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Influence of surface properties of filtration-layer metal oxide on ceramic membrane fouling during ultrafiltration of oil/water emulsion

Submitted by

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ABSTRACT

In this work, ceramic ultrafiltration membranes deposited with different metal oxides (i.e., TiO$_2$, Fe$_3$O$_4$, MnO$_2$, CuO, and CeO$_2$) of around 10 nm in thickness and similar roughness were tested for O/W emulsion treatment. Distinct membrane fouling tendency was observed, which closely correlated to the properties of the filtration-layer metal oxides (i.e. surface hydroxyl groups, hydrophilicity, surface charge, and adhesion energy for oil droplets). In consistent with the distinct bond strength of the surface hydroxyl groups, hydrophilicity of these common metal oxides are quite different. The differences in hydrophilicity consequently lead to different adhesion of these metal oxides towards oil droplets which consists very well with irreversible membrane fouling tendency. In addition, the surface charge of the metal oxide opposite to that of emulsion can help to alleviate irreversible membrane fouling in ultrafiltration. Highly hydrophilic Fe$_3$O$_4$ with lowest fouling tendency could be a potential filtration-layer material for the fabrication/modification of ceramic membranes for O/W emulsion treatment. To the best of our knowledge, this is the first study clearly showing the correlations between surface properties of filtration-layer metal oxides and ceramic membrane fouling tendency by O/W emulsion.
INTRODUCTION

Oily wastewater is produced in large volumes by many industries (e.g., oil and gas extraction, petroleum refining, food industry, and metal manufacturing). The oil in water is commonly classified as free oil (Dp > 100 µm), dispersed oil ((Dp = 100-10 um), emulsified oil (Dp < 10 µm), and dissolved oil, among which O/W emulsion and dissolved oil compounds are most difficult to be effectively removed. Oil-in-water (O/W) emulsions are usually stabilized by emulsifier (e.g., surfactant) which reduces the interfacial tension between oil and water. Most of environmental guidelines require that the maximum oil and grease concentrations in effluents should be less than 10-15 mg/L (in some countries < 5 mg/L), making efficient removal of O/W emulsion very critical in the treatment of oily wastewater. Most of the conventional processes for O/W emulsion treatment (e.g., gravity separation, chemical demulsification, air flotation, etc.), are not efficient enough in the treatment of stable O/W emulsions to meet the standards. These processes also have disadvantage such as significant recontamination and high operation cost.

Ultrafiltration (UF) has been widely studied for O/W emulsion treatment to replace traditional treatment because of its relatively low operation cost, steady quality of permeate, and small space requirement. Ceramic membranes are considered to be superior to polymeric membranes for the treatment of oily wastewater as they have higher mechanical, chemical, and thermal stability, as well as possibly overall lower lifecycle cost. However, like polymeric membranes, ceramic membranes also suffer from fouling during the treatment of O/W emulsions. Membrane fouling
(including reversible and irreversible fouling) leads to severe decline of permeate flux and thus compromises the membrane performance. During the filtration of oily wastewater, reversible fouling caused mainly by the accumulation and deposition of oil foulants on membrane surface can be effectively reduced by hydraulic washing (e.g., cross flow and back flush). In contrast, irreversible fouling cannot be effectively reduced merely by hydraulic washing, which therefore is one of the major challenges to ceramic UF membrane in O/W emulsion treatment. The irreversible fouling can be ascribed to: 1) blockage of oil droplets inside membrane pores, and 2) strong adsorption of oil foulant on membrane surface and pores. The first reason of irreversible fouling is mainly related to the structure and pore size of the membrane as well as the size of oil droplets. The second one is largely determined by the interaction between membrane filtration-layer material and oil foulant. For O/W emulsion treatment, strong oil adsorption could be the main reason causing irreversible fouling due to oil foulant properties such as high viscosity. In such circumstance, ceramic membrane filtration-layer material will play an important rule for the irreversible fouling.

