Water Supply

Self-forming dynamic membrane filtration for drinking water treatment

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ABSTRACT

Lab-scale continuous operation of self-forming microfiltration (MF) or ultrafiltration (UF) dynamic membranes were investigated simultaneously by applying iron oxide as an alternative treatment option in those waters having natural organic matter (NOM), iron and manganese. Both dynamic membranes gave high removal rates and effluent concentrations of pollutants were below the limit values in synthetic water. 60 and 62% (of DOC) and 75 and 78% (of UV_{254}) were removed in low dissolved organic carbon (DOC) synthetic (LS) water by MF and UF dynamic membranes, respectively. Although only 42 and 49% (of DOC) and 48 and 53% (of UV_{254}) could be removed by MF and UF dynamic membranes, respectively, a remarkable effect on fouling alleviation was observed in high DOC synthetic (HS) water. Iron oxide did not enhance the removal of organic matter in low DOC natural (LN) water as much as it did in synthetic water. Iron oxide led to the removal of high molecular weight organics, thus reversible fouling was reduced almost 2 orders of magnitude through both types of dynamic membranes in high DOC natural (HN) water. Reversible and irreversible resistances were reduced by iron oxide to some extent in LN water. Nevertheless the effect of iron oxide on fouling alleviation was much higher in HN rather than in LN water.

Key words: DOC, dynamic membrane, fouling, iron oxide, removal

HIGHLIGHTS

- The impact of self-forming MF and UF dynamic membranes on the removal process and fouling behaviour were investigated.
- Both dynamic membranes gave high removal rates and iron oxide led to a remarkable effect on fouling alleviation in artificial water.
- Iron oxide enhanced the removal of high molecular weight organics.
- Dynamic membranes caused a reduction in reversible and irreversible resistances, especially in HN water.

GRAPHICAL ABSTRACT
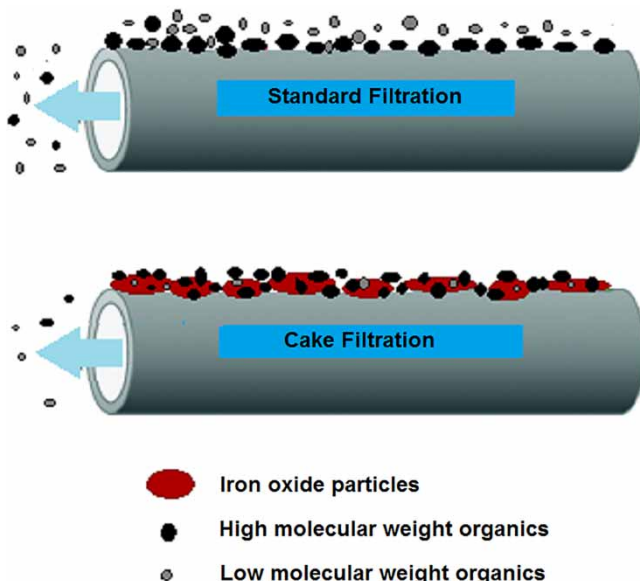
INTRODUCTION

Fouling is the major hindrance in membrane applications. The existence of natural organic matter (NOM) is an important issue affecting the performance and design of drinking water treatment plants. Manganese is also known to be one of the important components of water which causes fouling, along with NOM. Normally, microfiltration (MF) or ultrafiltration (UF) membranes alone are unable to remove soluble organics or manganese effectively. Various types of membranes have been applied to remove NOM and manganese in the past; however, it has been shown that membranes are subjected to severe fouling, in addition to their low retention rate (Cote *et al.* 1998; Choo *et al.* 2005; Zularisam *et al.* 2007; Choi *et al.* 2008; Park & Yoon 2009). A variety of pretreatment methods have been tested prior to membrane filtration to overcome fouling such as coagulation, adsorption, oxidation etc. Pre-coagulation has been shown as effective to some extent to control fouling (Miljatovic *et al.* 2004; Pikkarainen *et al.* 2004; Shon *et al.* 2005), but additional organic matter removal was poor. In-line coagulation (Konieczny *et al.* 2009a, 2009b; Meyn *et al.* 2012) or hybrid membranes (Park *et al.* 2002; Choi & Dempsey 2004; Konieczny *et al.* 2009a, 2009b) have been tried by some researchers, but resulted in significant increase in transmembrane pressure. Treguer *et al.* (2010) added ozone to powdered activated carbon (PAC) to remove the aromatic fraction of NOM in drinking water. However, it has been shown that PAC is unable to reduce fouling associated with low molecular weight organics. Actually, it was reported that PAC had adverse effects on fouling due to small particles left behind after PAC adsorption (Lin *et al.* 1999). Similarly, it has been shown that various pretreatment applications may reveal negligible or even negative impacts on fouling due to undefined factors, possibly depending on membrane material and water characteristics (Yuan & Zydney 1999). Additionally, oxidation with strong oxidants has not always had a positive effect on fouling control if elevated levels of algae population are present in water. In contrast, strong oxidant application may induce an adverse effect on algal cell breakdown, so resultant intracellular organics may be released (Fan *et al.* 2014).

On the other hand, chlorination has been known to form disinfection byproducts (DBPs) as a result of the interaction with NOM. However, NOM mostly exists in water sources associated with Fe(II) and Mn(II) and may form dissolved complexes with these constituents, especially with Fe(II). As a contrast example, if chlorination is applied, interaction of these constituents affects even the formation process of DBPs. Because the oxidation reaction of Fe(II) is much faster than that of NOM-chlorine reactions, this situation contributes to the control of DBP formation. A similar relationship was shown for manganese (Bazilio *et al.* 2016). Therefore, NOM requires a comprehensive evaluation to select proper treatment alternatives by taking into account water characterization.

Zhang *et al.* (2003) used heated iron oxide for adsorptive removal of NOM. They found that heated iron oxide formed a cake layer on the surface of the membrane, while other adsorbents led to pore fouling. Membrane coating with iron and

manganese oxides has been investigated and good results were observed in both control of fouling and removal of NOM (Byun *et al.* 2011; Park *et al.* 2012; Ma *et al.* 2015; Yu *et al.* 2016). Nanoparticle incorporated membranes have been fabricated and successful results have been yielded with these types of membranes (Gohari *et al.* 2014; Demirel *et al.* 2017).

Although UF is efficient in removing some fractions of NOM and partial algal organics, it exhibits severe fouling. Additional adverse effects of other constituents in water such as manganese worsen membrane fouling. MF membranes are known even to be unable to remove NOM. Recently, a low pressure membrane has been increasingly applied as a dynamic membrane since it can be operated without rapid fouling and maintains stable operation conditions. By using a dynamic membrane, efficient removal, as obtained by NF, can be achieved through a larger pore sized MF and UF membrane.

Studies have shown that the NOM concentration in dam water supplying water to Istanbul has been increasing. Furthermore, recently seasonal taste and odor problems have been experienced caused by an algal population increase during the periods between April through August. Powdered activated carbon has been applied using pre-ozonation to overcome this problem; however, TOC removal efficiency was found to be poor. In fact, according to the results of the analysis, effluent TOC concentration was found to be higher than that of the influent (Fakioglu *et al.* 2020), probably due to algal cell breakdown during ozone predosing. With the dynamic membrane approach, a cake layer is formed onto the membrane surface which prevents foulants accessing through the membrane pores. NOM, iron or manganese which normally result in membrane fouling are entrapped in the cake layer, preventing fouling of the membrane. In this study, lab scale continuous operation of both self-forming dynamic membrane MF and UF were evaluated simultaneously by applying iron oxide as a treatment alternative for surface and groundwater having NOM, iron and manganese. The impact of iron oxide on the removal process and the fouling behaviour of dynamic membranes was evaluated for various combinations of these pollutants. Thus, this research is mainly intended to give a comprehensive evaluation of dynamic membrane filtration using iron oxide for various pollutant combinations, and provide an alternative treatment method which prevents the fouling of membranes by a deposited cake layer on the membrane surface, acting as an additional barrier for pollutant removal without any of the adverse effects of strong oxidants. Experiments were conducted with synthetic and natural water samples. Natural water experiments were performed with high dissolved organic carbon (DOC) natural (HN) water (Omerli dam) and low DOC natural (LN) water (Danamandıra groundwater) samples. According to the characterization studies, both of the natural waters have moderate iron and high manganese concentrations. Considering the iron, manganese and DOC compositons of the natural waters, synthetic water samples with low DOC (LS) and high DOC (HS) concentrations were prepared similar to the natural water. Thus, natural and synthetic water samples were compared within dynamic membrane MF and UF applications in terms of pollutant removal and fouling alleviation.

