EREM 80/2
Journal of Environmental Research, Engineering and Management
Vol. 80 / No. 2 / 2024
pp. 49–55
10.5755/j01.erem.80.2.34789

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Received 2023/08 | Accepted after revisions 2024/03

https://doi.org/10.5755/j01.erem.80.2.34789

Performance Investigation of Surface Modified Ceramic Microfiltration Membranes of Ionic Water Treatment

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The ceramic membrane surfaces coated with cysteic acid were tested for efficacy and the fouling rate at constant crossflow velocities (CFV) and two transmembrane pressures (TMP). The crossflow mode was used during the filtration process to enable the membranes to perform for longer periods. The calculated variability and substance rejection were used to determine the performance of the membranes. In addition, cleaning in situ (CIP) was performed on the membranes to ensure that the flux recovery process was executed smoothly after each run. The current study uses ceramic microfiltration membranes to investigate the effectiveness of a 2600-ppm calcium carbonate solution and 260-ppm 4-nitrophenol extraction/removal from water samples. The concentrations of Ca^{2+} ions of the distinct concentration samples were reduced by 89–96% by non-coating and coating ceramic microfiltration membranes for a three-hour reaction time. At the end of the run, the concentration of the solution was at a TMP of 0.20 MPa with an efficiency of about 99.5% at t = 160 min with a sustainable flux.

Keywords: ceramic microfiltration membranes, hardness, water treatment, cysteic acid.

Introduction

An undesirable characteristic of some natural and groundwater sources is their hardness. Several health issues, including odd-tasting drinking water and atopic eczema, can be caused by hard water worldwide (Al-Dahhan and Al-Obaidi 2023). Natural water is hard due to dispersed minerals, primarily calcium and magnesium compounds. Most water facilities appraise a degree of water hardness ranging from 50 to 150 ppm of CaCO3 as suitable to the public (Tenget et al., 2023). The research focuses on treating groundwater and surface water with intensified ceramic microfiltration membranes. Numerous techniques for industrial wastewater and water have been documented in the literature. In addition to ion exchange, flotation, coagulation-flocculation, adsorption, advanced oxidation, chemical precipitation, and electro-oxidation, these techniques also involve flotation. The membrane process is a recent development in the field of wastewater treatment. This method uses polymeric or ceramic membranes to establish a selective barrier between the internal receiving phase and the wastewater they are treating. Due to ease of use, energy efficiency, simplicity and environmental friendliness, ceramic membrane processes are among the most effective liquid membranes for various applications of liquid including industrial water treatment.

Water and industrial wastewater have been documented using electrically stimulated membrane processes. The chemical, thermal, and mechanical stability of ceramic membranes makes them more popular than polymer membranes (Daches, 2019). Barone et al. have patented a method for altering pigment surfaces using cysteic acid to reinforce and improve ceramic membranes (Lee et al., 2019; Usman et al., 2021).

Chemical surface modification can make ceramic filtration membranes hydrophilic or hydrophobic, depending on the application. ABRF-funded 1989 and 1991 amino acid analysis studies found that core facilities most typically measured cysteine concentration with cysteic acid. The 1989 and 1991 amino acid analysis studies supported by the Association of Biomolecular Resource Facilities found that core facilities used cysteic acid analysis to measure cysteine concentration most often. An inadequate compositional analysis comes from cysteine oxidation and cysteine to cysteic acid (Cya). Other amino acids, such as His, Met, Tyr, and Trp, are also transformed by this procedure; however, the popularity of the method can be attributed, in large part, to the fact that it is both straightforward and efficient. Oxidation with volatile reagents such as performic acid covers both the surface and pores of the membrane with cysteic acid, which prevents particles from adhering to the membrane and fouling it. This results in the approach being particularly well-suited for micro-analysis. Additionally, the zwitterionic nature of the surface in the cysteic acid-functionalized alumina membrane creates a superhydrophilic layer that is easily wetted with water, resulting in low fouling. It has been demonstrated that the surface modification of filtration membranes enhances their performance by reducing membrane fouling, increasing separation efficiency, and increasing permeate fluxes. The results were compared with previously published work using a corresponding ceramic membrane arrangement and no alterations of the surface or with compounds other than cysteic acid (Gitis and Rothenberg, 2016) because the membranes used in these evaluations were acquired from Molecular Filtration Inc. and were modified in situ. This study tested the ability of the modified ceramic membranes to treat ground wastewater using alumina (Al_2O_3) membranes. An application of cysteic acid ($HO_3SCH_2CH(NH_2)CO_2H$) was By using $CaCO_3$ and 4-Nitrophenol, 20 liters of feed water containing 2600 ppm and 260 ppm in water, synthetic groundwater was created in the laboratory to test the performance of functionalized membranes. The pH was synthesized and changed from 5 to 4 by adding CH_3COOH. A magnetic stirrer mixer was used to mix the mixture with CO_2 with micro-bubbles to diffuse the CO_2 and capture the Ca to form $CaCO_3$ for 30 minutes. Then, the solution was run through the membranes, removing the particles as dewater and lowering hardness. Molecular Filtration Inc. (MFI) supplied the microfiltration ceramic membranes, and Sigma-Aldrich supplied all chemicals without purification. Molecular Filtration Inc. (MFI) provided the utilized filtration prototype rig (Kim et al., 2017). *Fig. 1* displays the main properties of membranes.