Polymeric membrane materials have been investigated intensively for their antifouling performances during oily wastewater treatment, and the influences of material properties have been widely reported. In contrast, roles of ceramic membrane materials in their antifouling performances have not been systematically studied. Knowledge on relationships between surface properties of filtration-layer metal oxide and ceramic membrane fouling tendency will be critical to select
appropriate materials for fabrication/modification of ceramic membrane to
successfully treat O/W emulsion.

In this research, five common metal oxides (i.e. TiO$_2$, Fe$_2$O$_3$, MnO$_2$, CuO, and CeO$_2$)
were selected for experiment due to their high stability in water and relatively low
prices. These metal oxides are also widely used as supports for catalysts,\textsuperscript{27, 28} thus
enabling future fabrication of catalytic membranes to mitigate membrane fouling for
the treatment of O/W emulsions.\textsuperscript{18, 29, 30} These metal oxides were deposited separately
on commercial ceramic membranes (the filtration layer is composed of ZrO$_2$) with
pulsed laser deposition (PLD) to achieve very thin deposition layers (around 10 nm)
while without changing membrane roughness and permeability. The irreversible
fouling on the deposited membranes was investigated through the treatment of crude
oil/water emulsion. Surface properties of these metal oxides were comprehensively
characterized in terms of surface hydroxyl groups, hydrophilicity, surface charge, and
adhesion energy for oil droplets. The irreversible membrane fouling tendency was
correlated to these surface properties of filtration-layer metal oxide. The relationships
between surface properties of the filtration layer and the membrane fouling tendency
in the treatment of O/W emulsion was, for the first time, clearly demonstrated for
ceramic membrane, which can provide a basic knowledge to select/prepare/modify
ceramic membranes for sustainable O/W emulsion treatment.

**EXPERIMENTAL SECTION**

**Preparation and characterization of O/W emulsion**
Crude oil (provided by Saudi Aramco) was used as base oil to prepare oil/water (O/W) emulsions. Sodium dodecyl benzene sulfonate (SDBS) (Sigma-Aldrich) was used as surfactant to disperse and stabilize the crude oil droplets in preparation of O/W emulsions. Details of the emulsion preparation procedure were provided in Text S1 of the Supporting Information (SI).

The O/W emulsion was characterized in terms of oil-droplet size distribution and zeta potential which were analyzed with a particle size and zeta potential analyzer (Nano ZS, Malvern). Microscopic configuration of the oil droplets was characterized with confocal laser scanning microscopy (CLSM) (LSM710, Carl Zeiss) using Nile red (Sigma-Aldrich) as a stain.\(^{31}\)

The emulsion has an average oil droplet size of 360 nm after 50 min sonication (Table S1 and Figure S1, SI). It was negatively charged with zeta potentials approaching -45.5 mV at pH 6.0. Figure S2 (SI) shows that the fine oil droplets distributed uniformly in the emulsion solution. During the experiments, the as-prepared emulsion was relatively stable in droplet size distribution and zeta potential.

**Ultrafiltration of O/W emulsion with ceramic membranes**

TiO\(_2\), MnO\(_2\), Fe\(_2\)O\(_3\), CuO, and CeO\(_2\) (Sigma-Aldrich) were deposited separately onto the filtration layer (composed of ZrO\(_2\)) of commercial ceramic membranes (50 kDa, TAMI Industries) by Pulsed-Laser Deposition (PLD) (COMPexPro201, Coherent) technique under specific conditions (Text S2, SI) with nearly the same coating thickness (around 10 nm). The coating of five metal oxides on membrane surface was
further tested by scanning transmission electron microscopy (STEM) (Titan 80-300, FEI) (Figure S3, SI). The elements of the coated metal oxide were confirmed with the Energy Dispersive Spectroscopy (EDS) accessory of the STEM equipment (Figure S4, SI). Morphologies of the virgin membrane and metal oxide-deposited membranes were characterized with scanning electron microscopy (SEM) (Magellan 400, FEI) and Atomic Force Microscopy (AFM) (Agilent 5500, Agilent). The surface roughness and zeta potential of these membranes were measured by AFM and Electrokinetic Analyzer for Solid Samples (SurPASS, Anton Paar), respectively. Details of the filtration procedure were provided in Text S3 (SI). Irreversible fouling of the membranes were evaluated with normalized initial permeate flux of each filtration cycle (NIF$_n$) which denotes the recovery extent of the permeability by hydraulic back flush. The higher NIF is, the less irreversible fouling the membrane has.

