Electronic Supplementary Information for

Competitive adsorption for simultaneous removal of emulsified water and surfactant from mixed surfactant-stabilized emulsions with high flux

Xiaoxia Ye, a Yaping Wang, a Le Ke, b Yiwen Cui, a Wei Luo, a Xiaoling Wang, b Xin Huang* a,b and Bi Shi a,b

a Department of Biomass Chemistry and Engineering, Sichuan University, Chengdu China, 610065.

b National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu China, 610065.

*Corresponding author: xhuangscu@163.com (X. Huang)
1. General information

Materials

CFM was provided by Ruixing Leather Co., Ltd (Haining, China). Non-functionalized MWCNTs (outside diameter: 10-20 nm, length: 20-100 μm) were purchased from Chinese Academy of Sciences Chengdu Organic Chemical Co., Ltd (Chengdu, China). Pump oil was purchased from Beijing Sifang special oil products factory. Polyamide porous membrane (with pore size of 0.45 μm) was purchased from Shanghai Xinya instruments Co., Ltd (Shanghai, China). Polytetrafluoroethylene porous membrane (with pore size of 0.45 μm) was purchased from Laisheng filter equipment factory (Haining, China). Polydimethylsiloxane (PDMS) prepolymer (Sylgard 184A) and curing agent (Sylgard 184B) were received from Dow Corning Corporation (Midland, USA). PDMS solution with concentration of 50 g L⁻¹ was prepared by dissolving Sylgard 184A (4.50 g) and Sylgard 184B (0.45 g) in 50 mL of dodecane, respectively, followed by mixing the two solutions together. All other chemicals were analytical grade reagents and were used as received without further purification.

Fabrication of MWCNTs(x)/CFM/PDMS membrane

CFM, with diameter of 9.0 cm and thickness of 1.0 mm, was rinsed with deionized water and ethanol successively. Then, 100 mL of ethanol suspension containing different amount of MWCNTs were ultrasonically dispersed in ethanol solution for 30 min, and then filtrated into CFM via vacuum filtration. The resultant membrane was immersed into 50 g L⁻¹ of PDMS solution (50 mL) for 5.0 min and dried at 105 °C for obtaining the MWCNTs(x)/CFM/PDMS
membrane, where $x$ is the content of MWCNTs, varied from 0 to 16 mg (0 mg, 4.0 mg, 8.0 mg, 12 mg, 16 mg).

**Fabrication of MWCNTs/PDMS**

The MWCNTs/PDMS was prepared by immersing 0.1 g of MWCNTs into PDMS solution (50 mL, 50 g L$^{-1}$) for 5.0 min and dried at 105 °C.

**Emulsion preparation**

Mixed nonionic surfactant-stabilized water-in-oil nanoemulsions were prepared, which were denoted as NE1 for Span80/Tween80 stabilized water-in-heptane nanoemulsion, NE2 for Tween80/Peregal stabilized water-in-octane nanoemulsion, NE3 for Peregal/OP-10 stabilized water-in-chlorobenzene nanoemulsion, NE4 for Tween80/OP-10 stabilized water-in-dodecane nanoemulsion, respectively. For the preparation of NE1, Span80 (0.25 g), Tween80 (0.25 g), heptane (450 mL) and water (50 mL) were mixed under sonication for 3.0 h. For the preparation of NE2, Tween80 (0.25 g), Peregal (0.25 g), octane (450 mL) and water (50 mL) were mixed under sonication for 3.0 h. For the preparation of NE3, Peregal (0.25 g), OP-10 (0.25 g), chlorobenzene (450 mL) and water (50 mL) were mixed under sonication for 3.0 h. For the preparation of NE4, Tween80 (0.25 g), OP-10 (0.25 g), dodecane (450 mL) and water (50 mL) were mixed under sonication for 3.0 h.

Mixed nonionic surfactant-stabilized water-in-oil nanoemulsions with high viscosity were prepared, which were denoted as NE5 for Span80/OP-10 stabilized water-in-olive oil nanoemulsion, NE6 for Span80/Tween80 stabilized water-in-pump oil nanoemulsion, respectively. Specifically, 0.25 g of Span80 and 0.25 g of OP-10 were added into 450 mL of olive oil, and then 50 mL of water was drop-wise added into above mixture under mechanical agitation at
1000 rpm. The resultant mixture was further stirred at 3000 rpm for 60 min, and the resultant emulsion was NE5. For the preparation of NE6, 0.25 g of Span80 and 0.25 g of Tween80 were added into 450 mL of pump oil, followed by the dropwise addition of 50 mL of water under mechanical agitation at 1000 rpm. The obtained mixture was further stirred at 3000 rpm for 60 min. The obtained emulsion was NE6. The viscosity of NE5 and NE6 was 33.2 and 76.2 mPa·s.