Fig. 1. *The properties of membranes*

Membrane functionalization with cysteic acid

Cysteine acid was applied to modify the surface of the membranes to modify them even further. During the time when the membranes were attached to the filtering apparatus, the coating was applied to them. A 1M solution of cysteic acid was produced by heating distilled water to temperatures ranging from 15°C to 65°C in the feed tank. Additionally, the permeate side of the filtration apparatus was left open for 12 hours while operating at 85°C. The procedure was deemed complete when the four conductivities were almost identical, as measured from the permeate side. Following functionalization, the membranes underwent multiple washes with distilled water (DW) before being allowed to dry. The filtration apparatus, meanwhile, was operated for around 40 minutes using distilled water (Daches, 2019).

Membrane cleaning

The following cleaning agents are illustrated in *Fig. 2*, and one can select one of them based on the characteristics of the feed material. The membranes were cleaned to guarantee adequate flux and separation efficiency (Zsirai et al., 2016). The membrane cleaning was performed under the parameters shown in *Table 1*. *Fig. 3* shows the tank after the high-concentration groundwater running for 3 hours.

Table 1. *The cleaning-in-place procedure*

Reagent (20 L)	Recirculation time and temperature
Water flushing	30 min, 25°C
2MNaOH	30 min, 60°C
Water rinsing	30 min, 25°C
1M oxalic acid	30 min, 60°C
Water rinsing	30 min, 25°C

Experimental setup and operation

Fig. 4 and *Table 2* (Molecular Filtration, Inc. USA) show the setup for the experiment. The experimental setup had a feed tank with a capacity of 50 L. To keep the feedstock concentration steady, concentrate and permeate were reused in the feed tank while the framework was in the crossflow mode (Maguire-Boyle et al., 2017). Working the framework in the crossflow mode as opposed to the dead-end mode considers longer filtration cycles because the shear following up on the film as the retentate streams across it keeps the layer from fouling. Two layers of a similar design were encased in two distinct lodgings and organized in series, as found in *Fig. 5*. (Molecular Filtration, Inc. USA)

Fig. 2. *Cleaning agents used for membrane cleaning*

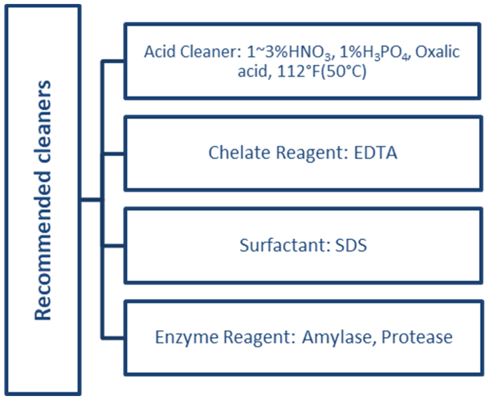
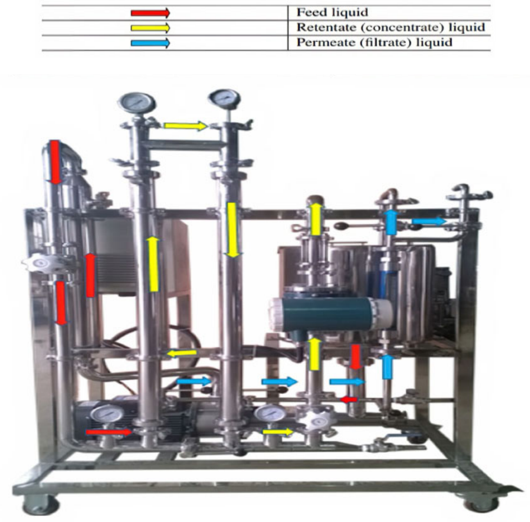


