CoFe$_2$O$_4$-peroxymonosulfate based catalytic UF and NF polymeric membranes for naproxen removal: The role of residence time

Tao Wang, Wiebe M. de Vos, Joris de Grooth *

University of Twente Institute for Nanotechnology, Universiteit Twente MESA*, The Netherlands, Enschede, Netherlands

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ABSTRACT

Micropollutants pose a significant threat to water quality, aquatic life, and public health. A catalytic polymeric membrane, combining membrane filtration and peroxymonosulfate (PMS) activation provides an alternative option to their treatment. In this work, CoFe$_2$O$_4$ based catalytic particles were blended with polyethersulfone (PES) polymer and catalytic UF (ultrafiltration) membranes were fabricated by non-solvent induced phase inversion. The catalytic UF membrane with 2.0% CoFe$_2$O$_4$ concentration can effectively degrade 70% naproxen in a batch experiment. Additionally, a stable selective layer was built by the layer-by-layer assembly of PDADMAC (poly(diallyldimethylammonium chloride)) and PSS (poly(styrenesulfonate)) on the surface of the catalytic UF membrane. Both the catalytic UF and NF (nanofiltration) membranes were measured in full-recycling mode and single-pass mode. In the full-recycling mode, the naproxen rejection of catalytic UF and NF membranes both increased after adding PMS due to the activation of PMS and increased adsorption. Naproxen removal at different fluxes indicates that longer residence time (i.e. lower flux) can effectively decrease the naproxen concentration in the permeate. The same effect of residence time was also observed in the single-pass mode. By prolonging the residence time of UF membranes to the same level of the NF membranes, the catalytic UF membrane exhibited 87.7% naproxen rejection which is comparable to that of the NF membranes. Significantly, the pressure used in the UF membrane was only 0.1 bar, showing a great advantage of reduced energy cost. These results reveal the important role of residence time on the treatment efficiency of micropollutants by catalytic membranes. Moreover, the application of catalytic UF membranes under low pressure provides an energy-friendly way of removing micropollutants.

1. Introduction

In the past decades, small organic micropollutants (MPs) have become an urgent global issue with ever-increasing concentrations in aquatic environments and the potential risks they pose to aqueous organisms and humans [1]. MPs typically end up in the environment via wastewater streams and consist of a wide variety of synthetic chemicals, including pharmaceuticals, personal care products, hormones, surfactants, industrial chemicals, and pesticides [2]. Since many of them are toxic, endocrine-disrupting, mutagenic or potentially carcinogenic even at trace levels, MPs pose a significant threat to aquatic life and even public health [3]. As a result, the elimination of MPs from wastewater has become a new challenge in water treatment processes.

Conventional physicochemical and biological processes, such as coagulation-flocculation, activated carbon adsorption, and bioreactors have only limited success regarding the removal of MPs due to the large variety and the recalcitrant nature of some MPs [4,5]. Advanced oxidation processes (AOPs) are considered promising alternative treatment methods, including ultraviolet (UV)/O$_3$, UV/H$_2$O$_2$, photocatalysis, sonochemical oxidation, photo-sonochemical oxidation, photo-Fenton, and Fenton based approaches [6–8]. The hydroxyl radicals or sulfate radicals generated in AOPs can degrade the complex organic molecules to smaller organics or ultimately to carbon dioxide and water [9]. The high reactivity and versatile applicability of hydroxyl and sulfate radicals are highly desired in the elimination of MPs [10,11]. Nevertheless, the formation of byproducts [2] and the difficulty of separating and recycling the catalysts from the treated water potentially limit their use in aqueous media [12,13].

Membrane separation is a promising approach to provide an adequate treatment of MPs. Reverse osmosis (RO) membranes have already been proven to have enough rejection (>99%) for most of the micropollutants [14,15]. However, the low permeability and thus high variety and the recalcitrant nature of some MPs [4,5]. Advanced oxidation processes (AOPs) are considered promising alternative treatment methods, including ultraviolet (UV)/O$_3$, UV/H$_2$O$_2$, photocatalysis, sonochemical oxidation, photo-sonochemical oxidation, photo-Fenton, and Fenton based approaches [6–8]. The hydroxyl radicals or sulfate radicals generated in AOPs can degrade the complex organic molecules to smaller organics or ultimately to carbon dioxide and water [9]. The high reactivity and versatile applicability of hydroxyl and sulfate radicals are highly desired in the elimination of MPs [10,11]. Nevertheless, the formation of byproducts [2] and the difficulty of separating and recycling the catalysts from the treated water potentially limit their use in aqueous media [12,13].

