Supporting Information for

Ceramic membrane fouling during ultrafiltration of oil/water emulsions: Roles played by stabilization surfactants of oil droplets

Submitted by

Dongwei Lu[a], Tao Zhang[b] and Jun Ma[a**]*

a.State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, People's Republic of China

b. Water Desalination and Reuse Center, King Abdullah University of Science and Technology, Thuwal 4700, Kingdom of Saudi Arabia

Thirteen pages. Four texts, five tables and nine figures are included in the supporting information.

Text S1 Preparation of the O/W emulsions

The surfactant and base oil were mixed together with a mass ratio of 1:10 in the pure water (Milli-Q Academic, Millipore) and sonicated (Q700 sonicator, Qsonica) for 15-40 min. Oil dosage was 100 mg L^{-1} for all the O/W emulsions. The prepared emulsions were stable in terms of droplet size distribution and zeta potential within 5 days.

Text S2 Characterization of the fluorescent organic contents before and after filtration with FEEM

The feeds and permeates of surfactant/crude oil emulsions were characterized with three-dimensional fluorescence excitation-emission matrices (FEEM) to compare fluorescent organic contents before and after filtration. The wavelength range of excitation and emission scans were 200-600 and 211.44-620.81 nm, respectively.

Text S3 Sample preparation procedure for the analysis of organic components in the feed and the permeate with GC/MS.

1) Analysis for aromatic compounds:

All feeds were filtered with a glass fiber membrane of 0.45 μm pore size. The permeates from the ceramic membrane were not further filtered. Decafluorobiphenyl (6 mg L^{-1}) of 100 μL was spiked into 50 mL of each collected samples as internal standard, followed by the addition of 10 g of NaCl and 3 mL of Hexane. Then, the samples were vigorously shaken for 5 min. The hexane extracts were measured using GC/MS (7890A gas chromatography and 5975C mass spectrometer, Agilent)

equipped with a DB-1701 column in (electron ionization) (EI) mode (splitness injection; injector temp.: 280 ^{o}C; oven temp.: 50 ^{o}C held for 5 min then ramped to 250 ^{o}C at 5 ^{o}C min^{-1}; aux temp.: 270 ^{o}C).

2) Analysis for the carboxylates of the permeate:

When the hexane layer was decanted, 60 μL of a surrogate internal standard (2-bromopropionic acid, 10 mg L^{-1}) was added into the remaining water samples. The samples were then acidified to pH < 0.5 with the addition of 0.8 mL H_2SO_4, followed by the addition of 10 g NaCl and 3 mL MTBE. Then, organic acids were extracted into MTBE by shaking for 5 min. The MTBE extract was methylated with 1 mL H_2SO_4/CH_3OH (10% v/v) at 50 °C in a water bath for 2 h. After neutralization with 4 mL saturated $NaHCO_3$, the MTBE solvent extracts were analyzed using GC/MS (Agilent 7890A) with a polar DB-Wax column following EPA Method 552.

Text S4 The filtration procedure of ceramic membrane in the treatment of O/W emulsions

A dead-end filtration setup connected with a nitrogen gas cylinder to maintain constant pressure was applied to evaluate ceramic membrane fouling in the treatment of the surfactant-stabilized emulsions. Before the filtration experiment, each membrane was initially dipped into pure water for 24 h and rinsed with pure water by filtration at 1.5 bar for 30 min. Each filtration test was conducted with 5 or 7 filtration cycles. Each cycle lasted for 30 min of forward filtration and 2 min of back flush as follows: 1) the pure water flux of clean membrane was measured at 1 bar for 1 h as

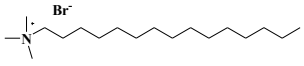
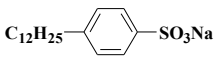
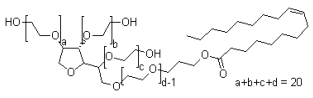
the first initial flux; 2) the emulsion was forward filtered for 30 min at 1 bar, meanwhile the permeate flux profile vs. time was recorded with an electronic balance connected to a desktop; and 3) after 30 min forward filtration, back flush with pure water was conducted at 2 bar for 2 min. Oil foulants removed from the membrane by back flush was discharged into a waste tank.

Table S1. Characteristics of ceramic membranes used for this study.

