Published in final edited form as:

Chem Eng J. 2017 November 1; 327: 573–583. doi:10.1016/j.cej.2017.06.128.

Naphthenic acids removal from high TDS produced water by persulfate mediated iron oxide functionalized catalytic membrane, and by nanofiltration

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Abstract

Oil industries generate large amounts of produced water containing organic contaminants, such as naphthenic acids (NA) and very high concentrations of inorganic salts. Recovery of potable water from produced water can be highly energy intensive in some cases due to its high salt concentration, and safe discharge is more suitable. Here, we explored catalytic properties of iron oxide (Fe_xO_y nanoparticles) functionalized membranes in oxidizing NA from water containing high concentrations of total dissolved solids (TDS) using persulfate as an oxidizing agent. Catalytic decomposition of persulfate by Fe_xO_y functionalized membranes followed pseudo-first order kinetics with an apparent activation energy of 18 Kcal/mol. Fe_xO_y functionalized membranes were capable of lowering the NA concentrations to less than discharge limits of 10 ppm at 40 °C. Oxidation state of iron during reaction was quantified. Membrane performance was investigated for extended period of time. A coupled process of advanced oxidation catalyzed by membrane and nanofiltration was also evaluated. Commercially available nanofiltration membranes were found capable of retaining NA from water containing high concentrations of dissolved salts. Commercial NF membranes, Dow NF270 (Dow), and NF8 (Nanostone) had NA rejection of 79% and 82%, respectively. Retentate for the nanofiltration was further treated with advanced oxidation catalyzed by Fe_xO_y functionalized membrane for removal of NA.

Keywords

persulfate; oil industry; advanced oxidation; nanoparticles; separation; degradation

1. Introduction

Increasing water scarcity and availability of safe water are critical challenges that need to be addressed in an energy efficient and sustainable way [1]. This demands minimization of water consumption by recycling, and treating effluent for safe discharge. Membrane-based

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technologies are extensively used for energy-efficient separations, which have shown immense potential in a wide variety of separations in aqueous and gas phase systems rejecting solutes with size ranging from few micrometers to nanometers [2–7]. Recently, membranes incorporated with some catalytic element have gained attention for decomposition of organic impurities owing to advantages, such as continuous mode of operation, along with their capability to separate solutes [8–10]. In this study, we explored the application of Fe_xO_y functionalized membranes and commercial nanofiltration (NF) membranes for remediation of the naphthenic acids (NA) from water containing high concentrations of total dissolved solids (TDS). Due to the presence of high TDS in the produced water samples used in this study, recovery of potable water by membrane separation can be energy intensive due to high osmotic pressure gradient and safe discharge with treatment (for remediation of NA) can be more feasible.

In a typical oil processing industry, approximately 2 m^3 to 3 m^3 of water is consumed per cubic meter oil produced during operations, such as the Clark process. During this process, NA and other oil extractible enters aqueous phase along with salts [11]. NA are one of the commonly found organic impurities in the oil sand process water and produced water from oil processing industries along with the high concentrations of dissolved salts [12–14]. NA is a mixture of surfactant-like molecules with a charged carboxylic group attached to the cyclic and acyclic aliphatic chains with molecular weights ranging from 200 g/mol to 500 g/mol . NA have been identified harmful to aquatic life due to their surfactant like nature. The mechanism of toxicity of NA has been identified through disruption of cell cytoplasmic membrane structure because of its surfactant-like properties with larger and more hydrophobic NA recognized as more toxic [15]. Study on mitigation of NA by different processes like biodegradation, photolysis, advanced oxidation, coagulation-flocculation, and adsorption have been carried out [16–19]. A combination of techniques also has been studied for the cost-effective remediation and full-scale implementation [20–22]. Microbial technology has shown promising results for mitigation of NA. However, high chlorine content and the need for faster throughput limits the application of this technology [12]. Advanced oxidation processes have proven to be useful in the oxidation of NA in several studies [12].

In this work, Fe_xO_y functionalized membrane catalyzed oxidation using persulfate as an oxidizing agent was investigated. Persulfate salts have attracted considerable attention in recent years as an in-situ oxidizing agent [23–26]. The persulfate ion has a reduction potential of 2.1 V ($\text{E}^\circ\text{S}_2\text{O}_8^{2-}|\text{SO}_4^{2-}$ vs. NHE) and generates sulfate free radicals with a higher reduction potential of 2.4 V ($\text{E}^\circ\text{SO}_4^{\bullet-}|\text{SO}_4^{2-}$ vs. NHE). Different modes of activation, such as UV light, heat, and transition metals have been investigated for decomposition of persulfate [23, 27]. Thermal fission of $-\text{O}-\text{O}-$ linkage in the persulfate to generate sulfate free radicals is slow at a lower temperature. Iron oxides are also known to catalyze the generation of sulfate free radicals and enables oxidation on shorter time scales [28]. Persulfate decomposition catalyzed by Fe_xO_y nanoparticles is a surface phenomenon. Fe(II) sites on iron oxides are responsible for the generation of sulfate free radical as shown in Eq. 1 [29]. Activation of persulfate by Fe_xO_y particle surface has been explained in analogy with Fenton's reaction as follows [30]:

$$, K_1^{[31, 32]} = 15.33 \text{ M}^{-1}\text{s}^{-1}$$

$$, K_2^{[31, 32]} = 4.6 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$$

$$, K_3^{[31, 32]} = 6.62 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$$

$$, K_4^{[31, 32]} = 9.4 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$$

Sulfate radicals produced in the process are also scavenged by Fe(II) sites as shown in Eq. 2. The efficiency of persulfate to decompose target organics depends on $Fe^{2+}/S_2O_8^{2-}$ ratio, and lower $Fe^{2+}/S_2O_8^{2-}$ ratio has shown more efficiency for overall degradation of the target molecule [33, 34]. Sulfate radicals can also interact with water generating hydroxyl radical (as shown in Eq. 4), which is also a strong oxidizing agent. However, it has been demonstrated in several studies that sulfate radicals are dominant in the system at acidic to near neutral pH [35, 36]. As reaction proceeds, Fe(II) sites will be converted to Fe(III) sites, and the catalytic activity of the Fe_xO_y particles will reduce. Regeneration of the catalytic activity therefore requires restoration of Fe(II) sites by reduction ($E^{\circ}Fe^{3+}/Fe^{2+} = -0.037 \text{ V}$ vs NHE and $E^{\circ}Fe^{2+}/Fe^0 = -0.447 \text{ V}$ vs. NHE). Reducing agents, such as ascorbic acid ($E^{\circ} = -0.104 \text{ V}$ vs. NHE at pH = 5.75) and sodium borohydride ($E^{\circ}BH_4^-/[H_2BO_3^-] = 1.24 \text{ V}$ vs. NHE) have been reported in various studies for reduction of Fe(III), and thus can enable regeneration of the catalytic systems. Also, to improve cost efficiency and lower contamination of water through catalyst leaching, recovery or immobilization of catalyst particle is important. We have demonstrated immobilization of iron nanoparticles by the capture of metal ions in the pores of membrane filled with polyelectrolyte followed by their reduction, and membrane regeneration by reloading iron through repeated cycles [8]. Aggregation of the nanoparticles was also minimized by the cross-linked polymer matrix thus availing high surface area of the particles enhancing catalytic properties. The immobilized nanoparticles enable application of advanced oxidation in a continuous mode through the generation of free radicals in membrane domain.

Reaction mechanism of sulfate free radicals with the carboxylic acids is proposed to be considerably different from the reaction of hydroxyl radical. Hydroxyl radical reacts with the aliphatic carboxylic acids through abstraction of hydrogen from the aliphatic chain of the

acids [37]. On the other hand, Madhavan et. al. [38] demonstrated that for saturated aliphatic acids, the reaction of sulfate radicals predominately proceeds through oxidation of the carboxylate group, resulting in decarboxylation. Authors observed higher yields of CO_2 for reactions of sulfate radical with saturated carboxylic acids as compared to hydroxyl radical reactions. The mechanism suggests reaction of sulfate radical with naphthenic acids will produce aliphatic chains which will have a considerably lower solubility in the water. Studies have reported a significant reduction in the concentration of NA by persulfate based oxidation using different model compounds, such as cyclo-hexanoic acid, commercial NA mixtures and produced water samples [39, 40]. The decomposition of the NA by iron is proposed through adsorption of NA on the iron surface forming complexes followed by sulfate radical based degradation. Drzewicz et. al. [40] observed cyclic NA, with 1 to 3 degree of unsaturation were preferentially removed at 20 °C by persulfate based oxidation using zerovalent iron. Degradation of similar NA was also observed by Sohrabi et. al. [41] in the initial period of extended study over 110 days, in the absence of a catalyst. Persulfate was able to degrade all the NA eventually, and the toxicity of oil sand produced water (OSPW) contaminated with NA was lowered.

Separation of NA from produced water using membranes can also be utilized to reduce the volume of produced water requiring advanced oxidation, thus improving the chemically efficiency of overall process. NF and Reverse osmosis (RO) membranes have the capabilities for separation of small organics from aqueous solutions [5]. However, it is essential that NF membranes should have a negligible rejection for monovalent ions to minimize the osmotic pressure gradient along with the high rejection for NA. Membranes with high rejection of salt, such as RO membranes, will require an operating pressure more than the osmotic pressure of the produced water. The estimated operating pressure of produced water samples used in this study is quite significant (120 bar, Sec. 3.4), and recovery of potable water (by separating salts as well) will demand high energy for separation and design of specific membrane modules for handling high operating pressure. NF membranes are suitable for the treatment of produced water because of their low rejection for monovalent ions at high ionic strengths and high rejection for NA [42, 43]. NA have molecular weights ranging from 200 g/mol to well over 500 g/mol along with the presence of the charged carboxylate group and branching. This feature of NA makes them a suitable candidate for separation by NF membrane. In this study, separation of NA by two commercial nanofiltration membranes and treatment of concentrated stream by membrane catalyzed advanced oxidation was also studied.