MATERIALS AND METHODS

Dynamic membrane system

MF and UF membranes were simultaneously operated with dynamic membrane application using iron oxide. The membranes tested for dynamic membrane applications were a hollow fiber polypropylene MF membrane (Zena Membranes, Czech Republic) and a polyvinylidene fluoride (PVDF) UF membrane (Zenon Environmental Inc., Canada). Both membrane modules were operated in 'outside-in' configuration. MF and UF membranes with nominal pore size of 0.1 μm and 40 nm were tested to compare their fouling tendencies and removal efficiencies. The surface area of both membranes was equal to 0.047 m^2.

Dynamic membrane experiments were performed with a lab-scale continuous operation submerged membrane system including automated control system (Figure 1). The system was supported by a UPS power supply and a generator. The membrane module was made of plexiglass and had a 6.6 litre volume. The raw water was fed into the membrane module by a peristaltic pump. The water level was controlled with a sensor to maintain a constant level in the module. A pressure gauge was placed in the vacuum line to measure transmembrane pressure (TMP). An automated control system monitored the pressure data online and the data was stored by a SC1000 data logger (Hach) in 5-minute intervals. Permeate was vacuumed from the reactor by a peristaltic pump for 72 hours. Backwashing operations were performed automatically during 60 seconds per hour through an automated control system. Air was supplied at the bottom of the membrane module by a porous ceramic plate in order to provide dissolved oxygen beside creating turbulence and keeping foulants away from the membrane. Permeate flow rate was kept constant at 20 ml/min (0.6127 m^3/m^2/day) and was monitored twice a day. Dynamic membrane filtration tests were performed with synthetic and natural water samples. Low and high levels of DOC were simulated using a predetermined amount (1 and 7 mg/l) of humic acid (Aldrich) stock solution for
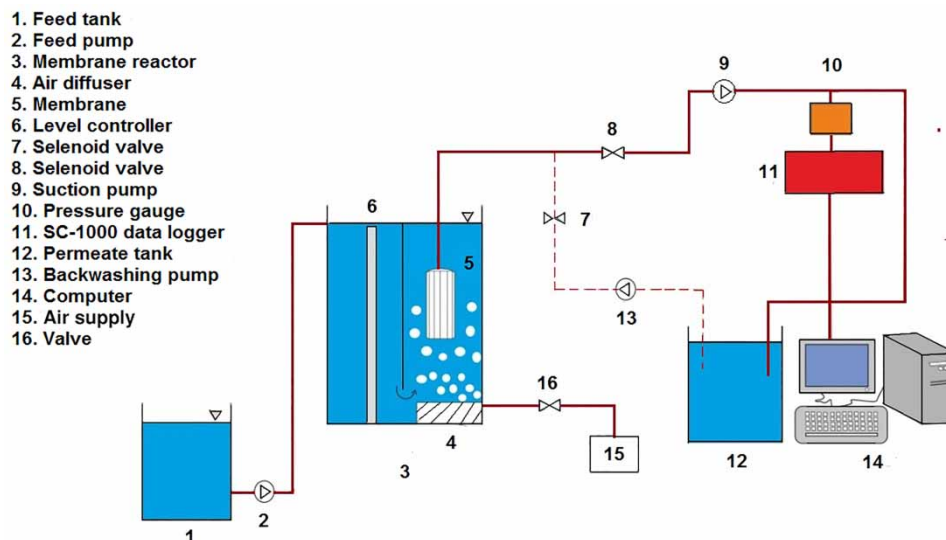
**Figure 1** | Schematic diagram of automated membrane system.

synthetic water. pH, alkalinity, Fe(II) and Mn(II) concentrations of the synthetic water were adjusted to natural water level. Synthetic solutions were prepared by 100 litre of volume to be fed into the continuous submerged membrane system. Iron oxide precipitate was obtained by slow addition of NaOH solutions into $FeSO_4.7H_2O$. The solution pH was fixed at 8.5 and aeration was maintained during 24 hours. Obtained iron oxide precipitate was used directly in pristine form without any purification, except washing with DI water. Point of zero charge (PZC) of synthesized iron oxide was determined according to the potentiometric titration method using 0.1 N NaOH and HNO_3 solutions. Iron oxide concentration in the reactor was adjusted to 50 mg/l.

Natural water experiments were performed with high DOC (HN) surface water (Omerli dam) and low DOC (LN) groundwater (Danamandıra water unit) samples. DOC concentrations of natural water samples were 4.8 and 0.65 mg/l; specific UV absorbance (SUVA) values were 4.15 and 1.5 l/mg/m; Fe(II) concentrations were 1.05 and 1.1 mg/l and Mn(II) concentrations were 0.9 and 1 mg/l for HN and LN, respectively. Natural water was fed into the membrane module and a self-formed dynamic membrane with iron oxide was investigated for 72 hours. Solutions in the feed tank were agitated continuously by a circulation pump to avoid precipitation. Samples were taken once a day from the reactor and permeate line. The samples were centrifuged and filtrated using a 0.45 μm cellulose filter immediately after the sampling period and were analysed directly for DOC and ultraviolet absorbance at 254 nm (UV_{254}). DOC were measured using a Total Organic Carbon Analyzer (Schimadzu TOC-VCPH) according to the Standard Methods/5310 B. UV_{254} was determined using a Perkin Elmer Lambda 25UV Visible spectrophotometer. ICP-OES was used to determine total iron and manganese. Characteristics of the fouling layer were examined using Scanning Electron Microscopy (SEM) (Celik 2011).