Membrane configuration	Discs with diameter of 47 mm
Active layer materials	TiO_2/ZrO_2 mixture
Support layer materials	TiO_2
Molecular weight cut-off/membrane pore size	50 kDa (8.6 nm),150 kDa (17.6 nm), and 0.14 μm
Surface zeta potential*	-24.8 ± 5 mV at pH 6.0
Maximum operating pressure	4 bar

* Zeta potential was measured in 10 mM L^{-1} NaCl solution at pH 6.0.

Table S2. Properties of the three surfactants

Surfactant	Molecular structure	HLB*	Molar weight (g/mol)	Emulsifier type
CTAB		15.8	364.5	cationic
SDBS		10.6	348.5	anionic
Tween-80		15.0	1310	nonionic

* HLB- Hydrophilic-lipophilic balance; the higher HLB, the more hydrophilic the surfactant is.

Table S3. Peak intensities of major aromatics identified in the feeds by GC/MS (the intensities were corrected by the internal standard)

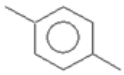
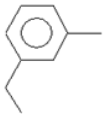
Feed emulsion			
Tween-80/crude oil	498295	156428	509537
SDBS/crude oil	517437	149453	521405
CTAB/crude oil	522376	115614	481419

Table S4. Peak intensities of major aromatics identified in the permeates by GC/MS (the intensities were corrected by the internal standard)

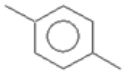
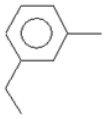
Permeate			
Tween-80/crude oil	48595	39157	59117
SDBS/crude oil	90503	61019	114139
CTAB/crude oil	38270	14121	20182

Table S5. Peak intensities of methyl esters (after methylation of carboxylates) identified in the permeates with GC/MS (the intensities were corrected by the internal standard)

Permeate	$C_{12}H_{17}N_3O_7$	$C_{16}H_{13}NO_2S$	$C_{12}H_{10}O_4$	$C_{11}H_{16}O_2$
Tween-80/crude oil	1411432	778076	3777423	1825602
SDBS/crude oil	2984607	1643048	8652794	1904298
CTAB/crude oil	2078905	1030485	7078656	1821495

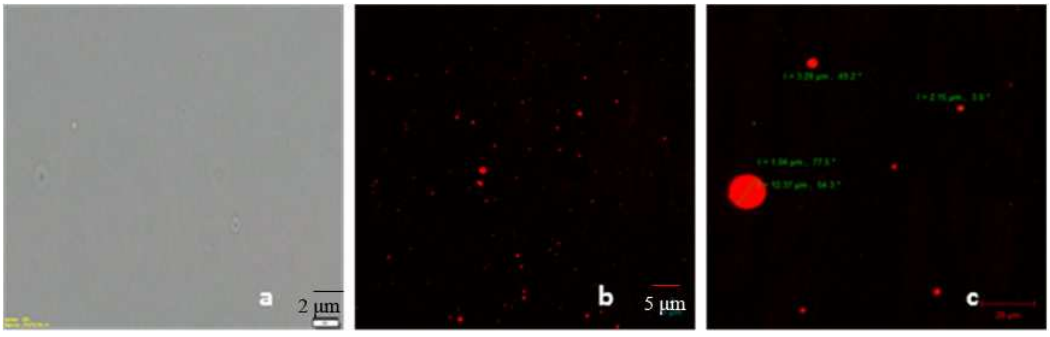


Figure S1. Microscopic images of oil droplets in emulsions prepared with diesel (a) and crude oil (b and c--- sonicated for 50 and 20 min, respectively): **picture a** was obtained with optical microscope; **pictures b** and **c** were taken with LSCM.