In our previous work, we reported the application of iron/iron oxide functionalized membrane for removal of selenium from scrubber water by reductive pathway [44]. Here, application of membrane-based technology for NA remediation from high TDS water was investigated. To the best of our knowledge, this is the first study reporting degradation of NA by Fe_xO_y functionalized membrane using persulfate as an oxidizing agent. The primary objective of the research was to reduce the oil extractible fraction from the produced water samples. For the same, Fe_xO_y functionalized membranes were synthesized by in-situ polymerization of acrylic acid in membrane pores followed by capture of Fe^{2+} and reduction to zerovalent iron nanoparticles. The immobilized Fe nanoparticles were then oxidized by hydrogen peroxide forming iron oxide (Fe_xO_y) nanoparticles in the membrane pores. The

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Fe_xO_y functionalized membranes were characterized by scanning electron microscopy, infrared spectroscopy, contact angle measurements, and energy-dispersive X-ray spectroscopy. Activation of persulfate and decomposition of NA catalyzed by Fe_xO_y functionalized membrane were studied with the model mixture and produced water samples. Commercial NF membranes were also investigated for separation of NA from produced water samples. Advanced oxidation of NA catalyzed by Fe_xO_y functionalized membranes combined with NF based separation for remediation of NA from high TDS water as demonstrated in this study can be a sustainable option.

2. Materials and Methods

2.1. Chemical reagents

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The NA mixture, magnetite particles, potassium persulfate, sodium chloride, ferrous chloride tetrahydrate, potassium persulfate, and ethanol, were obtained from Sigma-Aldrich. Acrylic acid, ammonium persulfate, and N,N'-methylene bisacrylamide (NNMA) were purchased from Acros Organics. Commercial membranes PVDF400HE, NF8 were supplied by Nanostone Water Co., Oceanside, California, and DOW FLIMTECH NF270 membrane was obtained from the DOW Chemical Company. Produced water samples were provided by Chevron (Refer SI, Table S2 for water composition). Deionized (DI) water used at all stages of the experiments was obtained (final resistivity $<18.2 \text{ M}\Omega$, TOC $<1 \text{ ppb}$) using a Purelab flex water purifier from ELGA Lab water. All chemicals were of reagent grade and were used with as received.

2.2. Membrane functionalization

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Functionalization of the PVDF membrane (refer SI, sec S3 for PVDF membrane details) was carried out by in-situ polymerization, as reported in our earlier research [8]. Polymerization solution composed of 10 ml acrylic acid, 1 mole% N,N'-methylene bisacrylamide (as a crosslinker) and 1 mole% ammonium persulfate (as initiator) in 50 ml of deoxygenated DI water. After soaking the membrane in polymerization solution for 10 min, the membrane was heated in a convection oven for 2 h at 90°C then cleaned with ethanol to remove any unpolymerized residues. Simplified scheme for the polymerization of acrylic acid is shown in Fig.1. These membranes are referred as polyacrylic acid functionalized (PAA) membranes. PAA functionalized membrane was then ion exchanged with sodium (1L of 2000 mg/L as NaCl) at pH 11 followed by an exchange with iron (200 ml of 200 mg/L as Fe^{2+}). Immobilized iron was further reduced to zerovalent iron by NaBH_4 (500 mg/L) over two h at 23°C to form zerovalent iron nanoparticles. Controlled oxidation with dilute H_2O_2 (76 mM) was carried out for 10 minutes to form a passive oxide layer with an iron core (referred as Fe_xO_y nanoparticles). Membranes with immobilized Fe_xO_y nanoparticles are referred as iron oxide (Fe_xO_y) functionalized membranes.

2.3. Membrane characterization

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The surface of the functionalized membranes was studied using scanning electron microscope (SEM, Hitachi S4300). X-ray photoelectron spectroscopy (XPS) characterization was conducted using the Thermo Scientific Al K-Alpha X-ray Photoelectron Spectrometer with a photon energy of 1486.6 eV. Each XPS spectrum was an

average of ten scans. X-ray diffraction patterns were obtained using SIEMENS D500 diffractometer with Al-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at an accelerating voltage of 40 kV and a current of 20 mA. Transmission electron microscopy characterization of the Fe $_x$ O $_y$ nanoparticles was carried out using TEM-JEOL 2010F. FTIR spectra of the membrane surfaces were obtained by Agilent 680 FTIR with an MCT detector scanned in the range of 900 cm $^{-1}$ to 4000 cm $^{-1}$. Iron content was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian VISTA-PRO) analysis of the nitric acid digested solution of the membrane. Contact angle measurements were done using a drop shape analyzer equipped with high definition camera (Kruss DSA100). The permeability of the membrane was measured with a Sterlitech HP4750 pressure stirred cell operated in a dead-end mode (refer SI, Fig. S1 for flow diagram).