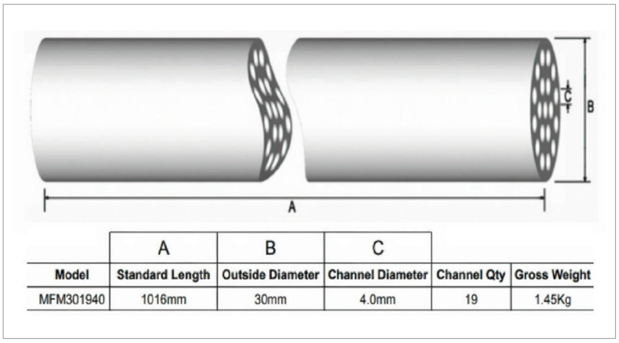
Fig. 3. *The tank after the high-concentration ground*

Fig. 4. *Liquid path flow in the machine*



With this arrangement, separation efficiency can be improved. A feed of 20 liters was moved through the system and into the feed tank using a circulation pump. The permeate flow rate (L/h) on the atmospheric side was monitored by a flow meter attached to the permeate line. The experiment was carried out at room temperature (27°C). The system's control valves adjust cross-flow velocity and operating pressure (Daches, 2019).

Fig. 5. *The configuration of ceramic membrane*



	A	B	C		
Model	Standard Length	Outside Diameter	Channel Diameter	Channel Qty	Gross Weight
MFM301940	1016mm	30mm	4.0mm	19	1.45Kg

Table 2. *Operating and design information and flux data*

Regular operating pressure	29–145 psi (2–10 bar)
Max operating temperature	302°F (150°C)
Max cleaning temperature	176°F (80°C)
Acceptable pH – continuous operation	1–14
Acceptable pH – clean-in-place (CIP)	0–14
Pure water flux	800 L/m²h.
Element water flux	192 LPH
Examination conditions	14 psi (1 bar), 86°F (25°C). pure water
Customizable length	From 500 mm to 1200 mm
Max operating pressure for MFM®UF membranes	145 psi (10 bar)
Max operating temperature shock ΔT	302°F (150°C) should not exceed 10°C per minute

Analytical method

The following equation was used to calculate the extraction percent:

$$\%\text{Extraction percent} = \\ = 100 - \left(\frac{\text{initial concentration} - \text{finalconcentration}}{\text{initial concentration}} X100\right) \quad (1)$$

Permeate flux (L/m²h)

The following equation was used to determine the permeate fluxes (Jp) of the membrane as a function of time:

$$\text{Jp} = \frac{Qp}{A * \Delta t} \quad (2)$$

Where: *QP* – volume of the permeate (L); A – effective surface area of membrane (m²); Δ*t* – time of sampling (h).

Results and Discussions

The carbonation process reduced the levels of hardness of the water samples. The pH of water samples was tested prior to and following carbonation. The CH_3COOH effect and the injection of CO_2 were crucial during the carbonation process for precipitating the Ca^{2+} carbonates and lowering the hardness of various water samples.

For the carbonation process, the closed-pressure reactor approach utilized an aqueous medium. First, the reaction bottle was filled with CO_2 gas at an 80 cc/min rate for 30 minutes. After that, it was filled with carbon dioxide. The carbonation reaction consists primarily of two steps: (i) carbon dioxide hydration, as depicted in *equations (3)–(5)*; ii) calcium carbonate precipitates are produced when carbonate ions react with calcium ions (Zhu et al., 2014).