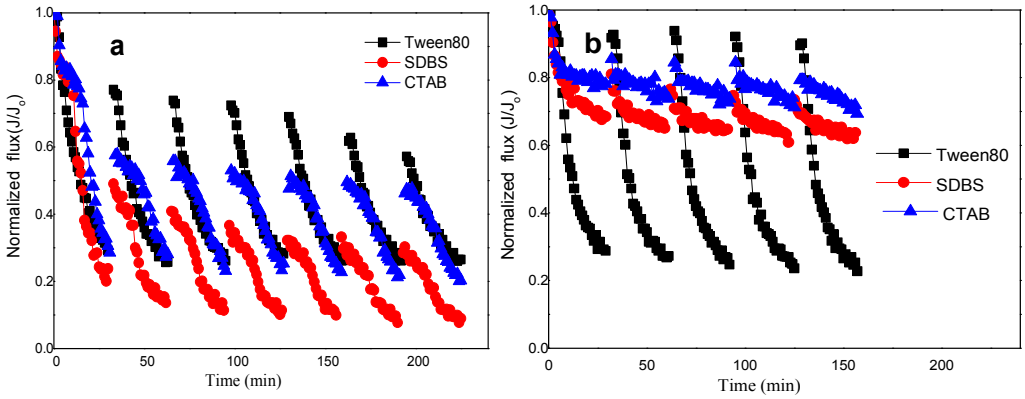


Figure S2. Decline of normalized permeate flux of 50 kDa ceramic membranes during the filtration of three crude oil/water emulsions (a) and three diesel/water emulsions (b) prepared with different surfactants.

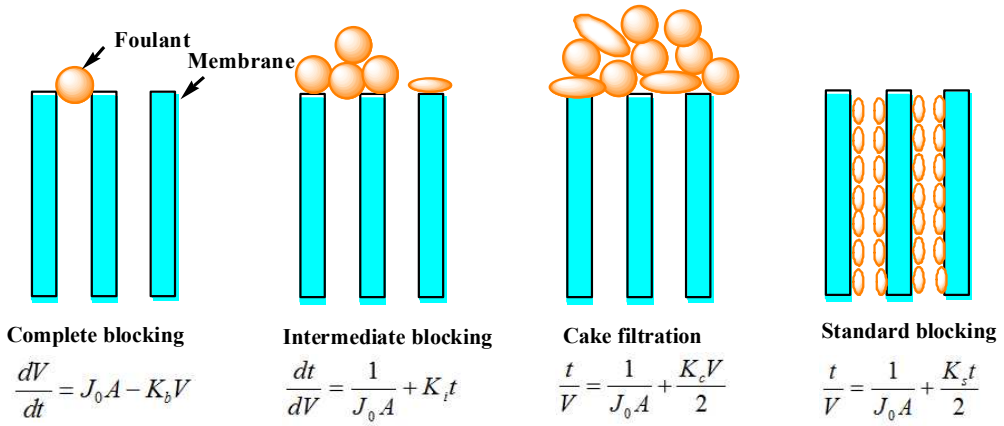
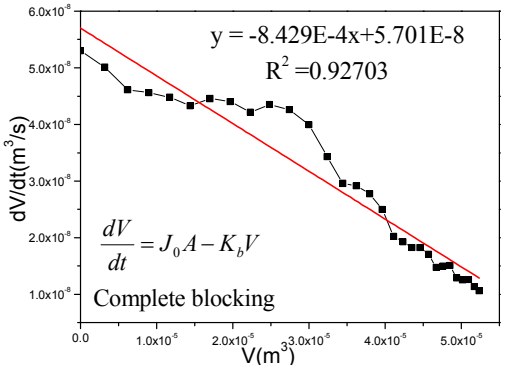
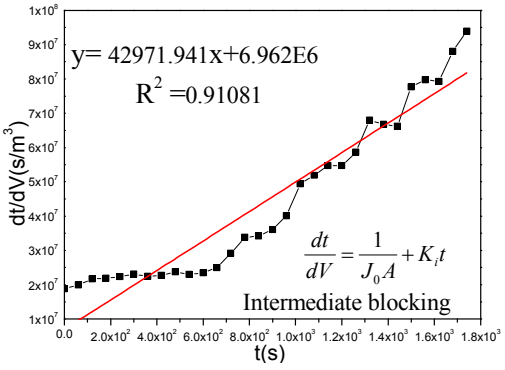
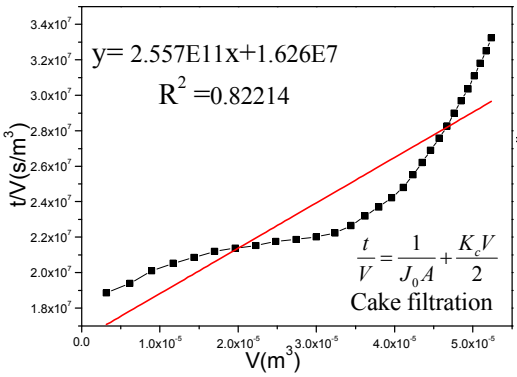