2.4. Persulfate decomposition and kinetic analysis

Persulfate analysis was carried out by spectroscopic analysis after the reaction of analyte solution with potassium iodide (refer SI, Sec S1.1 for details). Persulfate decomposition by Fe $_x$ O $_y$ functionalized membranes was studied at different temperature in the convective mode of operation in a dead-end filtration cell. Separate pieces of Fe $_x$ O $_y$ functionalized membranes were used to study decomposition at various temperatures. In a typical persulfate decomposition experiment, persulfate solution (50 ml of 500 mg/L) was passed through the Fe $_x$ O $_y$ functionalized membrane (13.2 cm 2) at different flow rates and temperature, and permeate concentration was determined. A lower concentration of persulfate (500 mg/L) as compared to the rest of the study (5000 mg/L) was used to lower the extent of oxidation of Fe $_x$ O $_y$ (Fe(II) to Fe(III)) immobilized in the membrane during kinetic analysis.

2.5. Naphthenic acid (NA) degradation

NA was analyzed using solvent extraction followed by infra-red adsorption measurements (refer SI, Sec S1.2 for details). Degradation studies of NA were carried out either with produced water, synthetic solution (NA obtained for Sigma-Aldrich dissolved in produced water samples, refer SI, Sec S1.4 for details) or NA in DI water. Prior to the degradation studies, produced water samples were prefiltered with 0.22 μm filter to remove suspended solids (refer SI, Fig. S8 for images). Reactions were carried out at 23 $^{\circ}\text{C}$ and pH around five unless stated elsewhere. No attempts were made to control the pH of the solution during degradation study. Reactions were carried out in batch mode for 24 h unless specified. Reactions were performed in the presence of persulfate (5000 mg/L) along with either 5 mM Ferric ion or 1000 mg/L of magnetite nanoparticles (as obtained from Sigma-Aldrich), or Fe $_x$ O $_y$ functionalized membrane (13.2 cm 2 with an average iron loading of 12 g/m 2), as specified. NA degradation studies in the convective mode were carried out in stirred pressure cell operated in a dead-end mode of filtration. Details of the residence time calculation can be found in SI, sec S1.5.

2.6. Naphthenic acid (NA) separation by nanofiltration (NF)

NA separations by NF membrane were studied in Sterlitech filtration cell operated in dead-end mode. Two commercial membranes, DOW FLIMTECH NF270 and Nanostone Water Co. NF8, were used for the study. Before every experimental run, the membranes were

rinsed with DIUF water and were tested for defects by measuring salt rejection using a magnesium sulfate standard. The rejection was defined as in Eq. 5:

$$R = \left(1 - \frac{C_{\text{per}}}{C_{\text{feed}}} \right) \times 100 \quad \text{Equation 5}$$

Where, C_{per} and C_{feed} are the permeate and feed concentration of the species. Pressure normalized water flux (permeability) of the membranes was determined before and after the experiments with produced water samples. The flux was measured, by recording the mass of the permeate through the RS232 output of the balance at a sampling rate of 50 sec^{-1} . Produced water flux by NF membranes was monitored for 20 h in cross-flow setup. 10 L of feed produced water was used, and 10 ml of the permeate (0.1% recovery) was taken out for analysis during each sampling (10 samples over the course of the experiment). Produced water flux was also monitored with increasing recovery (up to 80 %) in dead-end mode filtration cell.

3. Results and discussion

3.1. Membrane characterization

Polymerization of acrylic acid in the membrane pores was initiated by sulfate free radicals generated from ammonium persulfate at 90°C . In-situ polymerization resulted in an average weight gain of 12% of the final weight. The surface of the membranes was analyzed by FTIR to confirm the presence of carboxylic groups introduced by polyacrylic acid (PAA) in the membrane matrix. FTIR of the PVDF and PAA functionalized membrane are shown in Fig. 2, with nonwoven backing material as the substrate for the analysis. Absorption stretch for C-F bond from 1100 cm^{-1} to 1300 cm^{-1} was observed for both the membranes. Stretch at 1650 cm^{-1} was observed for the PAA functionalized membrane, indicating the presence of introduced carboxyl functionality in the functionalized PVDF membrane. An additional stretch between 3500 cm^{-1} and 2900 cm^{-1} for PAA functionalized membranes showed the presence of OH from the carboxylic functionalities in the membrane domain. In addition, elemental analysis of the surfaces of membranes showed an increase in O/C ratio from 3.52 % to 20 % after functionalizing PVDF membrane with polyacrylic acid (Refer SI, sec S4.1 for details).

PAA is pH sensitive polymer which tends to swell at $\text{pH} > 4.5$. The swelling of PAA gel in the membrane domain will lower the pore volume for water to flow and therefore, reduce its permeance [46]. The membrane flux was measured at different pH to confirm polymerization in the membrane pores, as indicated in Fig. S6. Higher flux was noted at pH four as compared to pH 6 suggesting successful polymerization in the membrane domain. Predicted effective pKa of the carboxylic group in the membrane pore was around 4.8 (refer SI, sec S5 for details).