RESULTS AND DISCUSSION

The impact of iron oxide on DOC and UV_{254} removal

Figure 2 shows the impact of iron oxide on DOC and UV_{254} removal in both synthetic and natural waters. In general, similar DOC and UV_{254} removal rates were obtained by MF and UF membranes, suggesting that the UF membrane was not superior to the MF membrane in terms of the removal of DOC and UV_{254}. For LS water, obtained DOC and UV_{254} removal rates by MF and UF membranes were 46–51% and 50–54%, respectively. Removal rates decreased to 37% of DOC and 40% of UV_{254} in HS water, depending on the increase in initial DOC concentration. On the other hand, although the Fe(II) concentration was low, aeration pretreatment resulted in 20% of DOC and 26% of UV_{254} removal in LS water. Herein, it must be emphasized that aeration results in in situ formation of Fe(III), which then adsorbs a certain amount of humic acid on its surface. It was revealed in our preliminary experiments that humic acid initially constitutes a soluble complex with ferrous iron; nevertheless these complexes are readily oxidized in later stages of the oxidation (Celik 2011). However, only 10% of DOC and 15% of UV_{254} could be removed in HS water performing aeration
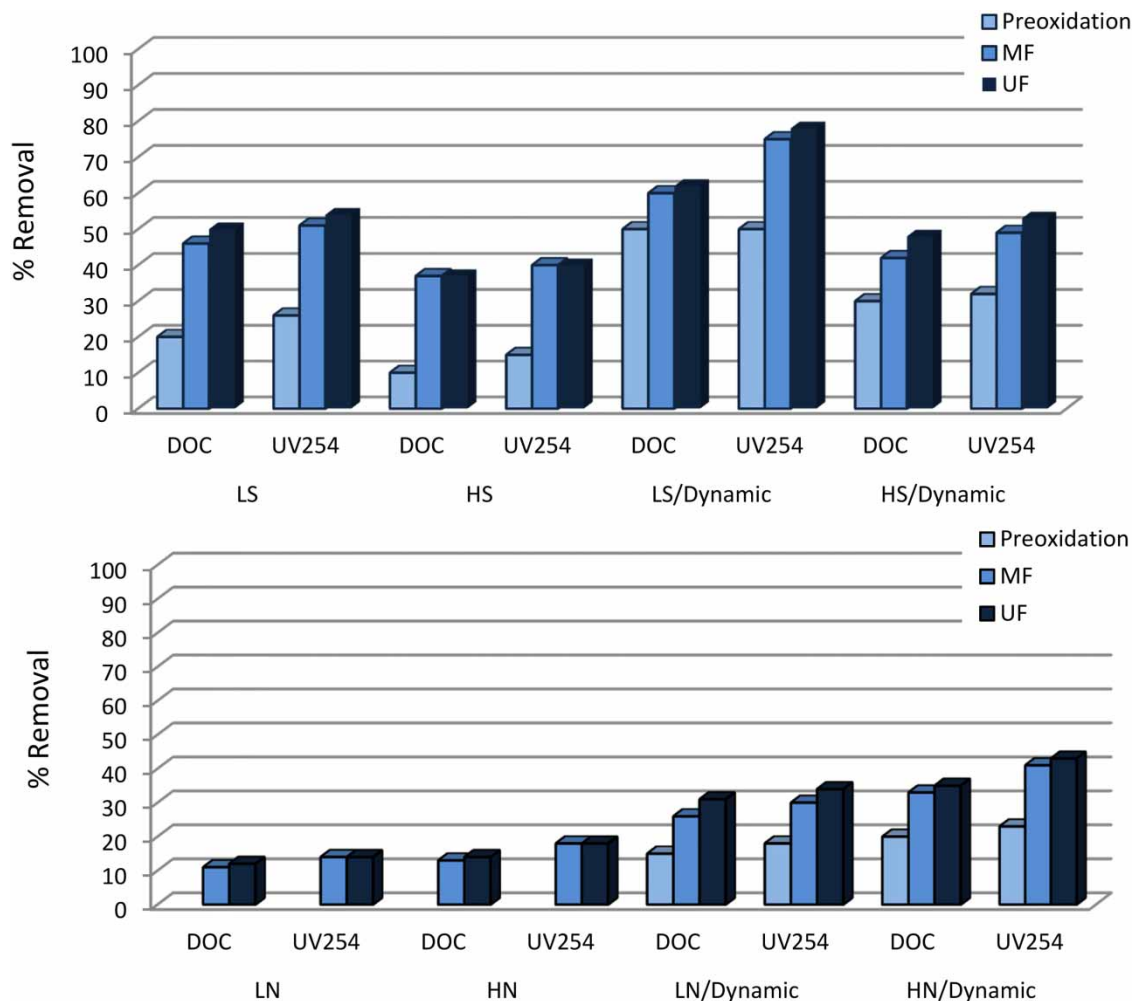
Figure 2 | DOC and UV$_{254}$ removal rates in synthetic and natural water.

pretreatment, individually. Thus, possibly due to the different pretreatment conditions performed, our findings are not in agreement with Qu *et al.* (2020), who imply that a low level of in situ formed Fe(III) contributes to the organic removal. Although the same concentration of Fe(II) is present in this combination, in situ formed iron oxide was not sufficient to remove high concentration of organics in HS.

Remarkable increase in removal rates was observed by dynamic membrane applications using iron oxide. As shown in Figure 2, DOC removal rates increased to 60–62% of DOC and 75–78% of UV$_{254}$ in LS by MF and UF dynamic membranes, respectively. However, dynamic membranes showed a moderate performance for HS, and removal rates decreased to 42–49% and 48–53% for DOC and UV$_{254}$, by MF and UF dynamic membranes, respectively. On the other hand, 50% of DOC and UV$_{254}$ removal could be achieved with iron oxide, performing aeration pretreatment individually for LS water. These relatively high removal rates arise from high affinity of humic acid to iron oxide. However, low removal rates could be obtained with iron oxide in HS water (30% of DOC and 32% of UV$_{254}$) performing aeration pretreatment individually. Although the surface of iron oxide has a relatively high positive electric potential at the pH level used in this study, it can remove humic acid just partially, so removal rates decreased in parallel to concentration increase in HS water. Nevertheless, 42 and 49% of DOC and 48 and 53% of UV$_{254}$ could be removed thanks to the additional sieving effect and adsorption mechanism of the dynamic membrane for HS water.

Although removal rates were slightly lower than those for the synthetic water, similar DOC and UV$_{254}$ removal rates could be obtained in HN water by a dynamic membrane. As shown in Figure 2, 13–14% of DOC and 18% of UV$_{254}$ could be removed in HN water by MF and UF membranes individually, without iron oxide. Iron oxide enhanced the removal rates, and 33 and 35% (of DOC) and 41 and 43% (of UV$_{254}$) could be removed by MF and UF dynamic membranes, respectively.

Similarly, only 11–12% of DOC and 14% of UV_{254} were removed by MF and UF membranes in LN water without iron oxide. Removal rates of DOC increased (to 26 and 30%) and UV_{254} increased (to 31 and 34%) by MF and UF dynamic membranes, respectively. Experiments conducted with natural water revealed that pretreatment individually had a lower effect on removal rates in natural water than it did in synthetic water. 20% of DOC and 23% of UV_{254} were removed in HN water, whereas only 15% of DOC and 18% of UV_{254} were removed in LN water through pretreatment only.

Since organic matter is formed as a result of complex biochemical processes in natural water, it is not surprising to find different results from those obtained with synthetic humic acid solutions used in the experiments. The SUVA value is calculated from the ratio of UV_{254}/DOC. The SUVA represents the aromaticity of the organic matter. Aldrich humic acid, used to prepare synthetic solutions has a high SUVA value (4–7 l/mg/m) (Karanfil et al. 2003; Pinkic 2014), representing its high aromatic and hydrophobic character. The SUVA of Aldrich humic acid is similar to the value of Omerli Dam water (4.15 l/mg/m) in the period of the experiments, which suggest that Omerli Dam (HN) water also has a humic-like hydrophobic character. Although a characterization study was not conducted within the scope of the study, prior studies performed on Omerli dam water revealed that a hydrophobic fraction is the dominant fraction, mainly consisting of hydrophobic neutral and hydrophobic acidic fractions (Kucukcongar et al. 2013; Avsar et al. 2014).

It can be concluded that in experiments conducted with the dynamic membrane, HN water showed similar trends to HS water, probably due to the similarity of NOM characteristics with HS water and its relatively higher aromatic content and molecular weight than LN water. Therefore, it must be emphasized that dynamic membrane application is more succesful for HN water than LN water, concerning DOC and UV_{254} removal. However, the dynamic membrane did not cause a significiant reduction in DOC and UV_{254} in LN water (SUVA <2), as it did in synthetic water.

The impact of iron oxide on iron and manganese removal

Figure 3 shows the impact of iron oxide on iron and manganese removal. As shown in the figure, both dynamic membranes gave almost complete iron removal in LS and HS water. Actually, ferrous iron was readily oxidized on a large scale through an iron oxide pretreatment step, giving 96 and 94% of iron removal for LS and HS water, respectively. Moreover, 86 and 84% of iron removal could be achieved by a pretreatment step without iron oxide. Following membrane application, effluent iron concentrations were found below the limit values in all combinations.