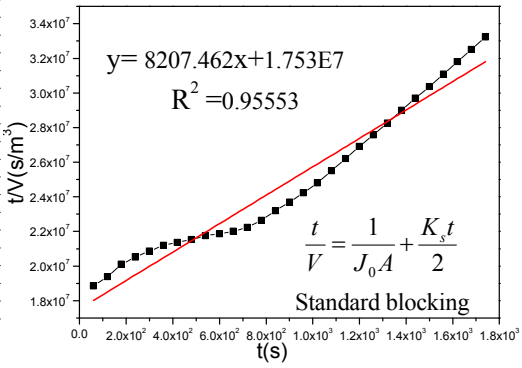
Figure S3. Schematic diagrams and equations of four fouling models adapted from references[1, 2]: A, membrane area; t, filtration time; V, cumulative permeate volume; J_0, initial permeate flux; K_b, K_i, K_c, and K_s, the coefficients of complete blocking, intermediate blocking, cake filtration and standard blocking, respectively.

SDBS/crude oil-prepared emulsion

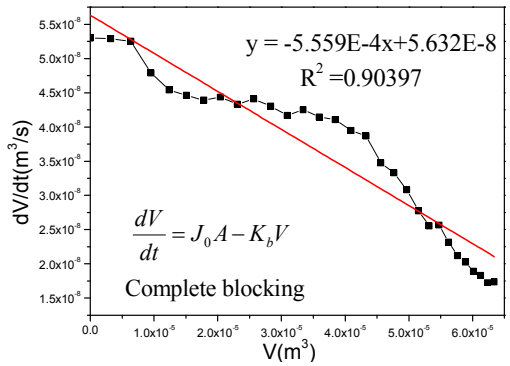


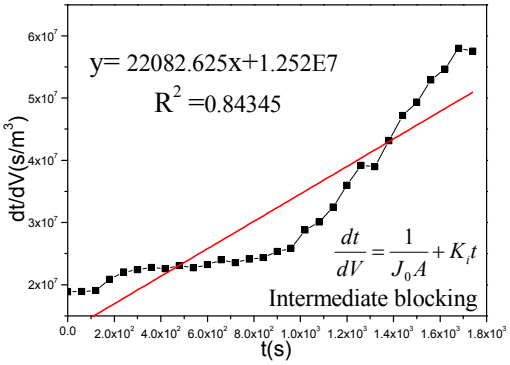


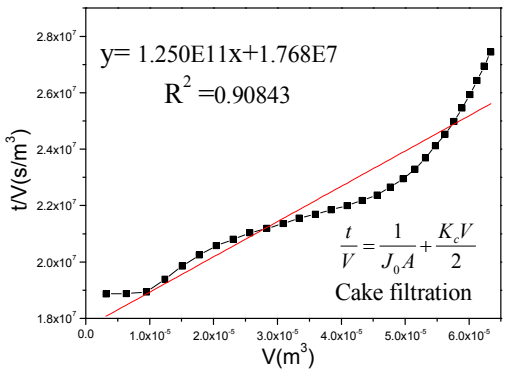


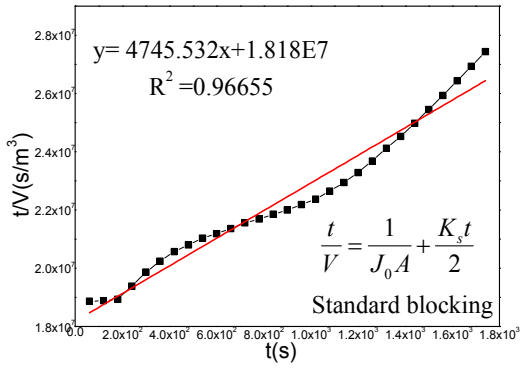


CTAB/crude oil-prepared emulsion

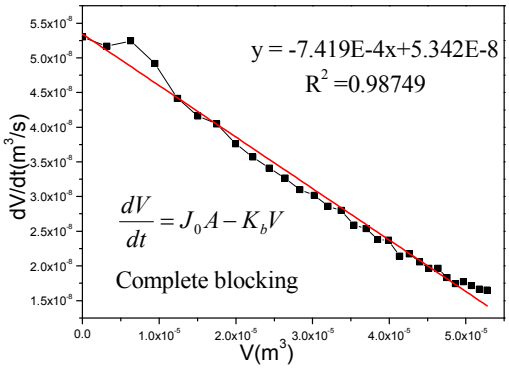


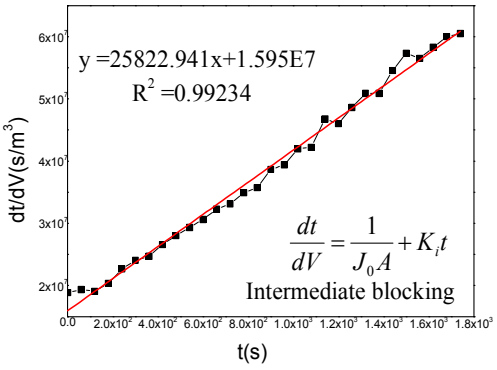


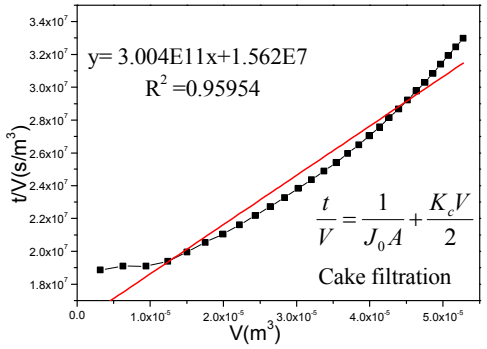