The permeability of the membrane was measured at different stages of functionalization. The permeability of the membranes reduced from $148.19 \text{ liters/m}^2/\text{h}/\text{bar}$ (LMH/bar) to $8.17 \text{ LMH}/\text{bar}$ (with a standard deviation of $3 \text{ LMH}/\text{bar}$) after functionalizing the PVDF

membrane with PAA (Fig. 3, e and f). SEM images of the membrane surface were obtained to study the changes in the pore geometry before and after functionalization of PVDF membrane with PAA. SEM of the top surface showed a decrease in surface porosity of the membrane after functionalization, suggesting the presence of polyacrylic acid on the membrane surface and in membrane pores (Fig. 3, a and b). The mean pore size of the membrane reduced from 37 nm to 14 nm after functionalization (Fig. 3, c and d). The observed lower permeability for functionalized membrane can, therefore, be explained by the lower volume of pores for water to flow through. In our earlier study, an excess of PAA layer on membrane surface was observed by studying surface morphology using the depth profile using X-ray photoelectron spectroscopy [44]. The excess of PAA layer on the membrane surface is due to polymerization of residual acrylic acid on the membrane surface.

The contact angle of the membrane at different stages of functionalization was measured using a sessile drop method. Contact angle lowered from $62^\circ \pm 5^\circ$ for PVDF membrane to $46^\circ \pm 8^\circ$ for PAA functionalized membrane. Lower contact angle suggests more hydrophilic surface of the PAA functionalized membrane, which is due to the presence of carboxylate functionalities. The contact angle of $43^\circ \pm 7^\circ$ was observed for Fe_xO_y functionalized membranes suggesting no significant change in hydrophilicity after nanoparticle immobilization.

Application of these membranes in advanced oxidation necessitates stable PAA network in the pores of substrate membrane in an oxidative environment. In this study, the polymeric (PAA) network was cross-linked with methylene bisacrylamide. Entanglement of the cross-linked polymeric network within the pores of PVDF membrane enabled confinement in the membrane pores. The stability of polymeric network in the membrane domain was investigated by soaking membrane in 5000 mg/L persulfate solution at 70°C for 3 h and monitoring its permeability. The permeability of the membrane (at pH 7) were 4.35 LMH/bar and 4.86 LMH /bar before and after soaking it in persulfate solution. The difference was within experimental error. Any loss in the polymer from the membrane domain should result in an increase in membrane permeability, and complete loss of polymer from the membrane pore should restore the permeability to its initial value (148 LMH/bar).

Cross section images were obtained by SEM and with integrated energy-dispersive X-ray (EDS) detector to confirm the presence of Fe_xO_y particles in the functionalized membrane matrix, as shown Fig. 4. The average size of the iron oxide particles was $66\text{ nm} \pm 17\text{ nm}$. Analysis of the solution after acid digestion of the Fe_xO_y functionalized membrane showed an iron content of 12 g/m^2 of the membrane. Iron content in the membrane matrix can be increased by repetitive ion exchange cycles, with Na and Fe as demonstrated in our earlier study [44]. For this study, only one cycle of ion exchange was performed with the PAA functionalized membrane.

TEM characterization (as shown in Fig.S7) of the iron oxide nanoparticles was carried out with the solution phase synthesized particles in the absence of membrane domain. Synthesized particles were spherical in shape (Fig. S7, a) and had a core-shell structure (Fig.

S7, c). SAED pattern was observed similar to magnetite particles (Fig. S7, d), suggesting the major fraction of oxide layer was magnetite. EDS line scan of the nanoparticle showed higher Fe/O in the core as compared to the shell (Fig. S7, e), confirming the presence of an oxide shell (about 5 nm) on the nanoparticles. To further analyze the content of iron by oxidation state, nanoparticles were dissolved in dilute HCL (5%) and analyzed by a spectroscopic technique using 1,10-phenanthroline as a complexing agent, as described SI, sec S1.3. The analysis showed 10.1 % Fe(III) content of the total Fe present in the nanoparticles.

3.2. Persulfate activation

Catalytic properties of the Fe_xO_y functionalized membrane was studied by the decomposition of persulfate in the membrane domain. In a typical persulfate decomposition experiment, persulfate solution (500 mg/L) was passed through the Fe_xO_y functionalized membrane at different flow rates and temperature, and concentration of persulfate in the permeate was determined. The residence time of solution in the membrane pores was controlled by changing the pressure difference across the membrane. A decrease in persulfate concentration was observed after passing persulfate solution through Fe_xO_y functionalized membrane, as shown in Fig. 5. Control study carried out with non-functionalized membrane showed a negligible decrease in persulfate concentration. Residence time of the solution in the membrane domain was calculated using plug flow reactor model to fit the kinetics of the reaction. Data was observed to fit pseudo-first order kinetics with the rate proportional to the concentration of persulfate anion as indicated by Eq. 6. The temperature dependent rate constants were determined from the slope of $\ln(C_t)$ vs. residence time at different temperatures. The apparent activation energy of 18 Kcal/mole, was obtained from the Arrhenius fit using the determined rate constants and corresponding temperature.

$$\frac{dS_2O_8^{2-}}{dt} = k \times [S_2O_8^{2-}] \quad \text{Equation 6}$$

Reduction of catalytic property happened with the repeated use of the Fe_xO_y functionalized membrane. The final conversion of persulfate decreased with each pass of persulfate solution (50 ml), for an average residence time of 5.2 sec, as shown in Fig. 6. Higher conversion of persulfate was observed on treatment of the Fe_xO_y functionalized membrane with NaBH_4 after the fourth pass indicating the catalytic property of the membrane was restored up to 90% of its initial activity.