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energy costs for treating fresh water sources limit its application in the treatment of MPs. Meanwhile, the currently reported nanofiltration (NF) membranes designed for the removal of dissolved ions exhibited only partial rejection for the MPs, with especially the small and uncharged molecules being hard to completely remove [16,17]. In addition to high energy consumption or the compromised retention, another inherent challenge of membrane technology is the production of a retentate which contains concentrated MPs levels that still need to be post-treated before discharge.

Aiming at increasing the efficiency of MPs treatment, more researchers have set their sights on the fabrication of catalytic membranes for the integration of AOPs and membrane filtration. In this integrated system, the membranes can work as support for the small-sized catalysts, avoiding the significant difficulty of having to separate the catalysts from wastewater after use [18-22]. Due to the catalytic degradation, MPs can be degraded within the, often porous, membrane matrix, thus decreasing the MPs concentrations in the permeate [23]. At the same time, the formation of a concentrated waste stream (retentate) is also preventing continuous MP degradation. As a result, post-processing can be effectively avoided, thereby lowering the treatment cost [27,28].

Among the reported catalytic membranes, titanium dioxide (TiO2) has been widely used as the photocatalyst because of its low cost, non-toxic, and photocatalytic performance [29-31]. However, due to the wide bandgap of TiO2 (3.0-3.2 eV), TiO2 can be activated only by UV light or near-UV light [32], resulting in higher cost compared to visible light [33]. On the other hand, the introduction of light components in membrane modules is almost impossible for large scale applications. Moreover, due to the short residence time of MPs in the membrane structure when pressure is applied in the separation process, the catalysts used in catalytic membranes are required to have high degradation efficiency. Recently, sulfate radical based AOPs have shown great potential in the use of catalytic membranes. With the activation of peroxysulfate (SO4O52-, PDS) or peroxymonosulfate (HSO5O4-, PMS), sulfate radicals can be generated, which were demonstrated to have a high redox potential (2.60–3.10V) and long lifetime (30–40μs) [34,35]. Besides the energy-based activation methods, like heat [36], UV irradiation [37], or ultra-sonication [38], diverse materials such as transition metal ions (Fe3+, MnO42-, Co3+, Cu2+, etc.) [39], carbon-based materials [40] and semiconductors [41,42] can all be used to effectively activate H2O2, PDS, and PMS. Catalytic membranes have recently been fabricated based on PMS/sulfate radical systems. For example, Cui et al. coated copper oxide on ceramic hollow fiber membranes and the fabricated membranes exhibited efficient bisphenol A degradation [19]. A cobalt ferrite impregnated ceramic membrane fabricated by Hu et al. also showed excellent sulfamate oxidation via PMS activation [43]. Currently, most of the catalytic membranes based on PMS/sulfate radicals are fabricated on ceramic substrates because of the stability of ceramic membranes under chemical oxidation. However, the downsides of ceramic membranes are the high unit price and the brittle failure under stress [44]. Typically, the separation ability of most of the reported catalytic membranes is around microfiltration and ultrafiltration levels suggesting that these membranes cannot reject MPs [24,45-48]. This means that the membrane only works as a substrate for catalysts in the treatment of MPs, rather than as a separating layer. The commonly used dense polyamide layer, fabricated by the interfacial polymerization, is shown to be easily damaged by the oxidative radicals [49,50]. However, the recent development of the Layer-by-Layer (LbL) assembly of polyelectrolytes provides an effective tool to fabricate selective layers that have been demonstrated to withstand an oxidative environment [51,52]. Depending on coating conditions, these NF membranes with a polyelectrolyte based selective layer have already shown decent to excellent rejections of different types of MPs [53,54].

In this work, CoFeO4 nanoparticles, which have already been demonstrated to effectively activate PMS [55,56], are employed as catalysts and mixed with polysulfone (PES) to fabricate the UF membranes. Subsequently, through the LbL assembly of poly (diallyldimethylammonium chloride) (PDADMAC) and poly (styrene sulfonate) (PSS) polyelectrolyte, a stable selective layer on top of the UF catalytic membranes was fabricated. Naproxen was chosen as the relevant model micropollutant in this work. As naproxen is widely used as an anti-inflammatory drug, it is frequently detected not only in sewage treatment plants effluents and surface water but even in drinking water, and is demonstrated to have harmful toxicological consequences [57-59]. Besides the catalytic measurement in the batch experiment, the membrane performance was evaluated by the removal efficiency of naproxen in both full-recycling mode and single-pass mode. By controlling the water flux of the membrane in full-recycling mode and single-pass mode, the residence time was manipulated to explore its effect on the treatment efficiency of both the UF and NF catalytic membranes. This work not only offers an effective method to build a stable selective layer on top of the catalytic UF membrane but also reveals the significant role of residence time that the degradation efficiency of the catalytic membranes can be easily improved by prolonging the residence time. As demonstrated here, the catalytic membranes containing CoFeO4 can provide an effective method regarding the treatment of MPs.