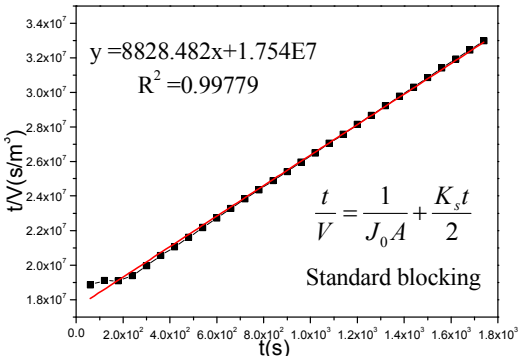


Tween80/crude oil-prepared emulsion

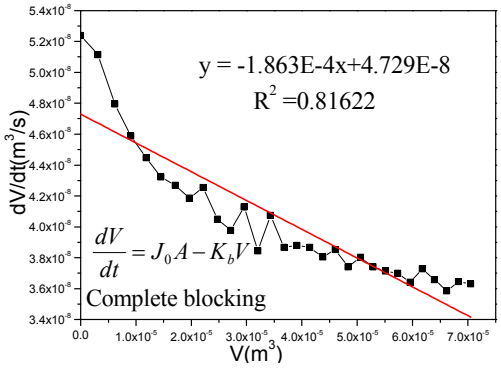


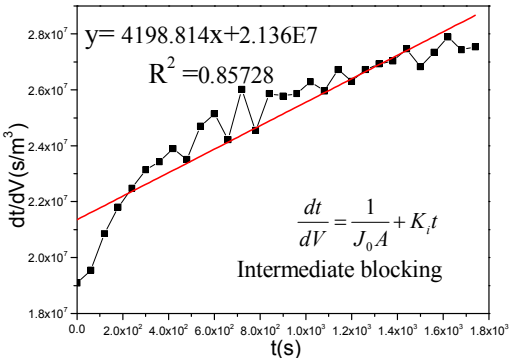


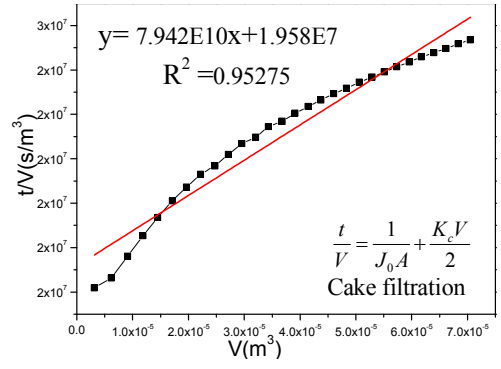


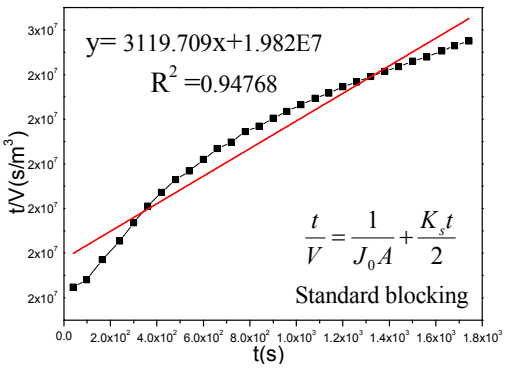


SDBS/diesel-prepared emulsion

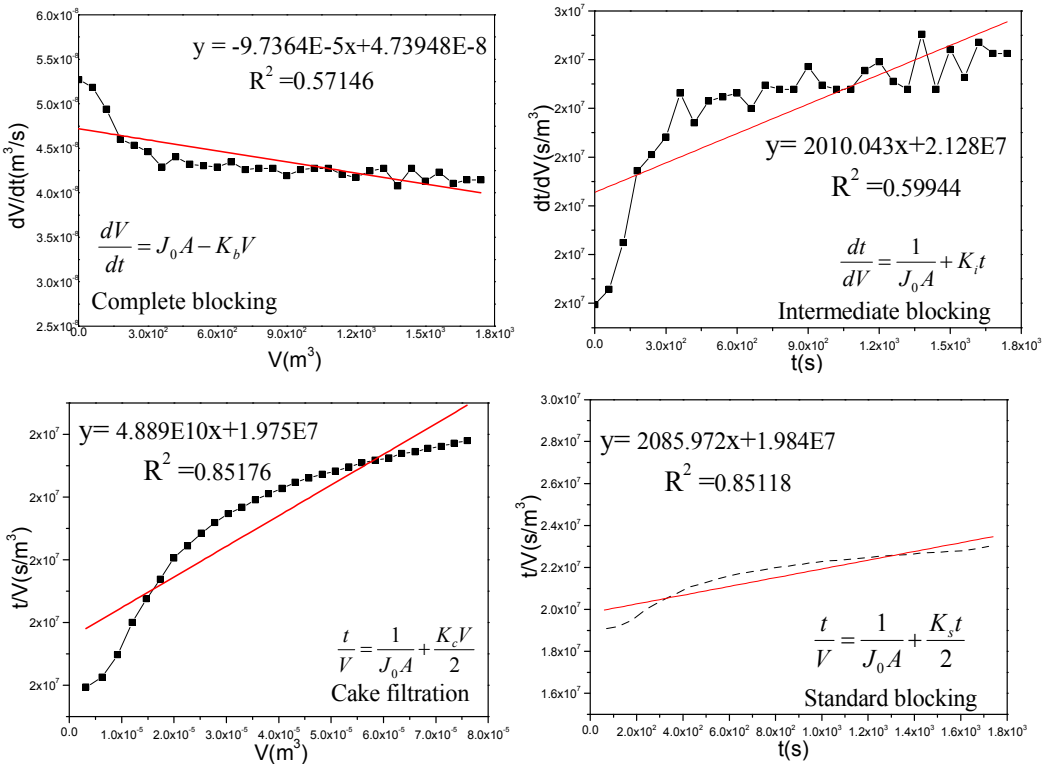








CTAB/diesel-prepared emulsion