The normalized initial permeate flux of each cycle (NIF$_n$) was calculated with equation (1).

$$NIF_n = \frac{J_n}{J_0} \times 100\%$$  \hspace{1cm} (1)

$J_n$ denotes the initial permeate flux after each back flush; $J_0$ is pure water permeate flux of the virgin membrane.

Instantaneous permeate flux $J$ (L m$^{-2}$ h$^{-1}$) was calculated with equation (2).

$$J = \frac{V}{A \Delta t}$$  \hspace{1cm} (2)

$V$ (L) is the permeate volume; $A$ (m$^2$) denotes the membrane filtration area; and $\Delta t$ (h) represents filtration duration.

Chemical oxygen demand (COD) of the feed and the permeate was measured in triplicate with a COD analyzer (DR2000, Hach). The COD rejection rate (R %) was
calculated with equation (3).

\[ R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (3) \]

R is the COD removal rate; \( C_f \) and \( C_p \) are COD concentrations of the feed and the permeate, respectively.

Characterization of surface properties of metal oxide

The surface properties of five metal oxides were investigated in terms of surface hydroxyl groups, hydrophilicity, surface charge, and adhesion energy for oil droplets. The surface hydroxyl groups were examined with Fourier Transform Infrared Spectroscopy (FTIR) equipped with an Attenuated Total Reflection module (ATR) (Nicolet 6700-continuum FT-IR Microscope, Thermo Scientific) with a procedure described in Text S4 (SI). Isoelectric points of metal oxides were measured with a Zeta potential analyzer (Nano ZS, Malvern) as detailed in Text S5 (SI). The hydrophilicity of metal oxide was characterized with contact angle measurement (Attension, KSV). Since the contact angle is influenced by surface roughness of the solid sample,\(^{32, 33}\) the metal oxides were deposited on smooth silicon wafers (roughness < 0.5 nm) separately with PLD to minimize the roughness effect.\(^{34, 35}\) The roughness of the deposited wafers was measured with Atomic Force Microscopy (AFM) (Agilent 5500, Agilent) to be below 10 nm (Table S2, SI). Contact angle of each deposited metal–oxide layer on the wafer was measured 10 times using a water-droplet volume of 5 ± 0.2 µL. Mean value of the contact angles was calculated, and the standard deviation was below 2°. Adhesion energy of the metal oxide for oil droplets was investigated also with AFM (Agilent 5500, Agilent). Details of the AFM
probe preparation, experimental setup, and adhesion energy calculation were provided in Text S6 (SI).