2. Materials and methods

2.1. Chemicals

Polyethersulfone (PES) (Ultrason 6020) and sulfonated polyethersulfone (SPES) (Ultrason 0559) were obtained from BASF. Cobalt iron oxide nanopowder (30 nm), glycerol, and di-deionized (DI) water, poly(styrenesulfonate) (PSS, 200 kDa, 30 wt% in water), poly(styrenesulfonate) (PSS, 200 kDa, 30 wt% in water), and (C14H21O2, Mw: 230.26gmol-1) were purchased from Sigma-Aldrich and used without further purification steps.

2.2. Fabrication and characterization of catalytic ultrafiltration (UF) membranes (PES@CoFeO4)

Non-solvent induced phase separation (NIPS) was used to fabricate flat sheet UF membranes. PES (14 wt%), SPEs (7 wt%), glycerol (12 wt %), and different amount of CoFeO4 (0.25 wt%, 0.50 wt%, and 2.00 wt%) were dissolved in N-methyl-2-pyrroldilone (NMP) under stirring for 12 h at 60 °C. The non-solvent additive, glycerol was used to form a thinner skin layer and narrow the distribution of the pores [60,61]. The polymer solution was stored in a desiccator for 12 h to remove air bubbles. A thin film of the obtained homogeneous polymer solution was cast on a clean glass plate, and then immediately immersed into a deionized (DI) water coagulation bath at 20°C. The gap height of the steel casting knife was controlled at 150 μm. The UF membranes with CoFeO4 were denoted as PES@CoFeO4. The UF membrane without CoFeO4 nanoparticles was also fabricated under the same conditions as a control. The morphologies and elemental composition of the membranes were characterized by field emission scanning electronic microscopy (SEM, JEOL JSM-6710F) with an energy-dispersive X-ray spectroscopy device (EDS). All the membrane samples were dried overnight in a vacuum oven at 30 °C and then sputter-coated with 5 nm platinum-palladium by a sputter coater (Quorum Q150 T ES). The water contact angle of the membrane surface was measured by an optical instrument (AD5300, Data Physics). A 2.0 μL DI water droplet was dropped on the membrane surface with a speed of 0.5 μL/s and the shape of the droplet was recorded after 3 s. To further explore the chemical composition variation of the membrane surface before and after the catalytic process, X-ray Fluorescence (XRF) (Bruker S8 Tiger 4 kW Wavelength Dispersive) measurement and X-ray photoelectron spectroscopy (XPS) (Quantera SXM (scanning XPS microprobe) from Physical Electronics) measurement were performed.
2.3. Micropollutant degradation in batch experiments

150 mL naproxen solution (10 mg L\(^{-1}\), 43 μM L\(^{-1}\)) was used as a model micropollutant solution. The initial pH value for each experiment was adjusted to 6 with NaOH (0.5 mol L\(^{-1}\)). The naproxen solution and membrane samples with an area of 4 × 4 cm\(^{2}\) were put into a beaker with stirring at 200 rpm for 24 h to reach the adsorption-desorption equilibrium (see Fig. 1c). To start the reactions, a PMS (500 mM L\(^{-1}\)) stock solution was injected into a naproxen solution to get a 2.0 mM L\(^{-1}\) concentration of PMS. 0.9 mL naproxen solution was taken from the beaker at specified time intervals (5, 15, 30, and 60 min) and then immediately mixed with 0.1 mL of methanol to quench the catalytic reactions [38, 39]. The naproxen concentration of all the samples was analyzed by HPLC (Dionex Ultimate 3000, water/acetonitrile, 0.1% phosphoric acid). A C18 column (Thermo Scientific Acclaim RSLC 120, 2.2 μm, 2.1 × 100 mm) was used to separate samples and then UV/vis detector was operated at 225 nm. To analyze the degradation kinetics of naproxen in the batch experiment, Langmuir-Hinshelwood model was used here [62]:

\[
\frac{dc}{dt} = \frac{kKC}{1 + KC} = -k_{app}t \quad \text{(1)}
\]

where \(r\) (mg L\(^{-1}\) s\(^{-1}\)) is the reaction rate, \(C\) (mg L\(^{-1}\)) and \(t\) (s) are the naproxen concentration and reaction time, respectively. \(k\) (mg L\(^{-1}\) s\(^{-1}\)) and \(K\) (L mg\(^{-1}\)) are the Langmuir-Hinshelwood reaction rate constant and Langmuir adsorption equilibrium constant, respectively. In a diluted system, \(KC << 1\), and thus pseudo-first-order kinetics model can be assumed as:

\[
\frac{dc}{dt} = \frac{kKC}{1 + KC} = -kKC \quad \text{(2)}
\]

where \(k_{app}\) (s\(^{-1}\)) is the apparent rate constant, and \(C_0\) (mg L\(^{-1}\)) is the initial concentration of pollutants. For every data point given in this paper, three individual membrane samples were measured, and errors margins are given as the standard deviation.

2.4. Layer-by-layer polyelectrolytes coating

LbL assembly of polyelectrolytes was conducted to form a selective layer on top of the UF membrane.

PDADMAC and PSS were chosen as the polycation and polyanion, respectively, due to the high stability of the polyelectrolytes. As SPES was added into the casting solution, which makes the membrane surface negatively charged due to the sulfonic acid groups, the positively charged polyelectrolytes, PDADMAC can be assembled on the membrane surface [51]. The Layer-by-Layer process was described as following [51–54]: The support membranes were firstly immersed in a 0.1 g L\(^{-1}\) PDADMAC solution in a 50 mM L\(^{-1}\) NaCl concentration. After 30 min, the membranes were rinsed in a solution of 50 mM L\(^{-1}\) NaCl for 15 min. The rinsing process was repeated three times in separate rinsing solutions. Subsequently, the membranes coated with polycation were immersed in a 0.1 g L\(^{-1}\) PSS (with 50 mM L\(^{-1}\) NaCl) solution for 30 min. After the same rinsing process, one bilayer of PDADMAC/PSS was successfully coated on the membrane surface. By repeating these same steps, membranes with the desired number of bilayers were obtained. All the coated membranes were stored in DI water at 4 °C before further characterization.
2.5. Micropollutant treatment in full recycling mode

The fabricated UF and NF membranes were measured in a full recycling mode (see Fig. 1a). In a crossflow setup, a membrane sample with an area of 42 cm$^2$ was mounted in the flat sheet membrane cell (CF 042, STERLITECH). The membrane samples were firstly filtered with 300 mL naproxen solution (10 mg L$^{-1}$, 43 μM L$^{-1}$) at 1 bar for 24 h to reach an adsorption-desorption equilibrium of the naproxen on the porous substrate. Subsequently, excess PMS (2.0 mM L$^{-1}$) was added to the feed solution. Samples from feed and permeate sides were collected before and after adding PMS. In this full recycling mode, the permeate was recycled back into the feed solution and thus the apparent reaction constant can be obtained from the naproxen concentration change in the feed solution. The membrane permeate flux ($J$, m/s) was calculated following equation (4):

$$J = \frac{V}{A\Delta t}$$  \hspace{1cm} (4)

Where $V$ (m$^3$) is the permeate volume, $A$ (m$^2$) is the membrane area, and $\Delta t$ (s) is the permeation time. Based on the equation following, an apparent residence time ($\tau$, s) in seconds can be calculated during the treatment process [63]:

$$\tau = \frac{l}{J}$$ \hspace{1cm} (5)

where $l$ (m) is the thickness of membranes, which is determined with the cross-section SEM images of three individual membrane samples. The removal rate and rejection of naproxen at different times were calculated following equations (6) and (7), respectively:

Removal rate (%) = (1 - $C_p / C_0$) × 100% \hspace{1cm} (6)

Fig. 2. Surface morphologies of PES@CoFe$_2$O$_4$ UF membranes with different CoFe$_2$O$_4$ concentrations: 0% (a), 0.25% (c), 0.5% (e), 2.0% (g) and cross-section morphologies of PES@CoFe$_2$O$_4$ membranes with different CoFe$_2$O$_4$ concentrations: 0% (b), 0.25% (d), 0.5% (f), 2.0% (h).
where \( C_0 \) (mg L\(^{-1}\)) is the initial naproxen concentration before adding PMS. \( C_p \) (mg L\(^{-1}\)) and \( C_f \) (mg L\(^{-1}\)) are the naproxen concentration of permeate and feed solution at different time intervals, respectively.