$$CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3(aq) \quad (3)$$

$$H_2CO_3(aq) \leftrightarrow H^+ + HCO_3^- \quad (4)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (5)$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \quad (6)$$

$$Ca^{2+} + CO_3^{2} \leftrightarrow CaCO_3 \quad (7)$$

Reactions regulating the pH of untreated water are mostly mediated by carbon dioxide species. Many of the natural mechanisms that control the pH of water include carbon dioxide species. The chemical equilibrium model is able to assess the relatively quick reactions between species that are connected to alkalinity (aqueous CO_2, H_2CO_3 (aq), HCO_3, and CO_2) and species that are directly related to pH (OH^- and H^+) (Zhu et al., 2014). Over a phase boundary, however, the equilibrium rates between gaseous CO_2 and solute species are slower. As a result, water bodies that are exposed to the air occasionally cooperate with it. The fundamental idea of the theory has been presented here. According to the calcium-carbon-dioxide equilibrium theory, Henry's law applies when carbon dioxide gas is pressed into water (Khair and Star, 2013).

Effect of cysteic acid on membrane

Improving the operational efficiency of ceramic membranes is directly correlated to treating their surfaces with cysteic acid, which increases the hydrophilicity of the membranes. Covalent connections are formed between the dirt of the layer body and the cysteic destructive, making the films organophilic. (Zhang et al., 2013). The cysteic acid coating on the membrane surface produced no extra separation layer. However, the component composition of the surface is altered as a result of the synthetic adsorption of cysteic acid on the surface of the film or into its pores. That does not affect the form or size of the pores of the ceramic membrane. The wettability is affected due to the surface harshness and arrangement of compounds in the film. The functionalized earthenware film is suitable for groundwater partition due to its wettability.

Flux monitoring

In membrane microfiltration, it is essential to maintain an adequate level of constant flux. This indicates how well the membrane functions in any circumstance. The performance of the membrane is greatly impacted by a variety of parameters, including the flux, crossflow velocity (CFV), and transmembrane pressure (TMP), as well as the feed concentration, feed composition, membrane pore size, and transmembrane surface properties. The transition additionally shows the film's fouling rate. The relationship between transition and fouling rate typically is the opposite. However, temperature, CFV, and TMP are often associated with motion. A membrane module can use either the constant pressure or constant flux modes of operation. Although the membrane had a constant flux, the TMP was still rising as the operation progressed. On the other hand, the operation with the constant pressure mode showed a decrease in flux (Roevens et al., 2017). While observing our framework's motion, the film module ran in the consistent tension approach. The motion's behavior was seen at two unmistakable transmembrane pressures (0.15 MPa, 0.20 MPa, and 0.25 MPa). Since pressure differentials typically drive membrane filtration, it was concentrated on the TMP. *Figs. 6* and *7* demonstrate the approach to acting on the system progress concerning the transmembrane strain with time. A stable permeate flux with TMP of about 0.20 MPa was observed in the first 20 minutes. Although there were flux fluctuations at t = 100 min and t = 140 min, the system continuously restored to a steady flux.

It is possible to provide an explanation for these changes by utilizing the strain differential across the membrane.

At the end of the run, the concentration of the solution was at a TMP of 0.20 MPa with an efficiency of about 99.5% at t = 160 min with a sustainable flux. The flux stayed at 95% of the initial flux, showing that membrane fouling is limited. The same pattern can be seen in the run at TMPs of 0.15 and 0.25 MPa. At t = 80 minutes, the underlying motion and a supported transition were accomplished. The fact that the constant flux was 78% of the initial flux proves the high efficiency of the membranes. The permeate had the same quality as the run at 0.20 MPa, even at the end of the run. The surface covered with cysteic acid permits the membrane to repel drops, which protects the membrane pores from deterrents and flow obstructions, resulting in the constant high flux observed for the two runs. In other words, there is no protection from the solution droplets, which keeps the flux going. Compared to other studies (Maguire-Boyle et al., 2017; Keskin et al., 2021), cysteinic acid has a greater potential to increase the hydrophilic properties of ceramic membranes for better performance. Studies (Hu et al., 2015; El Batouti et al., 2021; Keskin et al., 2021) indicate that fouling causes unfunctionalized layers to encounter fast transition declines. Unfunctionalized membranes showed a decline in their flux, which could reach up to 70% of the initial flux. Unfunctionalized membranes do not have the component that permits them to repulse arrangement drops. Consequently, the solution is readily absorbed onto the surface of the membrane, constricting the membrane's pores to prevent flow and speed up fouling.