**Results and Discussion**

**Fouling tendency of deposited ceramic membranes**

Dead-end ultrafiltration with periodical back flush was applied to investigate irreversible fouling of metal oxide-deposited ceramic membranes in the treatment of the emulsion. The deposited membranes have nearly the same pure-water permeability, surface roughness and microstructures as the virgin membrane (Table S3 and S4, Figure S5 and S6, SI). Figure S7 (SI) shows the permeate-flux decline of these membranes as a function of filtration duration. The deposited membranes all suffered permeate-flux decline of different extent during filtration, which can be ascribed to membrane fouling and concentration/polarization on the cake layer.\(^\text{36}\) Interestingly, two clear stages of the permeate-flux decline were observed before reaching a quasi-steady stage which has a relatively steady permeate flux (Figure S7, SI and Figure 1). The initial stage had a relatively slow decline of the permeate flux, being followed by a rapid permeate-flux decline stage. The development of the membrane fouling during the emulsion treatment was hypothesized in Scheme 1. At the beginning of the filtration, small oil droplets could directly penetrate and stuck inside membrane pores, which partially blocks the membrane pore leading to a slow decrease of the permeate flux (i.e., the first stage). Meanwhile, some oil droplets also deposit on the membrane surface. Then, the oil droplets would “pile-up” on membrane surface, which promotes the collision and coalescence of oil droplets as the
filtration further proceeds.\textsuperscript{37, 38} The membrane pore entrance will consequently be covered by the coalesced oil droplets leading to significant reduction of the effective pore size and a quick decline of the permeate flux (i.e., the second stage). Eventually, a compact oil layer of coalesced droplets spreads out on membrane surface and fully covers on the pore entrance as a “second membrane”.\textsuperscript{55} This uniform oil layer dominates permeate-flux and oil rejection, and leads to a steady permeate flux (i.e., quasi-steady stage).\textsuperscript{39, 40} Since the same O/W emulsion was used, the oil layer formed on each deposited membrane would be similar to each other, which would therefore lead to a similar oil rejection. COD rejection rates of the five deposited membranes (in \textbf{Table 1}) further confirmed our hypothesis. 93.2\%, 96.1\%, and 93.0\% of COD rejection (COD = 324 mg O\textsubscript{2}/L) were obtained by negatively charged TiO\textsubscript{2}-, CeO\textsubscript{2}-, and MnO\textsubscript{2}- membranes, respectively, while positively charged Fe\textsubscript{2}O\textsubscript{3}- and CuO-membranes rejected 95.4\% and 96.5\% COD, respectively. The COD rejection rates of the five metal oxide-deposited membranes were close to each other. In general, solute transmission can be enhanced if the membrane is oppositely charged.\textsuperscript{41, 42} The similar COD rejection of these deposited membranes here can be ascribed to a similar and compact oil layer formed on the membrane surface.\textsuperscript{39} \textbf{Figure 2} presents normalized initial permeate fluxes (NIF\textsubscript{n}, n represents the filtration cycles) of the deposited membranes in each cycle of O/W emulsion ultrafiltration. The NIF\textsubscript{n} of all the membranes declined as the number of filtration/backwash cycle increased, indicating that hydraulic irreversible membrane fouling increased gradually. In the six filtration cycles, the deposited membranes
suffered different extents of irreversible fouling. Fe$_2$O$_3$-membrane showed the best filtration performance and lowest irreversible fouling (NIF$_6$ = 60%), whereas MnO$_2$-membrane suffered the most severe fouling (NIF$_6$ = 34%) of all the membranes. In comparison, TiO$_2$-, CuO-, and CeO$_2$- membranes had moderate irreversible fouling (i.e., NIF$_6$ = 52%, 47%, and 44%, respectively). The irreversible fouling tendency of the deposited membranes follows the order of Fe$_2$O$_3$-membrane < TiO$_2$-membrane < CuO-membrane < CeO$_2$-membrane < MnO$_2$-membrane.

**Surface properties of the deposition metal oxides**

Since the surface roughness and structures are nearly the same, the significant difference in irreversible fouling extent of the deposited membranes is considered to be caused by distinct surface properties of the deposited metal oxides. To elucidate the relationship between metal oxide surface properties and the irreversible fouling tendency, these metal oxides were fully characterized in terms of their surface hydroxyl groups in water, hydrophilicity, surface charge, and adhesion energy for oil droplets.