\[ \text{Rejection (\%)} = (1 - \frac{C_p}{C_f}) \times 100\% \]  

(7)

3.2. Degradation ability of PES@CoFe\(_2\)O\(_4\) membranes

To evaluate the degradation ability of PES@CoFe\(_2\)O\(_4\) membranes, naproxen was used as the model organic micropollutant and initial batch experiments were performed (see Fig. 1c). During the experiments, the temperature was controlled at 25 \( \pm \) 1 \( ^\circ\)C, and the PMS concentration and initial pH value of naproxen solution were 2.0 mM/L and 6.0, respectively. It can be observed that the pH value decreased from 6.0 to 3.2 after adding PMS due to the acidity of PMS in water [16]. Fig. 3 illustrates the degradation efficiency of naproxen in our batch experiments by membranes with different CoFe\(_2\)O\(_4\) concentrations. For all experiments, the naproxen concentration declined with time after adding PMS, including the membrane without catalysts. For the membrane without catalysts, the naproxen concentration decreased 32% in 1 h, which is ascribed to some additional adsorption of naproxen. Although the membrane sample has already been stirred in the naproxen solution for 24 h to reach adsorption-desorption equilibrium, the decrease of the pH value, resulting from the adding of PMS, can lead to more adsorption on the membrane samples. Cuerda-Correa et al. showed that the decrease of pH value improved the capacity of naproxen adsorption by carbon black [66]. Sun et al. also proved that the naproxen adsorption by MOFs increased sharply when the pH value decreased [67]. To investigate if the naproxen adsorption by the membrane fabricated is indeed influenced by the pH value, a membrane sample was first immersed in naproxen solution (10 mg L\(^{-1}\), pH 6) for 24 h, and subsequently, HCl (1 mol L\(^{-1}\)) was used to adjust the pH value of the naproxen solution from 6 to 3.2. The concentration of naproxen solution was monitored for 1 h after adjusting the pH value. As shown in Fig. S5, when the pH value was adjusted from 6 to 3.2 by HCl, the naproxen concentration exhibited a similar decreasing trend as was observed after adding PMS. This demonstrates that the pH value plays an important role in the adsorption of naproxen by the PES membrane and explains the decrease of naproxen for the control membrane in Fig. 3. Even though the decrease of naproxen in Fig. 3 is influenced by the change of pH value, there is still a clear difference between the control membrane and the membranes with catalysts. Moreover, the membrane with a higher CoFe\(_2\)O\(_4\) concentration exhibited a higher naproxen degradation efficiency. The amount of catalyst embedded in the membranes can be influenced by the concentration of catalytic particles in the casting solution.

3.2.5. Micropollutant treatment in a single-pass mode

Fig. 1b illustrates the dead-end setup for the measurements in a single-pass mode. Before adding PMS, the membranes samples (12.56 cm\(^2\)) were filtered with naproxen solution at 1 bar for 24 h to reach adsorption-desorption equilibrium. After that, the stainless-steel tank was removed to eliminate the possible activation of PMS by residual transition metal ions leaching from the tank. 50 mL naproxen and PMS (2.0 mM L\(^{-1}\)) were added to the plastic membrane cell. To adjust residence time, different pressures were applied, and the results were taken when a specified amount of permeate passed through the membrane (5, 10, and 20g). The naproxen removal was calculated based on equation (6).