Tween80/diesel-prepared emulsion

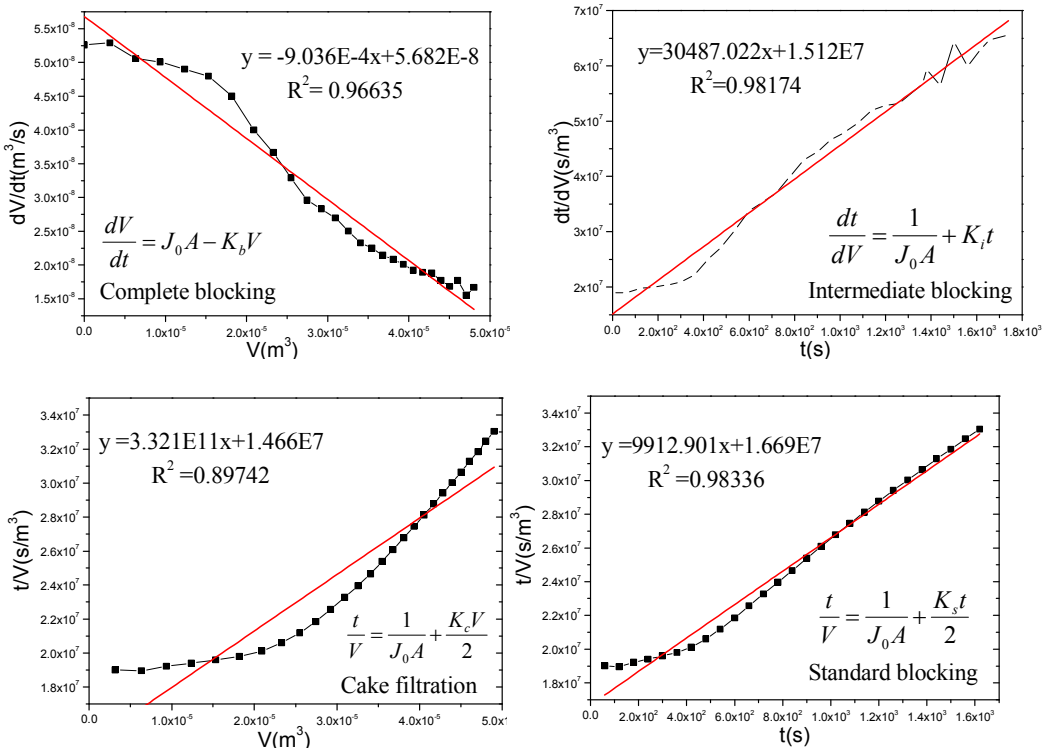


Figure S4. Fitting the flux decline of the first cycle of filtration with four fouling models (Black dots-the data obtained from Figure S2; red curve-the fitting result).

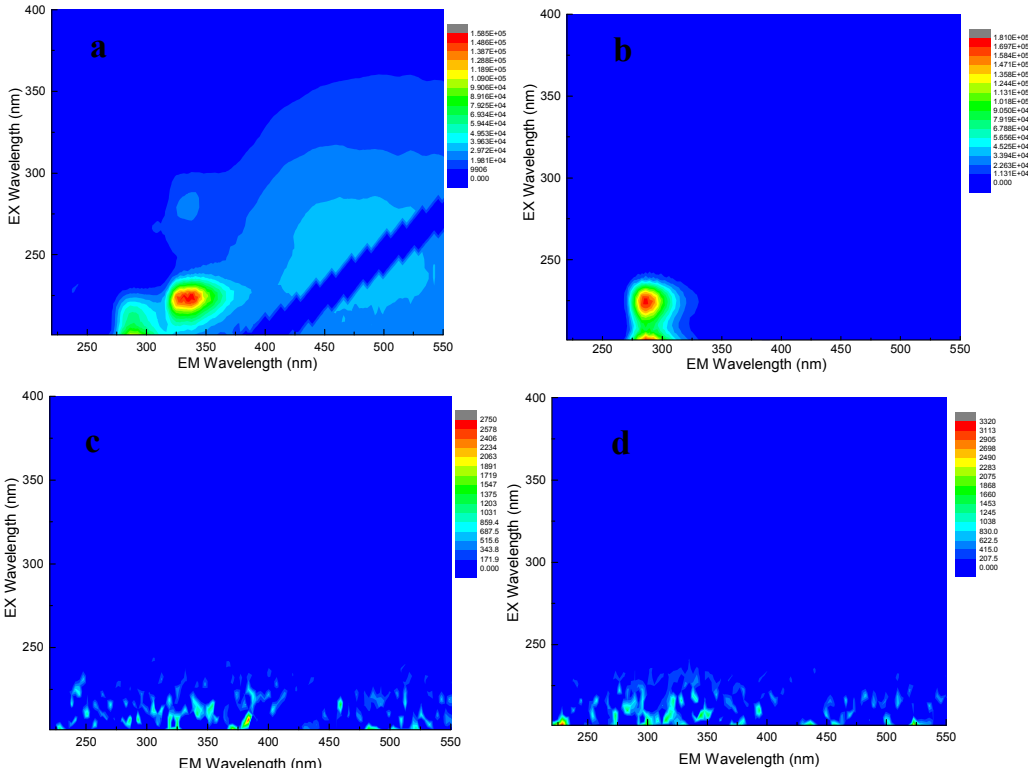


Figure S5. FEEM spectra of crude oil (a), SDBS (b), CTAB (c), and Tween-80(d).