**Surface hydroxyl groups** Surface hydroxyl groups of metal oxides (MeO-H) play an important role in influencing their surface properties. Hydroxyl groups can interact with water molecules through chemisorption or hydrogen-bond interactions. In addition, MeO-H formed Me-OH$_2^+$ or Me-O’ species through protonation/deprotonation at pH below or above pH$_{pzc}$ of the metal oxide. The surface hydroxyl groups of the metal oxides can be analyzed with ATR-FTIR. The stretching band
of MeO-H can be separated from that of the O-H of bulk water by using D$_2$O as solvent, where the surface hydroxyl group is deuterated.$^{45}$ The surface MeO-D has been reported to have characteristic IR stretching vibration in the range of 2200-2800 cm$^{-1}$.\textsuperscript{43, 46, 48} \textbf{Figure 3} shows the ATR-FTIR spectra of the surface MeO-D groups of the metal oxides in D$_2$O suspensions. The stretching frequencies of MeO-D of MnO$_2$, CuO, CeO$_2$, TiO$_2$, and Fe$_2$O$_3$ were 2337, 2339, 2456, 2545, and 2628 cm$^{-1}$, respectively, indicating that the bond strength of O-D in MeO-D groups of the metal oxides follows the order of MnO$_2$ < CuO < CeO$_2$ < TiO$_2$ < Fe$_2$O$_3$. A strong O-D bond of the MeO-D group indicates that the metal site (Me) has relatively weak bonding with the O atom of the surface O-D group. The strong O-D bond also implies high electron density of the O-D group and thus possibly high affinity for D$_2$O molecules through forming strong hydrogen bond. Therefore, the surface hydroxyl groups of Fe$_2$O$_3$ probably tend to strongly interact with water molecules through hydrogen bond (i.e. highly hydrophilic), whereas those of MnO$_2$ and CuO would be significantly less hydrophilic. This hypothesis is confirmed in the following hydrophilicity test.

\textbf{Hydrophilicity} Hydrophilicity is an important parameter for predicting fouling tendency of polymeric membranes: high hydrophilicity usually means low membrane fouling potential in filtration.\textsuperscript{49, 50} Metal oxides have been considered to be all hydrophilic. Differences in the hydrophilicity of metal oxides have never been realized until a recent study disclosed that some lanthanide oxides are relatively more hydrophobic than others.\textsuperscript{35} The hydrophilicity of the metal oxides used in this study was tested with contact angle measurement. In general, a small contact angle indicates...
a high hydrophilicity of the material. Contact angle images of the five metal oxide-deposited wafers taken within 30 s of interaction with water droplets clearly show the differences of their hydrophilicity (Figure 4a). The contact angles of the five metal oxides varied significantly from 26.6° to 71.7° (Table 1). The hydrophilicity of the five metal oxides increases with the order of MnO₂ < CeO₂ < CuO < TiO₂ < Fe₂O₃ (contact angles being 71.7°, 63.6°, 52.8°, 29.8°, 26.6°, respectively). This result supports the inferred order of IR stretching frequencies of the surface MeO–D bonds of these metal oxides, suggesting that the properties of surface hydroxyl groups largely influence the hydrophilicity of these metal oxides. Figure 4b schematically describes how water molecules attach on metal oxides by interaction with surface hydroxyl groups. A monolayer of water molecules interact directly with the surface hydroxyl groups of the metal oxide through hydrogen bonding, and then interact with outer-sphere water molecules also through hydrogen bonding forming multiple layers of water molecules.

Surface charge. Surface charge of membrane material influences electrostatic interactions between the membrane and the solutes. Membrane fouling can be enhanced or reduced through electrostatic interactions. As described above, the surface charge of metal oxides is developed through protonation/deprotonation of surface hydroxyl groups, which is pH dependent. At pH 6.0 of the experiments (i.e., the pH of the emulsion), MnO₂, CeO₂, and TiO₂ (pH_pzc being 3.8, 4.2, and 3.2, respectively, as shown in Table 1) were negatively charged, while Fe₂O₃ and CuO (pH_pzc being 6.4 and 9.5, respectively) were positively charged. The surface charge of
metal oxide-deposited membranes was consistent with that of the deposition metal oxides at pH 6.0 (Figure S8, SI). Because oil droplets were negatively charged (Table S1, SI), electrostatic repulsion between oil droplets and particles of MnO₂, CeO₂, and TiO₂ would occur, while electrostatic attraction would exist between oil droplets and particles of Fe₂O₃ and CuO.