Fe_xO_y functionalized membrane turned brown from black after its exposure to persulfate solution. The color change suggests conversion of iron (II) oxide to iron (III) oxide immobilized in the membrane. Oxidation state and iron leached at each stage of the regeneration process of Fe_xO_y functionalized membrane (1.25 cm^2 , Iron loading: 9.1 g/m^2) was analyzed by a colorimetric technique using 1,10-phenanthroline as a complexing agent (refer SI sec S1.3 for details). Fe_xO_y functionalized membrane showed an increase in Fe(III) content from 10.1 % to 67.3 % when exposed to 500 ppm persulfate solution for 3 hours. A

loss of 5% of the total Fe content was observed after the exposure to persulfate solution. During the regeneration process, using NaBH_4 as a reducing agent (1000 ppm, V: 20 ml, t: 12 h), Fe(III) content reduced from 67.3 % to 19 % and iron leached from the membrane was 3 % of the total Fe content. Also, the membrane had significant black stains on the surface, indicating partial restoration of Fe(II) oxide. XPS characterization of the Fe_xO_y functionalized membrane at various stages of treatment was also done (refer SI, sec S4.2). However, no significant change in nature of Fe2p spectra was observed for the membrane samples. Results indicate that regeneration cycle can actually restore the catalytic property of the Fe_xO_y functionalized membranes.

The Fe_xO_y particles formed under our experimental conditions are core-shell in nature with an oxide layer formed on the zerovalent iron core (SI, sec S6). In a detailed study carried out by Kusic et. al. [48] on iron-catalyzed persulfate decomposition, the author developed a model for persulfate decomposition catalyzed by ferrous ions and zerovalent iron. The rate of persulfate and hence the generation of sulfate radicals is significantly enhanced by the Fe(II) sites present on the Fe_xO_y nanoparticles. During the exposure of persulfate solution to the magnetite nanoparticles, Fe(II) sites on the surface will be depleted, and diffusion of the reactant to the particle core will limit the rate of reaction. After membrane regeneration, the proportion of Fe^0 and Fe(II) increased as determined by phenanthroline method, restoring the catalytic sites and improving the catalytic performance of the membrane.

3.3. Naphthenic acid (NA) degradation

3.3.1. Naphthenic acid (NA) oxidation in batch mode—Initial oxidation experiments for NA were carried out in the presence of ferrous ions. The pH of produced water samples was lowered to 3.5 to prevent the precipitation of iron in the form of $\text{Fe}(\text{OH})_3$. For produced water samples, 95% (5% - Detection limit of DTIR) degradation of NA was observed, with potassium persulfate (5000 mg/L) at 23 °C, in the presence of 5 mM Fe^{2+} and reaction time of 10 min. Ferrous ions were observed to be very efficient in oxidizing NA from produced water samples. Studies were further directed towards the heterogeneous catalysis by magnetite nanoparticles for persulfate based oxidation. The control run performed with magnetite nanoparticles (1000 mg/L) and no oxidizing agent, showed no significant adsorption of NA (<5 mg/L, detection limit) on magnetite nanoparticles. For produced water samples, 38% of NA was degraded in the presence of an oxidizing agent. Experiment repeated for the synthetic solution showed 46% degradation of NA. Lower NA degradation efficiency was observed for Fe_xO_y functionalized membrane in the batch-mode operation, as shown in Fig. 7, indicating diffusion resistance for reactants limiting the accessibility of the Fe_xO_y particles located inside the membrane matrix. The concentration of the dissolved Fe(II) concentration was less than 10 ppm (7% of the initial iron leached from the Fe_xO_y functionalized membrane) suggesting soluble iron should not have any significant contribution to the overall catalytic degradation. In summary, homogeneous catalysis showed the maximum potential for NA degradation. The nanoparticle/heterogeneous catalysis study showed a lower reactivity as expected (homogeneous vs. heterogeneous) followed by Fe_xO_y functionalized membranes.

As observed in Fig. 6, the catalytic property of the membrane reduced after exposing it to persulfate solution, due to conversion of Fe(II) oxide to Fe(III) oxide. Reduction in the catalytic effectiveness of the membrane was further investigated by a series of degradation experiments conducted for 8 h cycles, under similar conditions. After the first run, NA concentrations reduced by 50 %. However, only 15% reduction in concentration (by oil extraction method) was observed after the second run for the same membrane. Iron leached in first and second runs were 14.4 % and 12.3 %, respectively, which suggests loss in reactivity after the second cycle is due to complete oxidation of iron to Fe(III) state. Functionalized membrane was then treated with NaBH_4 for regeneration of catalytic activity by reduction of iron. The third run after regeneration resulted in 18% reduction in concentration, and a loss of 16.2 % iron. The lower efficiency observed even after regeneration was due to a significant portion of iron leached over its exposure to persulfate solution (slightly acidic media) over three runs. Therefore, an ion exchange cycle was performed on the same piece of the membrane as described in experimental section to restore the iron content. After restoration, reduction in NA concentration by 56 % was observed after the fourth run of degradation experiment. Thus, our study over repetitive cycles suggests restoration of lost iron is critical for catalytic activity of the membrane. SEM images of the membrane before and after the experiment (as shown in SI, S10) showed some aggregation of nanoparticles after PS exposure. Reduction in the effective surface area due to aggregation will also reduce the catalytic efficiency of the Fe_xO_y functionalized membrane to some extent. Additionally, the total organic content (TOC) of the solution measured before and after the first run of the mentioned degradation experiment showed a decrease by 12%. The reduction in TOC is due to partial mineralization.