Mixed nonionic surfactant-stabilized water-in-oil microemulsions were prepared, which were denoted as ME1 for Span80/OP-10 stabilized water-in-heptane microemulsion, ME2 for Span80/Peregal stabilized water-in-octane microemulsion, respectively. For the preparation of ME1, 0.25 g of Span80 and 0.25 g of OP-10 were added into 350 mL of heptane, and then 150 mL of water was drop-wise added into above heptane under mechanical agitation at 500 rpm. The resultant mixture was further stirred at 1200 rpm for 30 min. For the preparation of ME2, 0.25 g of Span80 and 0.25 g of Peregal were added into 350 mL of octane, and then 150 mL of water was drop-wise added into above octane under mechanical agitation at 500 rpm. The resultant mixture was further stirred at 1200 rpm for 30 min.

The ingredients of NE1-NE6 and ME1-ME2 are shown in Table S1.
Table S1. Ingredients of NE1-NE6 and ME1-ME2.

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Emulsifier</th>
<th>Emulsifier content</th>
<th>Oil content</th>
<th>Water content</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE1</td>
<td>Span80/Tween80</td>
<td>0.25 g/0.25 g</td>
<td>Heptane (450 mL)</td>
<td>50 mL</td>
</tr>
<tr>
<td>NE2</td>
<td>Tween80/Peregal</td>
<td>0.25 g/0.25 g</td>
<td>Octane (450 mL)</td>
<td>50 mL</td>
</tr>
<tr>
<td>NE3</td>
<td>Peregal/OP-10</td>
<td>0.25 g/0.25 g</td>
<td>Chlorobenzene (450 mL)</td>
<td>50 mL</td>
</tr>
<tr>
<td>NE4</td>
<td>Tween80/OP-10</td>
<td>0.25 g/0.25 g</td>
<td>Dodecane (450 mL)</td>
<td>50 mL</td>
</tr>
<tr>
<td>NE5</td>
<td>Span80/OP-10</td>
<td>0.25 g/0.25 g</td>
<td>Olive oil (450 mL)</td>
<td>50 mL</td>
</tr>
<tr>
<td>NE6</td>
<td>Span80/Tween80</td>
<td>0.25 g/0.25 g</td>
<td>Pump oil (450 mL)</td>
<td>50 mL</td>
</tr>
<tr>
<td>ME1</td>
<td>Span80/OP-10</td>
<td>0.25 g/0.25 g</td>
<td>Heptane (350 mL)</td>
<td>150 mL</td>
</tr>
<tr>
<td>ME2</td>
<td>Span80/Peregal</td>
<td>0.25 g/0.25 g</td>
<td>Octane (350 mL)</td>
<td>150 mL</td>
</tr>
</tbody>
</table>

Emulsion separation

Emulsion separation was carried out by an H-shaped device (Fig. a), where the MWCNTs(\(\chi\))/CFM/PDMS membrane with the area of 177 mm\(^2\) was vertically placed between the feed cell and collecting cell. Emulsion separation under gravity was initiated by adding the emulsion into the left feed cell, and the collected filtrate was obtained in the right collecting cell. The mixed nonionic surfactant-stabilized water-in-oil nanoemulsions with high viscosity were separated through vacuum filtration at 0.03 MPa, and the corresponding separation device was shown in Fig. b.
Fig. a Digital photo of an H-shaped separation device.

Fig. b Digital photo of an H-shaped separation device through vacuum filtration for emulsion separation.

**Static adsorption isotherms**

Static adsorption isotherms were carried out by suspending 0.1 g of MWCNTs/PDMS in 50 mL of water containing different concentration of Span80 from 100 to 800 mg L⁻¹. The resultant mixtures were kept under constant
shaking for 24 h at 30 °C. The concentration of Span80 at the adsorption equilibrium was measured by total organic carbon (TOC) analyzer, and the equilibrium adsorption capacity ($q_e$) was calculated according to the following equation: $q_e = V(C_o-C_e)/m$, where $C_o$ and $C_e$ represent the initial and the equilibrium concentration of Span80 (mg L$^{-1}$), respectively, $V$ is the volume of Span80 solution (L) and $m$ is the dosage of MWCNTs/PDMS (g). Measurements of $q_e$ for Tween80, OP-10 and Peregal were carried out by above similar procedures.