**Adhesion energy for oil droplets** The absorption fouling of oil on metal oxides is not only influenced by hydrophobic-hydrophilic interactions, hydrogen bonding and electrostatic interactions, but also by van der Waals interactions between metal oxide and oil foulant. AFM is a powerful tool that quantitatively measures the interaction forces/energies at the sub-nano Newton resolution between foulants and metal oxides. To further study the oil fouling potential towards metal oxides, adhesion energy of metal oxides for oil droplets was investigated with AFM. Figure 5 shows that the least hydrophilic MnO₂ has the highest adhesion energy for oil droplets, whereas the most hydrophilic Fe₂O₃ has the lowest adhesion energy of oil droplets. Adhesion energies of the metal oxides for oil droplets followed the order of Fe₂O₃ < TiO₂ < CeO₂ < CuO < MnO₂. It was noticed also that CuO had higher adhesion energy for oil droplets than CeO₂ while its hydrophilicity was higher. This means that the adhesion between oil droplets and metal oxides is also contributed by electrostatic interaction (CuO is oppositely charged to oil droplets, while CeO₂ is similarly charged to oil droplets). Lower adhesion energy between oil droplets and metal oxide indicates lower oil adsorption tendency on the metal oxide. Accordingly, adsorption fouling of oil on metal oxides would decrease with the decreasing adhesion energy in
order of $\text{Fe}_2\text{O}_3 < \text{TiO}_2 < \text{CeO}_2 < \text{CuO} < \text{MnO}_2$, which can be inversely correlated to
the hydrophilicity of the metal oxides.

**Relationship between the surface properties of filtration-layer metal oxide and
the irreversible membrane fouling tendency**

The irreversible fouling tendency of the five metal oxide-deposited membranes can
be correlated very well with surface properties of the metal oxides. The bond strength
of surface hydroxyl groups of the metal oxides (MeO–H) largely influences their
hydrophilicity, and the hydrophilicity mainly dominates the adsorption fouling of oil
on the metal oxides. The hydrophilicity of the metal oxides ($\text{MnO}_2 < \text{CeO}_2 < \text{CuO} <
\text{TiO}_2 < \text{Fe}_2\text{O}_3$) correlates inversely with irreversible fouling tendency of the deposited
membranes, and higher hydrophilicity is related to lower irreversible fouling tendency.

This result indicates that the hydrophilicity of the filtration-layer metal oxide is a
major factor influencing irreversible fouling tendency of ceramic membrane in the
O/W emulsion treatment. It is already known that hydrophilic polymeric membrane
has low fouling tendency.$^{55, 56}$ For ceramic membrane, this is the first time observing
the difference of these common metal oxides in hydrophilicity and clearly revealing
the dominance of the relative hydrophilicity of filtration-layer metal oxide in
membrane fouling tendency.

Surface charge of the metal oxide opposite to that of the emulsion helps to alleviate
irreversible membrane fouling in ultrafiltration, which is consistent with our last work
regarding the influence of surfactant on ceramic membrane performance in O/W
emulsion treatment.$^{30}$ The positively charged CuO-membrane suffered less
irreversible fouling than the negatively charged CeO$_2$-membrane in the treatment of
negatively charged emulsion (Figure 2), whereas its adsorption energy for oil was
higher than that of CeO$_2$ (Figure 5). Irreversible membrane fouling is caused by 1)
pore blockage by tiny oil droplets and 2) strong adsorption of oil droplets on
membrane surface and pores.$^{20}$ Although the CuO-membrane has more adsorption
fouling than the CeO$_2$-membrane, it may have less pore blockage fouling and thus
overall less irreversible fouling. Cross-section SEM images of the virgin and the
fouled CuO- and CeO$_2$- membranes support this hypothesis (Figure S9, SI). The
oxide particles in the filtration layer of CuO- and CeO$_2$- membranes (Figure S9b and
S9c, SI) showed larger sizes than that of the virgin membrane (Figure S9a, SI). This
indicates that oil droplets penetrated into membrane pores and covered on the oxide
particles during filtration. The oxide particle size of the CuO-membrane was smaller
than that of CeO$_2$-membrane (Figure S9b and S9c, SI), indicating less oil droplet
penetration into the CuO-membrane pores and covering on the oxide particles. Less
pore blockage fouling of positively charged CuO-membrane could probably be
ascribed to 1) the adsorption of some negatively charged surfactant-SDBS molecules
on membrane surface and pores, which prevent the penetration of some oil droplets
into the pores (i.e., surfactant barrier),$^{42}$ and 2) the subsequent coalescence of oil
droplets near membrane surface because of the less stabilization SDBS for oil droplets
(i.e., demulsification), which leads to more large oil droplets easily rejected on
membrane surface and less small oil droplets available to penetrate into membrane
pores (Scheme S1, SI).
It should be noticed that although the CuO-membrane oppositely charged to oil droplets may suffer less irreversible fouling caused by pore blockage, it still has overall more irreversible fouling than the TiO$_2$-membrane similarly charged to oil droplets. This is probably because the CuO-membrane suffered much more irreversible adsorption fouling than the more hydrophilic TiO$_2$-membrane (according to the adhesion energy shown in Figure 5). This fact again confirms that the hydrophilicity is a more significant factor influencing the irreversible fouling tendency of the ceramic membrane in O/W emulsion treatment.