### 3. Results and discussion

#### 3.1. Membrane morphologies and surface properties

In Fig. 2, we present the surface and cross-section morphologies of the produced UF membranes with varied catalysts concentrations. The membrane without CoFe\(_2\)O\(_4\) catalysts has a smooth surface. With the addition of CoFe\(_2\)O\(_4\), some particles appear on the membrane surface and increased numbers of particles on the membrane surface are observed with increasing CoFe\(_2\)O\(_4\) concentrations. The cross-section images of the membranes show that the sponge structure near the skin layer vanished with the increase of CoFe\(_2\)O\(_4\) particles and a more figure-like structure can be observed. Due to the higher affinity of CoFe\(_2\)O\(_4\) particles to non-solvent (DI water), the faster non-solvent/solvent exchange occurred during the phase inversion process. This accelerated demixing process results in the variation of membrane cross-section morphologies [64,65]. When the concentration of CoFe\(_2\)O\(_4\) is 2.0%, there are some particles on the wall of the finger-like structure, indicating that these particles are distributed throughout the whole membrane matrix. To confirm if these particles observed are indeed CoFe\(_2\)O\(_4\), the chemical composition of the membrane structure was determined via XPS and EDS. As the results shown in Table S1 and Fig. S1, cobalt and iron elements were both detected on the structure of membranes with catalysts. The mass percentage of these two elements also increased with the increase of CoFe\(_2\)O\(_4\) concentration and all the PES@CoFe\(_2\)O\(_4\) membranes exhibited the same atom ratio (2:1) between iron and cobalt, indicating that the CoFe\(_2\)O\(_4\) particles are successfully embedded in the membrane matrix. Additionally, the elemental composition of the cross-section was almost the same as the surface of the membrane with 2.0% CoFe\(_2\)O\(_4\), reconfirming the excellent distribution of the CoFe\(_2\)O\(_4\) particles. However, no cobalt or iron signal was detected by the survey spectrum of XPS (Fig. S2). As the detection depth of XPS is normally lower than 10 nm, this result indicates that the CoFe\(_2\)O\(_4\) particles that appeared in the surface SEM are covered by a polymer film whose thickness is higher than 10 nm. To explore the surface hydrophilicity of the membranes, water contact angle measurement was conducted and the results in Fig. S3 show that there is no big difference in water contact angle with the increase of CoFe\(_2\)O\(_4\) concentration. Meanwhile, as shown in Fig. S4, the pure water permeabilities of all the membranes were around 160–200 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). The results of water contact angle and water permeabilities indicate that the addition of CoFe\(_2\)O\(_4\) particles exhibits little influence on the membrane surface hydrophilicity and permeabilities. Our results show that CoFe\(_2\)O\(_4\) catalysts can be successfully immobilized in the membrane structure by NIPS and that the
PES@CoFe$_2$O$_4$ 2.0% membrane exhibited the best degradation efficiency, with nearly 70% naproxen degraded in 1 h with a $k_{app}$ of $(3.73 \pm 0.25) \times 10^{-4}$ s$^{-1}$. The catalytic ability of the UF membranes containing CoFe$_2$O$_4$ is thus successfully confirmed by the results of the batch experiments. Although the pH changes observed here in our study are substantial, it is expected that in practice this will be negligible due to lower PMS dosages and buffer capacity of waste water. Due to the strong metallic bonding between iron and cobalt atoms, the leaching of cobalt and iron ions from CoFe$_2$O$_4$ particles has already been proved very limited by several works [12,22,68]. To check the possible leaching from the PES@CoFe$_2$O$_4$ membranes, XRF measurement was employed to measure the elemental composition of the membrane before and after the batch experiment. As shown in Table S2, the decrease of cobalt and iron element composition was quite limited, proving that the CoFe$_2$O$_4$ particles were well embedded in the membrane structure. For further experiments, the PES@CoFe$_2$O$_4$ 2.0% UF membrane was chosen as the support membrane to fabricate the catalytic NF membranes.

3.3. The effects of residence time in a full-recycling mode

Layer-by-Layer assembly of PDADMAC and PSS polyelectrolytes was conducted on the surface of the PES@CoFe$_2$O$_4$ 2.0% membrane to endow the UF membrane with the capacity to reject MPs. To properly compare the performance of UF and NF membranes, both the catalytic UF membranes and NF membranes were measured at different flux ranges in the crossflow setup as illustrated in Fig. 1a. In this full-recycling mode, all of the permeate was recycled back into the feed solution. In this way, the influence of membrane separation is excluded and solely the catalytic performance of the membranes in the cross-flow setup is determined by monitoring the decrease of the naproxen concentration in the feed solution. Fig. 4 illustrates the change of naproxen rejection in 1 h. Due to the presence of the 9.5 polyelectrolytes bilayers, the initial naproxen rejection of the NF membrane was around 30–60%, which was much higher than that of the UF membrane. After adding PMS, the naproxen rejection of both UF and NF membranes dramatically increased within the first 15 min, which is explained by the combined effects of catalysis and adsorption. Due to the decreased pH value after adding PMS as discussed above, the adsorption of naproxen increased and thus the naproxen concentration in the permeate decreased. To further investigate the effect of initial adsorption on the NF membrane, these 9.5 bilayers were also deposited on UF control membranes without catalysts. The obtained membranes were used as the NF control membrane and then measured under similar conditions. As shown in Fig. S6, the naproxen rejection of the NF control membrane indeed increased in the first 15 min. Besides, the NF control membrane exhibited the same decrease of naproxen concentration in the feed solution as the UF control membrane in the batch experiment (Fig. S7). Even though partial improvement results from the adsorption on the membrane, the overall naproxen rejection of the NF membranes with catalysts was substantially higher than the control membranes, confirming the catalytic ability of the membranes containing CoFe$_2$O$_4$ in the filtration process. Moreover, the naproxen permeate concentration of the catalytic NF membrane was substantially lower than the UF membrane, which can be attributed to the existence of the selective layer and the longer residence time compared with the UF membranes. After 1 h, a clear decrease of naproxen rejection can be observed in both UF and NF membranes as shown in Fig. 4. This reduced rejection of naproxen can be attributed to the decrease of PMS concentration due to the ongoing reactions. In addition, poisoning of the catalysts caused by the adsorption of intermediates can also result in the decrease of naproxen degradation efficiency [41].