**Sandpaper abrasion**

Sandpaper abrasion was performed on a rub fastness tester (shown in Fig. c), where the MWCNTs(16)/CFM/PDMS membrane was fixed on the sample table, and a sandpaper (2#, 36 mesh, 1.5 cm × 1.5 cm) was stuck onto the fixed arm. One cycle of abrasion was defined as a round trip rubbing of the MWCNTs(16)/CFM/PDMS membrane against the sandpaper, and the corresponding abrasion distance for each cycle of abrasion was 6.0 cm.
Reusability test

The used MWCNTs(16)/CFM/PDMS membrane was cleaned by acetone and dried, and then reused for the next cycle of emulsion separation.

Characterizations

Water contact angle was measured on a contact angle goniometer (Krüss, DSA30, Germany), which was obtained from three measurements per sample. Water content in the filtrates was determined using a moisture titrator (Wo Ye technology, S-300, China). Optical microscopy images were obtained on a stereomicroscope (Leica, M205 C, Germany). Dynamic light scattering (DLS) analyses were performed by a particle size analyzer (Brook haven, NanoBrook, America). We carried out scanning electron microscopy observation of samples using a field emission SEM (FESEM, Nova Nanosem 450, America). Sandpaper
abrasion was performed by using sandpaper (2#, 36 mesh) on a rub fastness tester (FEK-VESLIC, Switzerland). N₂ adsorption/desorption curves were taken from an automated physisorption analyzer (Quantachrome Instruments, Autosorb 1MP, America). The tearing strength and tensile strength were determined using a tensile testing machine (Gotech, AI-7000 SN, China). Bending test was carried out by using a flexing endurance tester (Bally, Flexometer, Britain). TOC measurement was carried out using a TOC analyzer (TOC, Vario, Elementar, Germany).
2. Supporting figures

**Fig. S1** Digital photo of CFM after 10000 times of bending.
Fig. S2 N$_2$ adsorption/desorption isotherm curves of CFM.
**Fig. S3** FESEM images of (a,b) the MWCNTs(16)/CFM membrane and (c,d) MWCNTs(16)/CFM/PDMS membrane.
**Fig. S4** Digital photo showing the MWCNTs(16)/CFM/PDMS membrane immersed in water by external force with a silver mirror-like appearance.
Fig S5 Digital photos of an H-shaped separation device at $t = 0$ and $t = 5.0$ min after the addition of 50 mL of nanoemulsion NE1 into the left feed cell.
Fig. S6 DLS curves of NE1-NE4 nanoemulsions (a-d) before and after separation by (e-h) the MWCNTs(16)/CFM membrane and (i-l) MWCNTs(16)/CFM membrane abraded by 30 cycles of abrasion with sandpaper.
Fig. S7 Static adsorption isotherms of different surfactants on MWCNTs/PMDS at 30 °C.
Fig. S8 Optical microscopy images of (a) ME1 and (c) ME2, and the corresponding particle size distributions of (b) ME1 and (d) ME2, respectively.
Fig. S9 Optical microscopy images of ME1 and ME2 (a-b) before and after separation by (c-d) the MWCNTs(16)/CFM/PDMS membrane and (e-f) MWCNTs(16)/CFM/PDMS membrane abraded by 30 cycles of abrasion with sandpaper.
**Fig. S10** Digital photo of MWCNTs(16)/CFM/PDMS membrane after 10000 times of bending.
Fig. S11 Digital photos of NE5 and NE6 (a,c) before and (b,d) after the filtration for 60 min by the MWCNTs(16)/CFM/PDMS membrane under gravity.
Fig. S12 Digital photos of NE5 and NE6 (a,c) before and (b,d) after the vacuum filtration (0.03 MPa) for 30 min by the polytetrafluoroethylene porous membrane.
Movies for electronic supplementary information

Movie S1. CFM was repeatedly bent on a flexing endurance tester.

Movie S2. The running water washed away starch powder placed on the surface of MWCNTs(16)/CFM/PDMS membrane abraded by 30 cycles with sandpaper (2#, 36 mesh).