On the other hand, as expected, insignificant manganese removal rates were obtained through the pretreatment step without iron oxide. With an MF membrane, 63 and 74% of manganese still existed in LS and HS water without iron oxide. Using
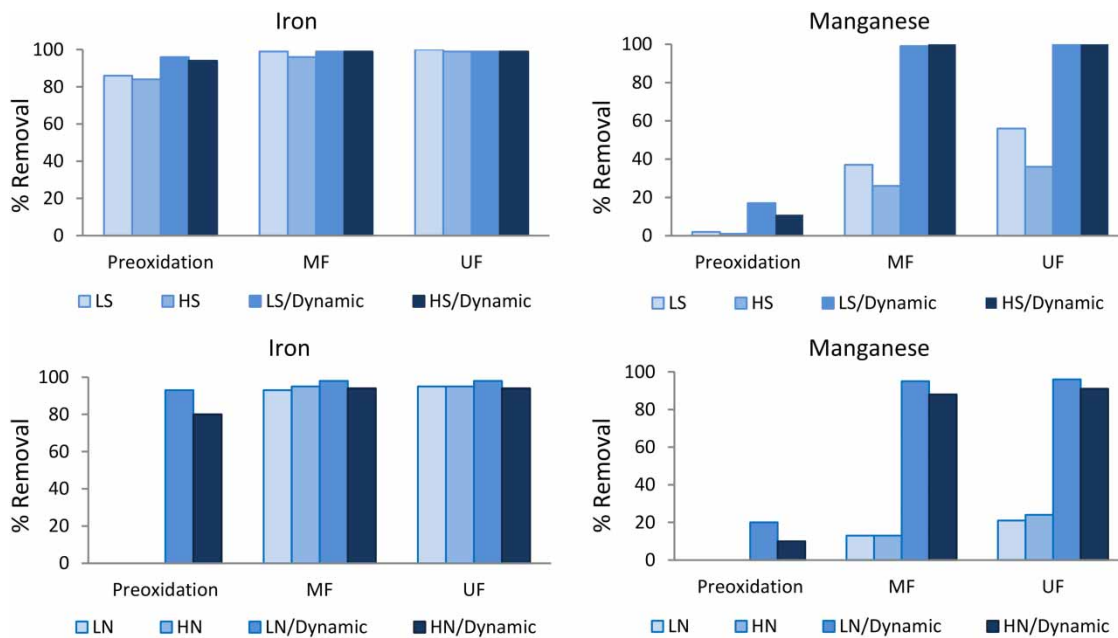

Figure 3 | Iron and manganese removal rates in synthetic and natural water.

MF and UF dynamic membranes, $\geq 99\%$ of manganese could be removed and manganese was reduced to below limit value for both synthetic waters. Iron oxide, known for its excellent catalytic effect on Fe(II) oxidation, is moreover just as effective as manganese oxide for catalytic oxidation of Mn(II) (Sung 1980; Sung & Morgan 1981; Davies & Morgan 1989). As a result of this catalytic effect on oxidation, iron oxide significantly enhanced iron and manganese oxidation due to its adsorption/surface oxidation mechanism. Obtained results were in good agreement with prior studies (Tufekci & Sarikaya 1996; Unal et al. 2011; Cheng et al. 2020; Van Beek et al. 2020).

Dynamic MF and UF membrane applications using iron oxide led to 98 and 94% of iron removal in LN and HN water. Although manganese was not oxidized on a large scale through the pre-oxidation step (10–20%), 95 and 88% of manganese removal could be achieved by an MF dynamic membrane in LN and HN water, and 96 and 91% of manganese were removed by a UF dynamic membrane in LN and HN water. Results suggested the success of both dynamic membranes in LN water in terms of iron and manganese removal. However, although dynamic membrane application resulted in high iron removal, 88% of manganese removal by the MF dynamic membrane couldn't meet the standards in HN water. Effluent manganese concentration for the dynamic UF membrane were also found slightly above the limit value for HN water.

Effect of iron oxide on membrane fouling

TMP trends of bare and dynamic membranes are shown in Figure 4. The remarkable fouling mitigation obtained through dynamic membranes is noteworthy. The TMP of the MF membrane reached $\cong 0.3$ bar without iron oxide for LS and HS water. On the other hand, the dynamic MF membrane with iron oxide operated quite stably around 0.1 and 0.2 bar for LS and HS water.

According to the results, a remarkable reduction in fouling potential of organic matter was observed in the dynamic MF membrane for LS water, possibly due to significant DOC, UV_{254}, iron and manganese removal in the pre oxidation step. Additionaly, it must be emphasized that 60% of DOC and 75% of UV_{254} could be removed by the MF dynamic membrane in LS water in parallel to the stable TMP level. For HS water, relatively low DOC (42%) and UV_{254} (49%) removal rates were obtained with a dynamic membrane in spite of its stable and low TMP trend.

On the other hand, the TMP of the dynamic UF membrane reached $\cong 0.55$ bar and <0.2 bar for HS and LS water, respectively. Figure 4 shows that the UF dynamic membrane had greater effect on fouling alleviation for LS water compared to bare membrane. It is worth remembering that iron and manganese were removed almost completely by dynamic membrane for both synthetic waters. Also, 78% of UV_{254} and 62% of DOC removal could be achieved by the UF dynamic membrane in LS water. Therefore, it can be concluded that the UF dynamic membrane led to a low and stable TMP trend, as well as high removal efficiency for LS water.

Regarding natural water experiments, a dynamic MF membrane led to 0.3 bar and 0.2 bar of TMP for LN and HN water. On the other hand, a UF dynamic membrane gave a quite low level of TMP ($\cong 0.05$ bar) for LN water, in contrast to HN water ($\cong 0.5$ bar). According to the TMP results, an MF dynamic membrane is superior to a UF dynamic membrane for high DOC water, while a UF dynamic membrane is a more viable option for low DOC water in the view of fouling alleviation. However, compared to the remarkable effect on membrane fouling mitigation, low removal rates concerning DOC and UV_{254} were obtained for natural water even with a UF dynamic membrane, possibly due to the presence of low molecular weight organics in groundwater. The MF dynamic membrane showed more stable and low TMP trend in comparison to the UF dynamic membrane for HN water. Similar removal rates of MF and UF dynamic membranes in HN water to the rates in HS water concerning DOC and UV_{254} were noteworthy, in addition to high iron and manganese removal. It is known that humic acid has high affinity to iron oxide (Baalousha et al. 2008; Genz et al. 2008). The PZC of synthesized iron oxide used in this study was determined as 9.2. Therefore, the surface of iron oxide is positively charged at operation pH, which is lower than the PZC (Illes & Tombacz 2006), and adsorbs a significant amount of NOM, especially the humic-like, high molecular weight fraction. Thus, adsorption reaction resulted in cake formation on the membrane surface which acts as an additional barrier for foulants. Iron oxide used in this study was obtained at pH 8.5 maintaining aeration during 24 hours. Therefore, obtained iron oxide was transformed to goethite (Yoshinaga & Kanasaki 1993; Hove et al. 2008). The obtained PZC value of synthesized iron oxide was in line with Kosmulski et al. (2003), who imply that the PZC of synthesized goethite in various studies were reported in the range of 7–10.

Figure 5 shows an amplified graph of Figure 4 between the 12th and 15th hours to compare the fouling trend of bare and dynamic membranes based on TMP.