The influence of residence time within the spongeous structure of the membrane on the degradation efficiency was also explored in this full-recycling mode. A higher residence time can lead to a higher reaction efficiency of non-selective porous membranes [19,69,70]. To investigate the effect of residence time on the NF membrane with a selective layer, the feed pressure was adjusted. The results of naproxen rejection in Fig. 4 show that both the UF and NF membranes exhibited a similar trend under different residence times: the naproxen rejection increased with the higher residence time, indicating that the degradation performance of catalytic NF membranes in the porous structure can be tuned by controlling the residence time. For catalytic membranes processes, this is a relevant finding, as it states that the efficacy of the degradation process is effectively increased by decreasing the membrane flux.

As the permeate was recycled back into the feed solution in this full recycling mode, $k_{app}$ values can be calculated based on the decrease of the normalized naproxen concentration in the feed side, which are shown in Fig. 5. Compared with the NF membranes, UF membranes exhibited higher naproxen removal based on a higher $k_{app}$ in the feed solution. This shows again the influence of membrane flux in this full-recycling mode. On the one hand, the increase of water flux can shorten the residence time, decreasing the water quality in the permeate side as shown in Fig. 4; on the other hand, due to the higher flux of UF membranes, more naproxen solution can go through the membrane matrix where the catalytic reactions occur. Providing more opportunities for the catalytic reactions by keeping the naproxen concentrations in the membrane high. Even though the naproxen rejection of UF membranes in Fig. 4a was much lower than the NF membranes, the naproxen removal of UF membranes, as shown in Fig. S8, was still comparable to the NF membranes, resulting from the high water flux of UF membranes in this full-recycling mode. Additionally, due to the partial rejection ability of the selective layer (67 ± 3% MgSO$_4$ rejection), the retention of PMS may also contribute to this phenomenon. When PMS is partially rejected by the selective layer of NF membranes this
lowers the PMS available for the catalytic reaction in the membrane structure. As mentioned above, PDADMAC and PSS were chosen as the polycation and polyanion, respectively due to their good stability under oxidative environment [51]. To confirm the stability of PDADMAC/PSS multilayers, the flux change of the catalytic NF membrane was monitored during the measurement. If the multilayers were damaged by the hydroxyl and sulfate radicals generated in the catalytic reactions, an increase in water flux can be expected due to the defects within the multilayers. As shown in Fig. S9, the flux of the catalytic NF membranes remains stable during the experiments, which indicates the stability of PDADMAC/PSS multilayers under these catalytic reactions. Moreover, the surface morphologies of the catalytic NF membrane before and after catalytic reactions were also characterized by SEM, which are shown in Fig. S10. Compared with the surface before the measurement, there is no difference that can be observed on the membrane surface after the measurement.

3.4. The effect of residence time in a single-pass mode

The results in the full-recycling mode demonstrate the importance of residence time on the degradation efficacy of the catalytic membranes. As the catalysts in the membrane can only react while the PMS is in (near) contact with the catalysts in the support, increasing the residence time during filtration favors the activation of PMS during single pass filtration. Subsequently, a dead-end setup (Fig. 1b) was used to further investigate the effect of residence time in a single-pass filtration mode. As the initial naproxen rejection of NF membrane with 9.5 bilayers was around 30–60% under different residence times in the full-recycling mode, NF membranes with 15.5 bilayers were fabricated to explore the catalytic efficiency when a thicker or denser selective layer was used. In this single-pass mode, three types of membranes including the catalytic UF membrane, catalytic NF membrane with 9.5 bilayers and 15.5 bilayers were measured in a dead-end cell. The permeate was collected based on the amount of permeate passing through the membranes to

Fig. 5. The normalized concentration changes of naproxen in the feed solution: (a) catalytic UF membrane: PES@CoFe$_2$O$_4$ 2.0%; (b) catalytic NF membrane with 9.5 polyelectrolytes bilayers. For every data point, three individual membrane samples were measured, and errors were given as the standard deviation.