3.3.2. Naphthenic acid (NA) oxidation in convective mode—In a series of experiments, produced water samples were passed through the Fe_xO_y functionalized membrane in dead-end mode filtration for an average flux of 2 LMH to simulate realistic process conditions. In the batch mode of the study, diffusion of the reactant to the catalytic sites is a major factor limiting the rate of kinetics. Convective flow through the membrane pores exposes water to the Fe_xO_y particles in the membrane pore more than the batch process by lowering mass transfer resistance. The preliminary run showed 44% reduction (34 mg/L to 19 mg/L) in the concentration of NA from the produced water samples (Fig. 8). No significant adsorption of NA on Fe_xO_y functionalized membrane was observed in a control experiment in the absence of $\text{K}_2\text{S}_2\text{O}_8$. NA concentrations for the synthetic solution were lowered by 47% (38 mg/L to 20 mg/L) further verifying oxidation of NA in the produced water matrix. Produced water samples were passed through the Fe_xO_y functionalized membrane twice at a controlled temperature (22 °C or 40 °C) with the addition of persulfate (5000 mg/L) at each pass with a goal of further reducing NA concentrations. A significant drop in NA concentration (by 42%) was observed during the second pass, lowering final concentration to less than 10 mg/L at 40 °C. In-series oxidative treatment by Fe_xO_y functionalized membrane can thus be employed to meet the discharge standards.

3.4. Naphthenic acid (NA) concentration by nanofiltration (NF) membranes

Organic and inorganic contents of the produced water used in this study are summarized in table S1. Produced water samples had high concentrations of monovalent ions (Na^+ and Cl^-). Lower activity of ions has been observed for high ionic strengths in several studies. For the ionic strength of 3 mole Kg^{-1} (ionic strength of produced water), Bates et.al. [49] observed an activity coefficient of 0.71 and 0.50 for NaCl and CaCl_2 , respectively. Using these activity coefficients, we estimated an osmotic pressure of approximately 120 bar for the produced water. Nanofiltration membranes have a low rejection for monovalent ions at such high ionic strengths. Two commercially available NF membranes, NF8 (Nanostone water co.) and NF270 (DOW-FLIMTEC) were investigated for separation of NA from aqueous solutions. Both membranes are polyamide membranes with negative surface potential at neutral pH. The observed pure water permeabilities for the two membranes were 13.4 LMH/bar and 16.7 LMH/bar, respectively.

3.4.1. Nanofiltration (NF) membrane performance for Naphthenic acid (NA)

separation—Separation of NA by NF was carried out with NA (Sigma-Aldrich) in DI water, synthetic solution and produced water samples (prefiltered by 0.22 μm filter). High rejection of NA was observed for both membranes, as shown in Fig. 9. Rejection studies carried out with the synthetic solution further validated rejection of NA from the produced water. NA molecules contain negatively charged carboxylate group at neutral pH, and therefore, the exclusion of NA by NF membrane is governed by both size and charge exclusion principles [50]. The lower observed rejection of NA (from Sigma-Aldrich) in the produced water matrix is due to the screening of surface charge. Produced water samples have high TDS content, and surface charge of the membrane is shielded to a greater extent in the presence of high concentration of monovalent and divalent ions.

3.4.2. Water flux and salt rejection—Rejection of salt and water flux was monitored in the cross-flow cell over 20 h, as shown in Fig. S10 (SI). The rejection of various salts is summarized in table 1. Filtration process was operated at near 0% recovery to avoid any significant change in the composition of the feed water over the course of the experiment. Lower ion rejection was observed for produced water samples as compared to the studies with single salt solutions in DI water, which is mainly due to the screening of membrane charge [51]. Despite the low rejection of NaCl of 6.8% and 5% for NF8 and NF270 membranes, the estimated osmotic pressure difference due to NaCl rejection were 4.2 and 2.8 bar, respectively. The major fraction of the applied pressure gradient (6.8 bar) was, therefore consumed to overcome the osmotic pressure gradient. A decline in flux was also observed over the course of experiment with the produced water (80.4 % and 90% of the initial flux for NF8 and NF270, respectively). After the course of operation, the membrane was washed with DI water, and a flux recovery of 90% and 94% was observed for NF8 and NF270 membrane, respectively. Flux behavior of the produced water with increasing water recovery was also studied for both the membranes in stirred filtration cell operated in dead-end mode.