Water treatment

The change in pressure (DP) over the ceramic membrane is the driving force behind its use to separate impurities from water. The membrane's purpose and treatment mode (MF, UF, NF, RO) and MWCO determine the separation efficiency. The rejection efficiency is higher when the droplet size is larger in microfiltration (MF). Following this, there is a significant drop in the permeate flux due to solution droplets being deposited on the surface of the membrane, creating a resistant layer to flow. However, due to the droplets' ease of deformation through the membrane pores, a droplet's rejection efficiency decreases with a decreasing droplet size (Abdullah et al., 2022; Abdullah et al., 2021a; Abdullah et al., 2021b). Therefore, surface functionalized membranes are used in the best condition of 45 Hz, P1 = 1.2 KPa, and P2 = 0 after three hours of treatment, as shown in *Figs. 6* and *7*, to reduce fouling and low rejection efficiency. Since the surface of the membrane has captured the Ca^{+2} ions, the membranes will prevent the Ca^{+2} ions from passing through their pores and will prevent droplets from adhering to their surface. The obtained permeate had a rejection efficiency of 99.5% and a permeating quality of pp. The fact that the permeate was obtained in a single pass with no prior treatment makes this result promising (Hu et al., 2015; El Batouti et al., 2021, Keskin et al., 2021).

Conclusions

This study demonstrated that to observe the phenol compound passing through the membrane and the capture of Ca2+, commercial Al_2O_3 ceramic microfiltration membranes were treated with 2600 ppm and 260 ppm groundwater, respectively. The concentration of the solution was at a TMP of 0.20 MPa with an efficiency of about 99.5% at t = 160 min with a sustainable flux. Cysteic acid improved membrane performance more than any other compound, exhibiting high rejection efficiency and a prolonged, stable, sustained flux. The result obtained in this work supports the use of a ceramic membrane process for hardness removal, which can be extended to remove another non-polar component efficiently. $CaCO_3$ cannot be dissolved in water using a batch reactor alone; it needs injection gas with pressure to help the $CaCO_3$ to dissolve in water, and this is the idea used to separate it from the water using the membrane unit since it is working on the non-polar component only. It mimics the water hardness since it is available in the southern area of Iraq in dissolving in water with the percentage of the phenol and because of the pressure and the higher percentage of the gases. Furthermore, the tanks will finally get a milky white foam, indicating that the $CaCO_3$ has not passed through the membrane.

Fig. 6. *The impact of MPa on the performance of the membranes*

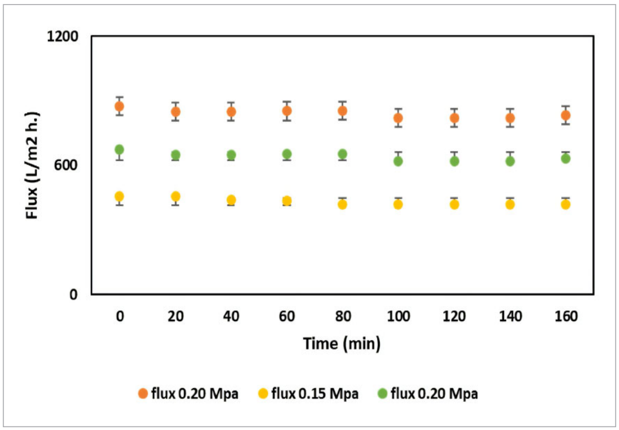
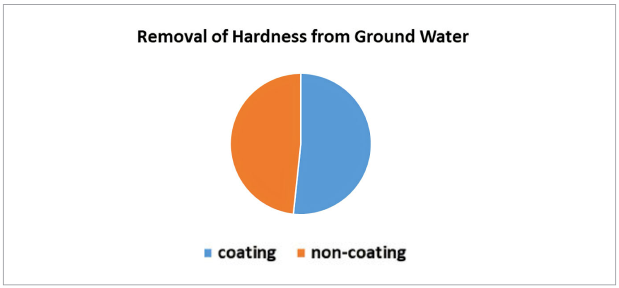


Fig. 7. *The effects of coating the membranes with cysteic acid depend on their performance*



Acknowledgments

The authors would like to thank the Chemical Engineering Department at the University of Technology-Iraq and the Multiphase Flow and Reactors Engineering, and Education Laboratory (mFReel), Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO, USA for their invaluable collaboration and support. Their contributions have significantly enhanced our research efforts in chemical engineering.

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