Fig. 6. The naproxen removal of different membranes under different residence times: (a) catalytic UF membrane; (b) catalytic NF membrane with 9.5 bilayers; (c) catalytic NF membrane with 15.5 bilayers; (d) the influence of residence time on the naproxen removal. To adjust the residence time, the UF membranes were measured at 0.1, 0.2 and 0.5 bar; the NF membranes with 9.5 bilayers were measured at 2, 4, and 6 bar; the NF membranes with 15.5 bilayers were measured at 3, 4, and 6 bar. For every data point, three individual membrane samples were measured, and errors were given as the standard deviation.
make sure that the amount of permeate is the same. As shown in Fig. 6a-c, the removal of naproxen all significantly increased after adding PMS. The single-pass naproxen removal is highly influenced by the residence time, with increased removal rates at higher residence time. Our results show that this impact of residence time is most dominant for the more open UF membranes. This can be explained by the low residence time in the more open membranes, as they can easily be operated at higher fluxes. To clearly show the influence of residence time on naproxen removal, Fig. 6d illustrates the naproxen removal of the different membranes as a function of residence time. With the increase of residence time from 4.6 s to 18.6 s, the naproxen removal of the UF membrane significantly improved from 43.5% to 87.7%. Compared with the UF membrane, the NF membranes with 9.5 and 15.5 bilayers only exhibited 5% and 9% of improvement, respectively, when the residence time increased from 11 to 27.9 s and 15.3–35.3 s, respectively. Remarkably, the naproxen removal of the UF membrane can be comparable to the NF membrane if the residence time is similar to that in the NF membranes. These results indicate that high naproxen removal can be easily achieved by adjusting the residence-time of the membrane separation process. When the residence time of UF membranes is comparable to the NF membranes, also the UF membranes can reach a high naproxen removal. It is important to notice that significantly less pressure is needed for the UF membrane to reach these residence times as the membrane with a selective layer. This means substantially less energy consumption is needed that lowers operating costs, which is a big advantage in the practical application of water treatment.

4. Conclusions and future prospects

In this work, catalytic UF membranes containing CoFe₂O₄ catalysts were fabricated by non-solvent induced phase inversion and were shown to be able to effectively degrade naproxen in batch experiments. The membrane with 2.0% CoFe₂O₄ exhibited the best degradation efficiency where 70% of the naproxen could be degraded in 1 h under the conditions used. To explore the effect of residence time, the catalytic UF membranes and catalytic NF membranes were measured in both full-recycling mode and single-pass mode. In the full-recycling mode, the naproxen concentration in both feed solution and permeate solution significantly decreased after adding PMS, proving the benefits of introducing the PMS-based catalysis process. In the single-pass mode, both catalytic UF and NF membranes showed high and stable naproxen removal which were higher than 80%. The significant role of residence time is revealed in that prolonging the residence time of the catalytic UF membrane can effectively increase the naproxen rejection. An increase in residence time favors the kinetics of radical formation and MP degradation. Due to the low pressure needed in UF membranes, the catalytic UF membranes show the possibility of treating MPs in a highly efficient and energy-friendly way.

To have a better understanding of the catalytic polymeric membranes, several further studies are highly required. Firstly, as mentioned in the results of the batch experiment, the decrease of pH after the addition of PMS plays an important role in both the degradation efficiency and MP adsorption, deeper insight into the effect of pH on catalytic efficiency and MP adsorption will help achieve an improved performance of the catalytic polymeric membranes. Secondly, besides the doping method used in this work, different methods of loading catalysts can be investigated to achieve a high loading rate of catalysts or enhance the accessibility of the loaded catalysts. In addition, the building of the modelling of the catalytic membranes is meaningful and beneficial for the development of catalytic polymeric membranes, which not only provide the fundamental understanding of the process combining with separation and catalysis but also guide the design of membrane structure.

Supporting information

The supporting information is available.

CRediT author statement

T. Wang: Funding acquisition, Methodology, Conceptualization, Investigation, Writing - Original Draft.W.M. de Vos: Supervision, Writing - Review & Editing. J. de Grooth: Conceptualization, Formal analysis, Supervision, Writing - Review & Editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.120209.

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