Environmental significance:

Ceramic membrane ultrafiltration is an ideal treatment process for O/W emulsions daily produced in many industrial activities. Severe irreversible membrane fouling compromises the performance of ceramic membrane in O/W emulsion treatment, where filtration-layer material plays a crucial role. The filtration-layer material of low fouling tendency is highly desirable for sustainable O/W emulsion treatment. This study clearly shows the relationship between the surface properties of the filtration-layer metal oxides and the membrane fouling tendency, which provides a theoretical foundation to guide the selection/preparation/modification of ceramic membranes for sustainable O/W emulsion treatment. In addition, the result suggests that highly hydrophilic metal oxides (e.g., Fe$_2$O$_3$) can be potential filtration-layer materials of the ceramic membrane for O/W emulsion treatment.

ASSOCIATED CONTENT

Supporting Information.
Six texts, four tables, ten figures and one scheme are included in the supporting information. This information is available free of charge via the Internet at http://pubs.acs.org/

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Literature Cited


Table 1. Surface properties of the metal oxides and COD rejection rates of ceramic membranes deposited with these metal oxides for the O/W emulsion

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Contact angle (degrees)</th>
<th>pH$_{pzc}$</th>
<th>Surface charge$^a$</th>
<th>COD rejection %</th>
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</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>26.6 ± 1.6</td>
<td>6.4</td>
<td>+</td>
<td>95.4</td>
</tr>
<tr>
<td>CuO</td>
<td>52.8 ± 1.6</td>
<td>9.5</td>
<td>+</td>
<td>93.2</td>
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<tr>
<td>TiO$_2$</td>
<td>29.8 ± 1.5</td>
<td>3.2</td>
<td>-</td>
<td>96.5</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>63.6 ± 1.9</td>
<td>4.2</td>
<td>-</td>
<td>96.1</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>71.7 ± 1.1</td>
<td>3.8</td>
<td>-</td>
<td>93.0</td>
</tr>
</tbody>
</table>

$^a$ Surface charge of metal oxides under experimental filtration conditions (pH = 6.0).

Figure 1. Normalized permeate-flux decline of Fe$_2$O$_3$-membrane for O/W emulsion treatment in a long run without back flush.
Figure 2. Decline of normalized initial permeate-flux of ceramic membranes deposited with different metal oxides in seven cycles of O/W emulsion filtration.

Figure 3. ATR-FTIR spectra of surface MeO-D groups of metal oxides immersed in D$_2$O (pD = 6.0).
Figure 4. Optical images and contact angle images of metal oxides deposited on silicon wafers (a). A scheme of interaction between water droplet and metal oxide surface (b).

Figure 5. Adhesion energy between metal oxides and oil droplets.
Scheme 1. Possible membrane fouling stages of ceramic membrane during O/W emulsion treatment.