It can be clearly seen from Figure 5 that formation of the cake layer with iron oxide alleviated membrane fouling. Resistance values of the membranes are given in the next section, but it can also be seen from Figure 5 that reversible fouling was
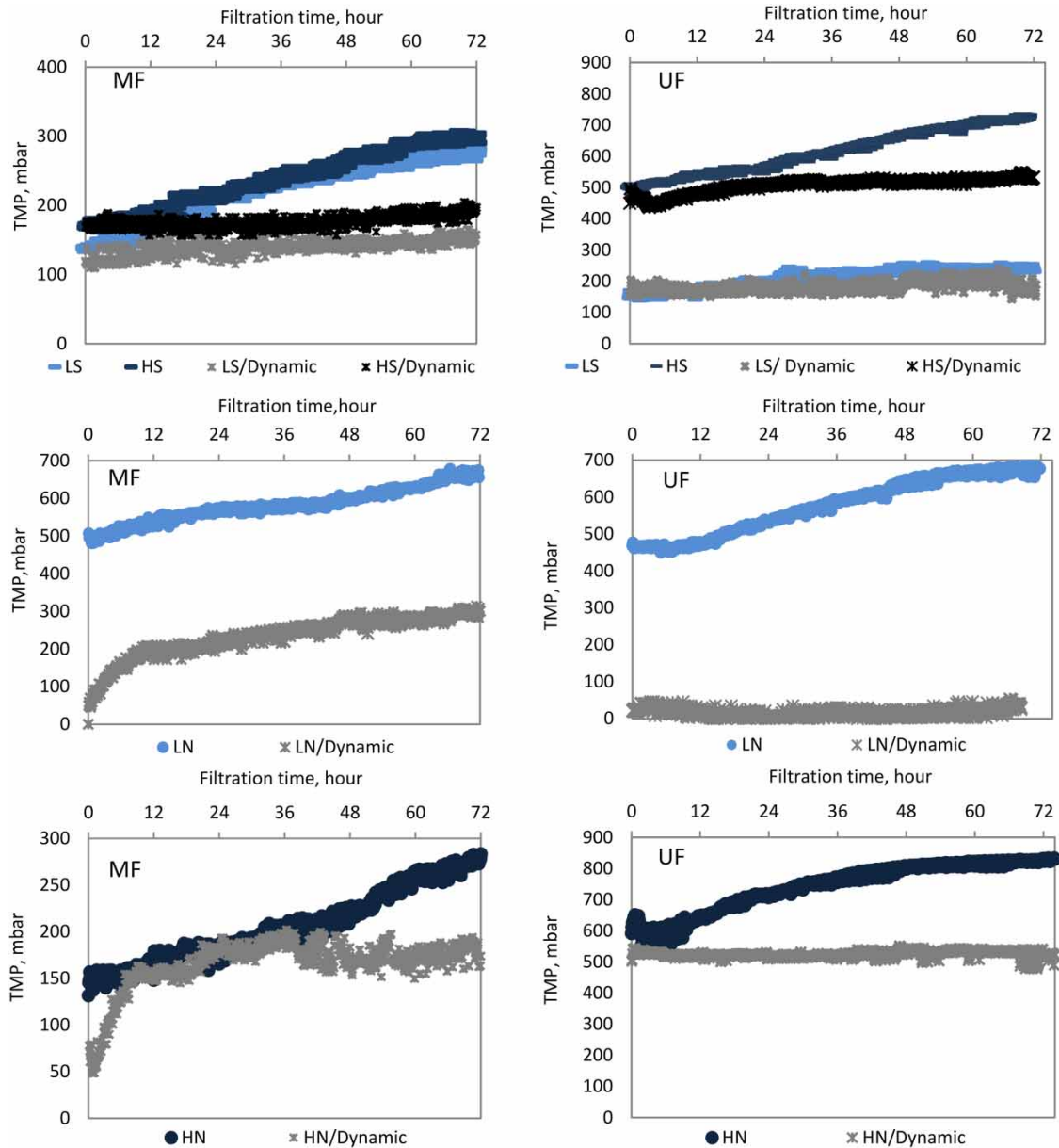
Figure 4 | Transmembrane pressure (TMP) values of the membranes for synthetic and natural water.

decreased using iron oxide when hydraulic backwashing was applied. The formed cake layer was relatively easily detached from the dynamic membrane by hydraulic backwashing in comparison to the sticky fouling layer of the bare membrane. Accordingly, low flux values were obtained with bare MF and UF membranes; on the other hand, the flux of the UF dynamic membrane decreased only 30% in LN and 38% in HN water (Figure 6). Regarding the MF dynamic membrane, the flux was decreased only 32% for HN and 42% for LN water.

As shown from Figure 6, flux initially declined over time for both types of membrane. The continous trend during the filtration with bare membranes indicated severe fouling, possibly due to pore blocking. But both dynamic membranes showed stable flux trends following the completion of the cake formation phase. High permeate fluxes, obtained by both dynamic membranes, can be explained by hindering as a result of pore blocking through the accumulation of cake layer on the membrane surface.
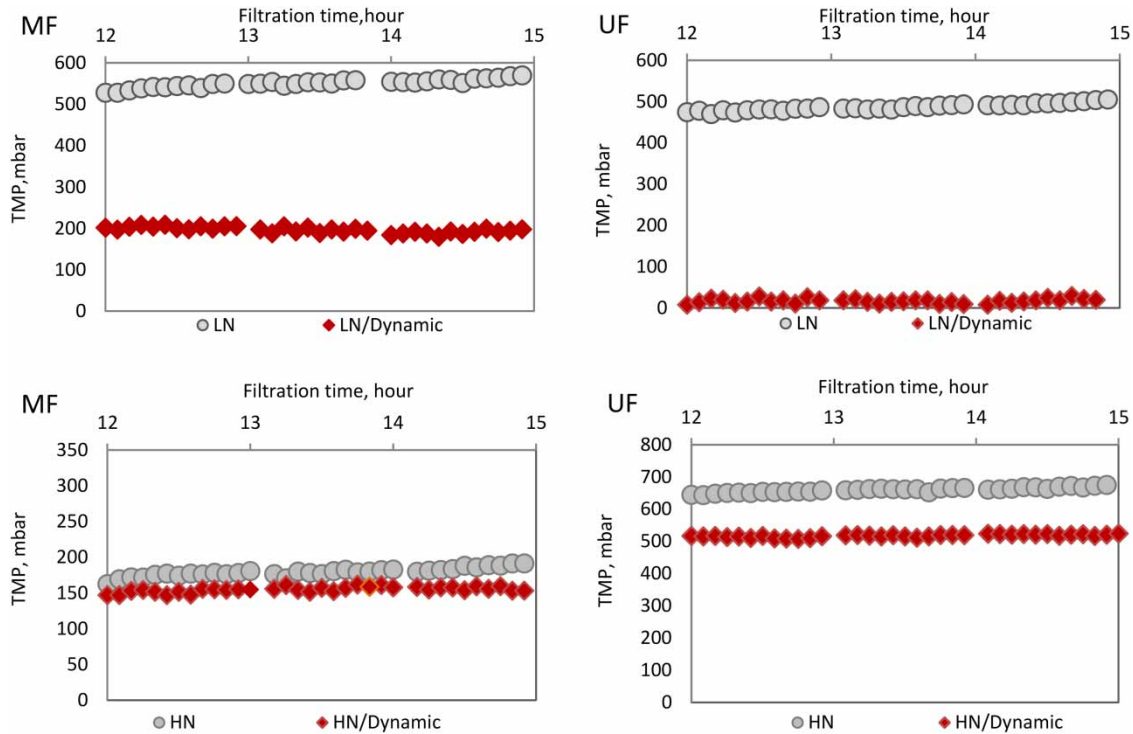
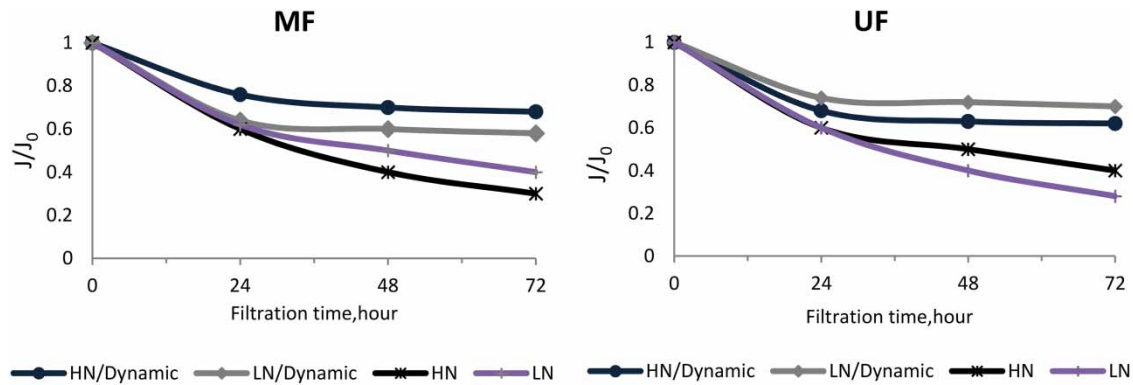**Figure 5** | Amplified graph of TMP between the 12th and 15th hours.

Figure 6 | Specific flux values.