3.5. Integration of Nanofiltration (NF) with advanced oxidation catalyzed by Fe_xO_y functionalized membrane for Naphthenic acid (NA) remediation

A combination of NF and Fe_xO_y functionalized membrane based oxidation can also be employed to lower concentration of NA in a more cost effective way, as shown in Fig. 10. NF membranes can reduce NA concentration from large volumes of the produced water. Oxidative treatment can further treat the retentate from the same before discharge. Produced water used in this study contained 35 mg/L NA. In one of the study, oxidative treatment of the concentrate stream after 70 % recovery using NF8 reduced NA content from 75 ± 10 mg/L to 31 ± 7 mg/L (refer SI, sec S9.2 for details). Thus NF membrane can treat 80% of the water to create a discharge quality water (<10 mg/L), and Fe_xO_y functionalized membrane (advanced oxidation process) can treat the retentate stream to reduce NA concentrations.

4. Conclusions

We herein have demonstrated the application of catalytic membranes for oxidation of NA using persulfate as an oxidizing agent. In this study, Fe_xO_y functionalized membranes were synthesized by in-situ polymerization of acrylic acid within the pores of a commercial MF membrane followed by ion exchange, reduction, and controlled oxidation. Persulfate decomposition on the Fe_xO_y functionalized membrane followed pseudo-first order kinetics with an activation energy of 18 Kcal/mol. In the study, the catalytic property of the Fe_xO_y functionalized membrane to decompose persulfate decreased over repetitive use. The NaBH_4 treatment restored the catalytic property of the Fe_xO_y functionalized membrane up to 90% of the initial activity. NA concentration was reduced to 8 mg/L (from 34 mg/L) after the second pass through Fe_xO_y functionalized membrane in the presence of persulfate at 40 °C. Exclusion of NA from produced water samples by NF membranes was also investigated. DOW FLIMTECH NF270 and Nanostone NF8 membrane had 79% and 82% NA rejection, respectively, and thus proving to be a promising alternative for NA treatment. We proposed a combined process of nanofiltration-based separation followed by treatment with Fe_xO_y functionalized membrane for lowering concentrations of NA to meet the discharge standards.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors acknowledge the funding support of Chevron and Nanostone Corporations, NSF EPSCOR Program (Grant no. 1355438), and NIH-NIEHS-SRC (Award no: P42ES007380). Authors are thankful to DOW FLIMTECH and Nanostone water co. for providing the flat sheet nanofiltration membranes. Joseph Papp was also supported by the NSF-REU program. The authors also acknowledge the technical help of Michael Detisch, Dr. Rupam Sarma, Dr. M. Gui, John May and Tricia Coakley.

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Figure 1.
Simplified reaction scheme for polymerization of acrylic acid in the membrane domain

Figure 2. FTIR spectra of polyester support for Polyvinylidene fluoride microfiltration (PVDF 400HE, Nanostone water co.) membrane (3), PVDF membrane active layer (2) and PAA functionalized PVDF membrane (1).

Figure 3.

SEM of top surface (a,b), pore size distribution (c,d) and permeability (e,f) of PVDF 400 and PAA functionalized PVDF 400 membrane.

Figure 4. SEM and EDS of the Fe_xO_y functionalized membranes. a) Cross-section, b) Fe_xO_y nanoparticles on the membrane surface, c and d) immobilized Na and Fe in the cross section of the membrane.

Figure 5. Decomposition of persulfate by Fe_xO_y functionalized membrane at different temperatures. Average iron loading: 1.2 mg/cm^2 , Initial persulfate concentration: 1.8 mM .

Figure 6.

Change in reactivity of the Fe_xO_y functionalized membrane after several passes of persulfate solution. Average residence time: 5.2 sec, Iron loading: 1.2 mg/cm^2 , Persulfate feed: 1.8 mM, pH: 5, temperature: 23°C . *persulfate conversions were normalized with the conversion after first pass.

Figure 7.

Batch mode degradation of naphthenic acid (NA) in different water matrices. Feed persulfate= 17 mM, NA in DI water= 48 mg/L, NA in synthetic solution= 38 mg/L, NA in produced water= 34 mg/L, Magnetite= 1000 mg/L, Membrane area exposed= 13.2 cm², (time: 24 hr and initial pH 5 for heterogeneous reactions),

Figure 8.

Conversion of NA in different water matrix on passing through Fe_xO_y functionalized membrane convective flow. Iron loading = 1.2 mg/cm^2 , Persulfate = 17 mM. Average flux = 2 LMH

Figure 9.

Naphtheneic acid (NA) rejection by nanofiltration membranes from different water matrices.

Synthetic solution: NA concentrations: synthetic solution (mixture from Sigma-Aldrich dissolved in produced water): 38 mg/L, DI solution: 48 mg/L, Produced water: 34 mg/L.

Figure 10. Schematic representation of the integration of nanofiltration membranes and Fe_xO_y functionalized membranes for treatment of Naphthenic acid (NA) from produced water.

Table 1

Rejection of naphthenic acids, monovalent and divalent ions by NF8 and NF270 membrane.

	Produced water Feed	NF8 permeate	NF270 permeate
Naphthenic acids (mg/L)	34	< 5	< 5
Na (mg/L)	66,246	61,677	62,922
Ca (mg/L)	3382	2607	2894
Mg (mg/L)	1110	403	629