Membrane resistance

The membrane resistance (Rm), cake resistance (Rc) and pore resistance (Rp) were calculated using the resistance in series model. Total resistance (Rt) can be expressed by Darcy's law:

$$R_t = \frac{\Delta P}{\mu.J} = R_m + R_c + R_p \tag{1}$$

where ΔP is the TMP; μ is the dynamic viscosity; and J is the permeate flux. Prior to each experiment, the pure water flux of the membrane was recorded by filtering 250 ml of Milli-Q water (J_o). R_m was calculated from the measurement of flux and TMP of the virgin membrane. R_t was calculated from the data at the end of the experiment. The cake layer on the membrane surface was wiped away with a sponge and TMP and flux were measured again with Milli-Q water ($Rm + Rp$). Fouling resistance for natural water filtration was given in Figure 7. As shown from Figure 7, reversible and irreversible resistance values in
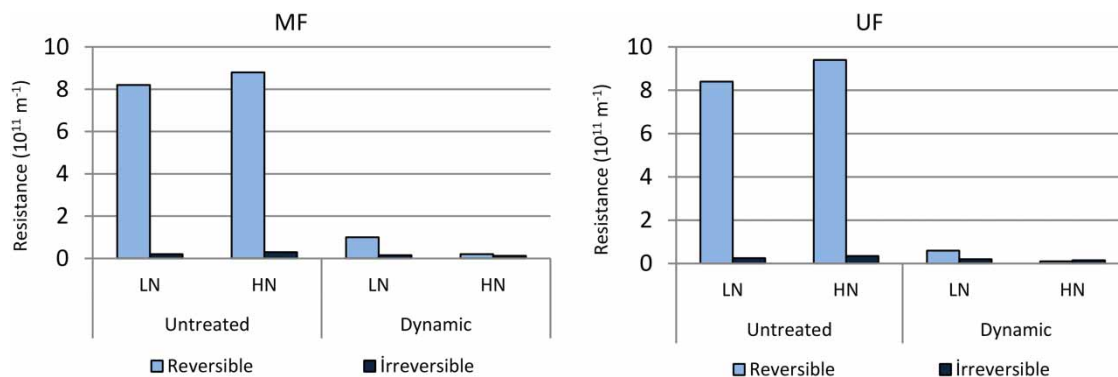
Figure 7 | Resistance values of raw and dynamic membranes.

HN water were $8.8 \times 10^{11} \, \mathrm{m}^{-1}$ and $0.3 \times 10^{11} \, \mathrm{m}^{-1}$, respectively, for MF. Reversible and irreversible resistances were decreased to $0.2 \times 10^{11} \, \mathrm{m}^{-1}$ and $0.12 \times 10^{11} \, \mathrm{m}^{-1}$, respectively, by the MF dynamic membrane. Similarly, reversible resistance was reduced to $0.6 \times 10^{11} \, \mathrm{m}^{-1}$ by the UF dynamic membrane. Irreversible resistance was also reduced to $0.2 \times 10^{11} \, \mathrm{m}^{-1}$ from $8.4 \times 10^{11} \, \mathrm{m}^{-1}$. By applying a dynamic membrane, reversible fouling reduced almost 2 orders of magnitude. Similar results were obtained by several researchers using dynamic membranes (Kim *et al.* 2017; Kim & Jang 2018; Qu *et al.* 2020). Reduction in irreversible resistances implies that iron oxide is a viable option that does not have an adverse affect on fouling, in contrast to strong oxidants. It is known that the dominant mechanism in membrane filtration by MF and UF membranes is sieving. However, following the cake layer formation on the membrane surface, cake filtration may become important for membrane filtration. The cake layer formed on the membrane surface reduces the access of small particles through the membrane pores and acts as a second barrier in membrane filtration. This phenomenon leads to the reduction in irreversible resistance, as well as reversible resistance. However, the efficiency of cake filtration may vary during the filtration period. A detailed model can be used to analyse further each component of membrane filtration such as filtration time, filtration volume, back washing period etc. to reveal relative balanced filtration conditions (Szwast *et al.* 2013; Qu *et al.* 2020).
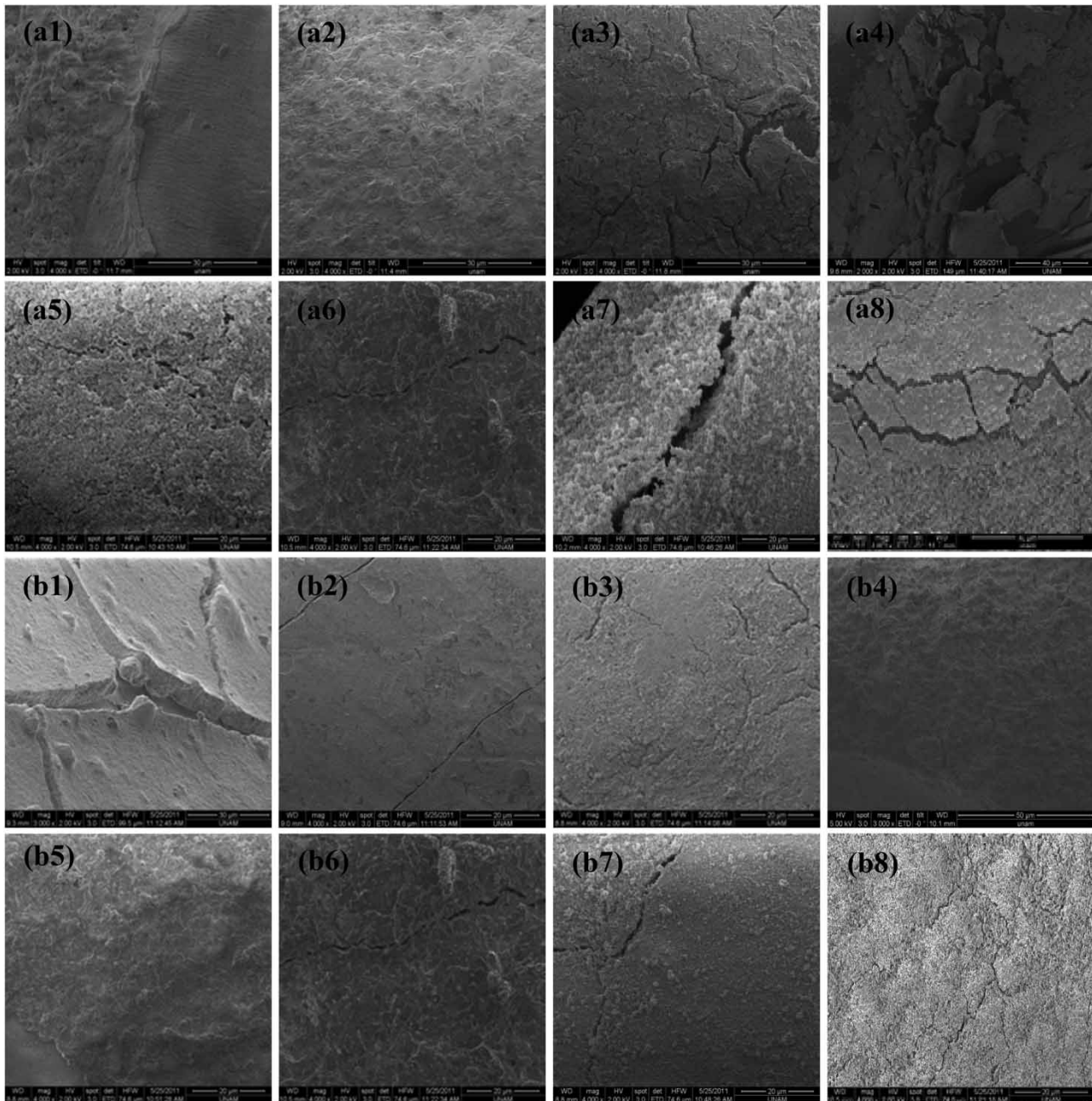
SEM micrographs

According to the results of the experiments, low flux and high resistance values were obtained without a dynamic membrane. On the other hand, dynamic membranes have lower resistance and significantly high flux values suggesting that iron oxide had a positive effect on both flux and resistance values. SEM micrographs of the fouled membrane appear in Figure 8. According to the micrographs, a loose and highly porous cake layer was formed by the dynamic membranes. The cake layer formed on the surface of the membranes did not cause any reduction in flux and could even be easily detached from the membranes through hydraulic backwashing. The significant decrease in reversible resistance contributes to membrane lifetime due to retardation of fouling. Moreover, the decline in irreversible resistance shows that iron oxide has a significant impact on fouling alleviation, thus the membrane can be used for a long time without significant pore blockage.

According to the SEM micrographs, the obtained loose porous structure indicates that iron oxide led to the accumulation of the flocs on the membrane surface rather than pores and acted as a second membrane layer contributing to the filtration. By contrast, foulant accumulation mainly occured in membrane pores without iron oxide.

CONCLUSION

In this study, lab-scale continuous operation of self-forming MF and UF dynamic membranes were investigated simultaneously by applying iron oxide as an alternative treatment option in those waters having NOM, iron and manganese. When the results were evaluated, the following conclusions were drawn from the results.

Iron oxide enhanced iron and manganese oxidation due to its adsorption/surface oxidation mechanism. Both dynamic membranes gave high removal rates and effluent concentrations of iron and manganese were below the limit values in synthetic water. Iron oxide led to significant DOC and UV_{254} removal, possibly due to floc formation in synthetic water. Thus,

Figure 8 | SEM micrographs of the fouled membranes in different water: (a) MF membranes: (a1) LS, (a2) HS, (a3) LS/Dynamic, (a4) HS/Dynamic, (a5) LN, (a6) HN, (a7) LN/Dynamic, (a8) HN/Dynamic; (b) UF membranes: (b1) LAS, (b2) HS, (b3) LS/Dynamic, (b4) HS/Dynamic, (b5) LN, (b6) HN, (b7) LN/Dynamic, (b8) HN/Dynamic.

iron oxide caused a significant increase in membrane productivity, maintained a stable TMP trend and retarded membrane fouling via cake layer formation on the membrane surface, acting as a second layer (cake filtration). It can be clearly shown from the flux and resistance values, as well as SEM observations that iron oxide resulted in deposition of particles on the membrane surface, forming reversible fouling by relatively large flocs with high porosity, while without iron oxide, foulants deposited mainly in membrane pores forming membrane fouling by small particles.

But iron oxide had a moderate effect on dynamic membranes regarding DOC and UV_{254} removal when they were operated with natural water. As for natural water, though dynamic membranes caused a significant reduction in membrane fouling, the

obtained DOC and UV$_{254}$ removal efficiencies were low. Furthermore, manganese concentration slightly exceeded the standards in HN water. Nevertheless, it is important to note that the removal results of DOC and UV$_{254}$ obtained in HN water are similar to those obtained in HS water. Dynamic membrane application is more succesful for HN than for LN water concerning DOC and UV$_{254}$ removal. MF and UF dynamic membranes contributed to a high flux for both types of natural water. The effect of iron oxide on TMP control resulted in reduction in reversible and irreversible fouling, thus contributed to fouling alleviation as well. Although there is no significant difference between MF and UF membranes in terms of the removal rate, they show different trends with regard to membrane fouling. The UF dynamic membrane gave high flux and maintained low and stable TMP for LN water, while MF was superior to UF for HN water. Dynamic membrane application led to the reduction of reversible and irreversible resistances to some extent in LN water. Nevertheless the effect of dynamic membrane application on fouling alleviation is much higher in HN water than in LN water. It seems that iron oxide led to the removal of high molecular weight fraction of organics, thus reversible fouling reduced almost 2 orders of magnitude through both types of dynamic membranes in HN water. Results suggested the success of both dynamic membranes in LN water in terms of iron and manganese removal.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Avsar, E., Toroz, I. & Hanedar, A. 2014 Chemical characterization of natural organic matter and determination of disinfection by product formation potentials in surface water of Istanbul (Omerli and Buyukcekmece Water Dam), Turkey. *Fresenius Environmental Bulletin* **23** (2A), 494–501.

Baalousha, M., Manciulea, A., Cumberland, S., Kendall, K. & Lead, J. R. 2008 Aggregation and surface properties of iron oxide nanoparticles: influence of ph and natural organic matter. *Environmental Toxicology and Chemistry* **27** (9), 1875–1882. https://doi.org/10.1897/07-559.1.

Bazilio, A. A., Kaminski, G. S., Larson, Y., Mai, X. & Tobiason, J. E. 2016 Full scale implementation of a second stage contactor for manganese removal. *Journal of American Water Works Association* **108** (12), 606–614. https://doi.org/10.5942/jawwa.2016.108.0184.

Byun, S., Davies, S. H., Alpatova, A. L., Corneal, L. M., Baumann, M. J., Tarabara, V. V. & Masten, S. J. 2011 Mn oxide coated catalytic membranes for a hybrid ozonation-membrane filtration: comparison of Ti, Fe and Mn oxide coated membranes for water quality. *Water Research* **45**, 163–170. https://doi.org/10.1016/j.watres.2010.08.031.

Celik, S. O. 2011 *Fe (ıı) ve mn (ıı)' nin birlikte giderimine dom etkisi ve batık membran filtrelerle ileri arıtımı (Effect of nom on the Removal of fe(ıı) and mn(ıı) and Advanced Treatment with Immersed Membrane System)*. PhD Thesis, Istanbul University, Turkey.

Cheng, Y., Zhang, S., Huang, T., Hu, F., Gao, M. & Niu, X. 2020 Effect of alkalinity on catalytic activity of iron manganese cooxide in removing ammonium and manganese: performance and mechanism. *International Journal of Environmental Research and Public Health* **17** (3), 784. https://doi.org/10.3390/ijerph17030784.

Choi, Y. H., Kim, H. S. & Kweon, J. H. 2008 Role of hydrophobic natural organic matter flocs on the fouling in coagulation-membrane processes. *Separation and Purification Technology* **62**, 531–536. https://doi.org/10.1016/j.seppur.2008.03.001.

Choi, K. Y. & Dempsey, B. 2004 In-line coagulation with low-pressure membrane filtration. *Water Research* **38** (19), 4271–4281. https://doi.org/10.1016/j.watres.2004.08.006.

Choo, K. H., Lee, H. & Choi, S. J. 2005 Iron and manganese removal and membrane fouling during uf in conjunction with prechlorination for drinking water treatment. *Journal Of Membrane Science* **267**, 18–26. https://doi.org/10.1016/j.memsci.2005.05.021.

Cote, P., Mourato, D., Gungerich, C., Russel, J. & Houghton, E. 1998 Immersed membrane filtration for the production of drinking water: case studies. *Desalination* **117** (1–3), 181–188. https://doi.org/10.1016/S0011-9164(98)00090-3.

Davies, S. H. R. & Morgan, J. J. 1989 Manganese (II) oxidation kinetics on metal oxide surfaces. *Journal of Colloid and Interface Science* **129**, 63–77. https://doi.org/10.1016/0021-9797(89)90416-5.

Demirel, E., Zhang, B., Papakyriakou, M., Xia, S. & Chen, Y. 2017 Fe$_2$O$_3$ nanocomposite PVC membrane with enhanced properties and separation performance. *Journal of Membrane Science* **529**, 170–184. https://doi.org/10.1016/j.memsci.2017.01.051.

Fakioglu, M., Karpuzcu, M. E., Toroz, I., Yildiz, F. & Oztürk, I. 2020 Removal of taste and odor from drinking water performance evaluation and upgrade options for the treatment plants in Istanbul. *Pamukkale University Journal of Engineering Science* **26** (3), 505–512. https://doi.org/10.5505/pajes.2019.78949.

Fan, J., Hobson, P., Ho, L., Daly, R. & Brookes, J. 2014 The effects of various control and water treatment processes on the membrane integrity and toxin fate of cyanobacteria. *Journal of Hazardous Materials* **264**, 313–322. https://doi.org/10.1016/j.jhazmat.2013.10.059.

Genz, A., Baumgarten, B., Goernitz, M. & Jekel, M. 2008 NOM removal by adsorption onto granular ferric hydroxide: equilibrium, kinetics, filter and regeneration studies. *Water Research* **42**, 238–248. https://doi.org/10.1016/j.watres.2007.07.005.

Gohari, J. R., Halakoo, E., Nazri, N. A. M., Lau, W. J., Matsuura, T. & Ismail, A. F. 2014 Improving performance and antifouling capability of PES UF membranes via blending with highly hydrophilic hydrous manganese dioxide nanoparticles. *Desalination* **335** (1), 87–95. https://doi.org/10.1016/j.desal.2013.12.011.

Hove, M., Hille, R. P. & Lewis, A. E. 2008 Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH. *Chemical Engineering Science* **63** (6), 1626–1635. https://doi.org/10.1016/j.ces.2007.11.016.

Illes, E. & Tombacz, E. 2006 The effect of humic acid adsorption on pH-dependent surface charging and aggregation of magnetite nanoparticles. *Journal of Colloid and Interface Science* **295** (1), 115–123. https://doi.org/10.1016/j.jcis.2005.08.003.

Karanfil, T., Erdogan, I. & Schlautman, M. A. 2003 Selecting filter membranes for measuring DOC and UV_{254}. *Journal of American Water Works Assosiation* **95** (3), 86–100. https://doi.org/10.1002/j.1551-8833.2003.tb10317.x.

Kim, B.-C., Nam, J.-W. & Kang, K.-H. 2017 Dynamic membrane filtration using powdered iron oxide for SWRO pre-treatment during red tide event. *Journal of Membrane Science* **524**, 604–611. https://doi.org/10.1016/j.memsci.2016.11.081.

Kim, K.-J. & Jang, A. 2018 Effect of heated aluminum oxide particles dynamic membranes on polymeric and ceramic microfiltration membrane. *Desalination and Water Treatment* **135**, 314–322. https://doi.org/10.5004/dwt.2018.22698.

Konieczny, K., Rajca, M., Bodzek, M. & Kwiecińska, A. 2009a Water treatment using hybrid method of coagulation and low-pressure membrane filtration. *Environment Protection Engineering* **35** (1), 5–22.

Konieczny, K., Sakol, D., Plonka, J. & Rajca, M. 2009b Coagulation-ultrafiltration system for river water treatment. *Desalination* **240**, 151159. https://doi.org/10.1016/j.desal.2007.11.072.

Kosmulski, M., Maczka, E., Jartych, E. & Rosenholmb, J. B. 2003 Synthesis and characterization of goethite and goethite–hematite composite: experimental study and literature survey. *Advances in Colloid and Interface Science* **103**, 57–76. https://doi.org/10.1016/S0001-8686(02)00083-0.

Kucukcongar, S., Sevimli, M. F. & Yel, E. 2013 Fractionation of natural organic matter (nom) by resin adsorption chramatography (rac). In: *2nd International Conference On Chemical, Environmental and Biological Sciences (ICCEBS)*, Dubai. UAE.

Lin, C. F., Huang, Y. J. & Hao, O. J. 1999 Ultrafiltration processes for removing humic substances: effect of molecular weight fractions and Pac treatment. *Water Research* **33** (5), 1252–1264. https://doi.org/10.1016/S0043-1354(98)00322-4.

Ma, B., Yu, W., Jefferson, W. A., Liu, H. & Qu, J. 2015 Modification of ultrafiltration membrane with nanoscale zerovalent iron layers for humic acid fouling reduction. *Water Research* **71**, 140–149. https://doi.org/10.1016/j.watres.2014.12.034.

Meyn, T., Altmann, J. & Leiknes, T. 2012 In-line coagulation prior to ceramic microfiltration for surface water treatment – minimisation of flocculation pre-treatment. *Desalination and Water Treatment* **42** (1–3), 163–176. https://doi.org/10.1080/19443994.2012.683106.

Miljatovic, I., Matosic, M., Cerneha, B. H. & Bratulic, D. 2004 Removal of natural organic matter by ultrafiltration and nanofiltration for drinking water production. *Desalination* **169** (3), 223–230. https://doi.org/10.1016/j.desal.2004.01.002.

Park, H., Kim, Y., An, B. & Choi, H. 2012 Characterization of natural organic matter treated by iron oxide nanoparticle incorporated ceramic membrane-ozonation process. *Water Research* **46**, 5861–5870. doi: 10.1016/j.watres.2012.07.039.

Park, P., Lee, C., Choi, S.-J., Choo, K., Kim, S.-H. & Yoone, C.-H. 2002 Effect of the removal of DOMs on the performance of a coagulation-UF membrane system production for drinking water. *Desalination* **145** (1–3), 237–245. https://doi.org/10.1016/S0011-9164(02)00418-6.

Park, S. & Yoon, T. 2009 Effects of iron species and inert minerals on coagulation and direct filtration for humic acid removal. *Desalination* **239**, 146–158. https://doi.org/10.1016/j.desal.2008.03.015.

Pikkarainen, A. T., Judd, S. J., Jokela, J. & Gillberg, L. 2004 Pre-coagulation for microfiltration of an upland surface water. *Water Research* **38** (2), 455–465. https://doi.org/10.1016/j.watres.2003.09.030.

Pinkic, S. 2014 *Development of Methods for the Separation and Characterization of Natural Organic Matter in dam Water*. Master Thesis, Durban Unviersity of Technology, Durban, SA.

Qu, F., Yang, Z., Yu, H., Zhou, H., Fan, G., He, J. & Rong, H. 2020 Algae-laden water treatment with ultrafiltration: effects of moderate oxidation by Fe(II)/ permanganate on hydraulically irreversible fouling and deposition of iron and manganese oxides. *Environmental Science: Water Research& Technology*. https://doi.org/10.1039/d0ew00833 h.

Shon, H. K., Vignesvaran, S., Aim, R. B., Ngo, H. H., Kim, I. S. & Cho, J. 2005 Influence of flocculation and adsorption as pretreatment on the fouling of ultrafilration and nanofiltration membranes: application with biologically treated sewage effluent. *Environmental Science and Technology* **39** (10), 3864–3871. https://doi.org/10.1021/es040105s.

Sung, W. 1980 *Catalytic Effects of the ϒ-FeOOH (Lepidocrite) Surface on the Oxygenation Removal Kinetics of Fe(II) and Mn(II)*. PhD Thesis, California Institute of Technology, Pasadena, California.

Sung, W. & Morgan, J. J. 1981 Oxidatif removal of mn(II) from solution catalyzed by the γ-FeOOH (lepidocrocite) surface. *Geochimica et Cosmochimica Acta* **45**, 2377–2383. https://doi.org/10.1016/0016-7037(81)90091-0.

Szwast, M., Szwast, Z., Grądkowski, M. & Piątkiewicz, W. 2013 Modelling of postproduction suspensions' concentration processes by 'batch' membrane microfiltration. *Chemical and Process Engineering* **34** (3), 313–325. https:// doi.org/10.2478/cpe-2013-0025.

Treguer, R., Tatin, R., Couvert, A., Wolbert, D. & Tazi-Pain, A. 2010 Ozonation effect on natural organic matter adsorption and biodegradation – application to a membrane bioreactor containing activated carbon for drinking water production. *Water Research* **44** (3), 781–788. https://doi.org/10.1016/j.watres.2009.10.023.

Tufekci, N. & Sarikaya, H. Z. 1996 Catalytic effects of high Fe(III) concentrations on Fe(II) oxidation. *Water Science and Technology* **34**, 7–8. 389-396. https://doi.org/10.1016/S0273-1223(96)00770-6.

Unal, A., Tufekci, N., Cakmakci, M. & Kinaci, C. 2011 Effect of organic and inorganic matters on the oxidation of Fe(II) in raw water from Omerli Dam. *Desalination and Water Treatment* **26**, 1–3. 194-200. https://doi.org/10/5004/dwt.2011.2151.

Van Beek, C. G. E. M., Hofman-Caris, C. H. M. & Zweere, G. J. 2020 Drinking water treatment and chemical well clogging by iron(II) oxidation and hydrous ferric oxide (HFO) precipitation. *Journal of Water Supply: Research and Technology-AQUA* **69** (5), 427–437. https://doi.org/10.2166/aqua.2020.140.

Yoshinaga, N. & Kanasaki, N. 1993 Synthesis of ferrihydrite and feroxyhte. *Clay Science* **9**, 43–51.

Yu, W., Brown, M. & Graham, N. J. D. 2016 Prevention of PVDF ultrafiltration membrane fouling by coating MnO_2 nanoparticles with ozonation. *Nature, Scientific Reports* **6**, 30144. doi: 10.1038/srep30144.

Yuan, W. & Zydney, A. L. 1999 Effects of solution environment on humic acid fouling during microfiltration. *Desalination* **122**, 63–76. https://doi.org/10.1016/S0011-9164(99)00028-4.

Zhang, M., Li, C., Benjamin, M. M. & Chang, Y. 2003 Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment. *Environmental Science & Technology* **37** (8), 1663–1669. https://doi.org/10.1021/es0260418.

Zularisam, A. W., Ismail, A. F., Salim, M. R., Sakineha, M. & Ozaki, H. 2007 The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes. *Desalination* **212**, 191–208. https://doi.org/10.1016/j.desal.2006.10.010.