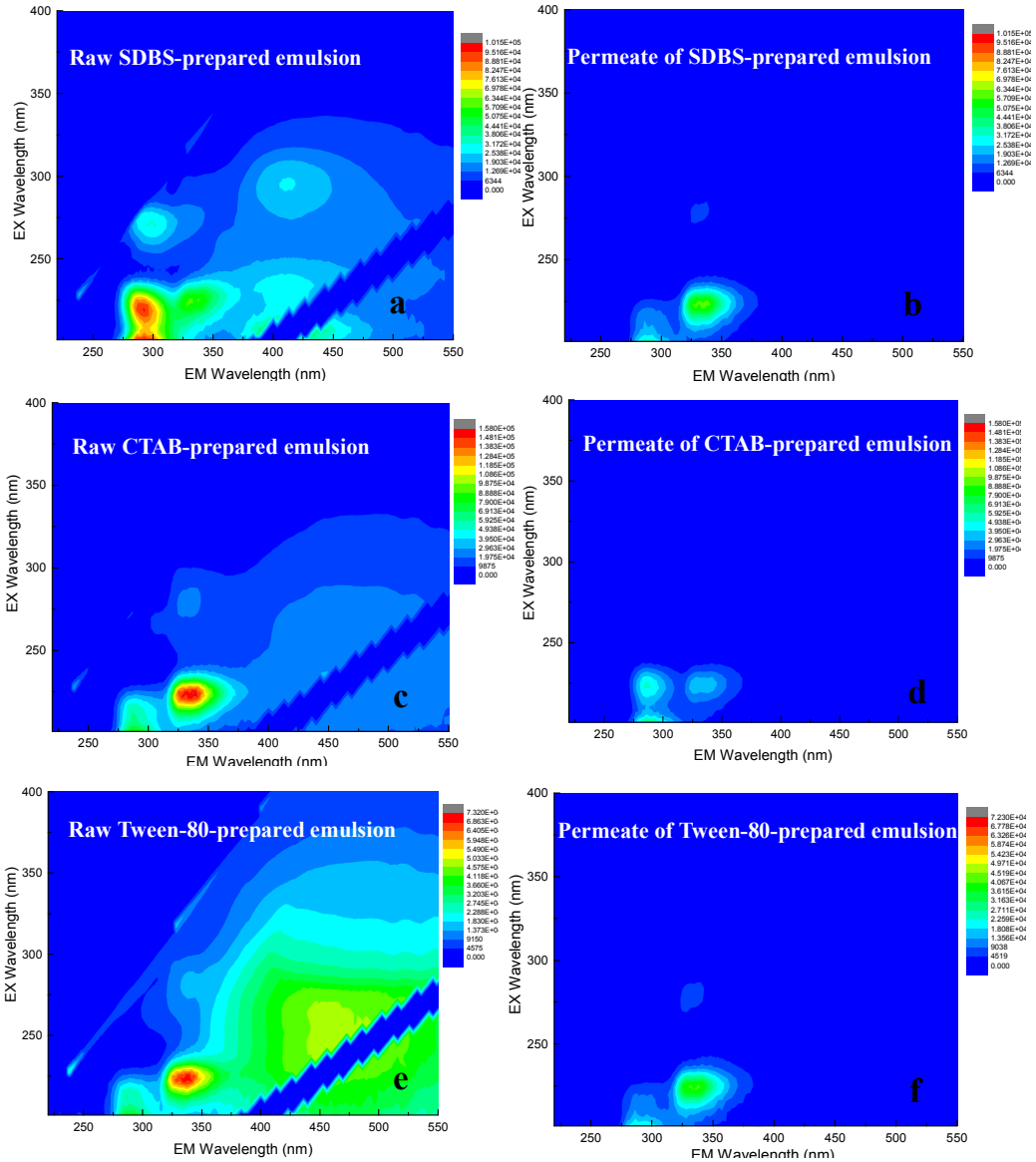


Figure S6. FEEM spectra of the feeds (Left) and the permeates (Right) of three crude oil/water emulsions.

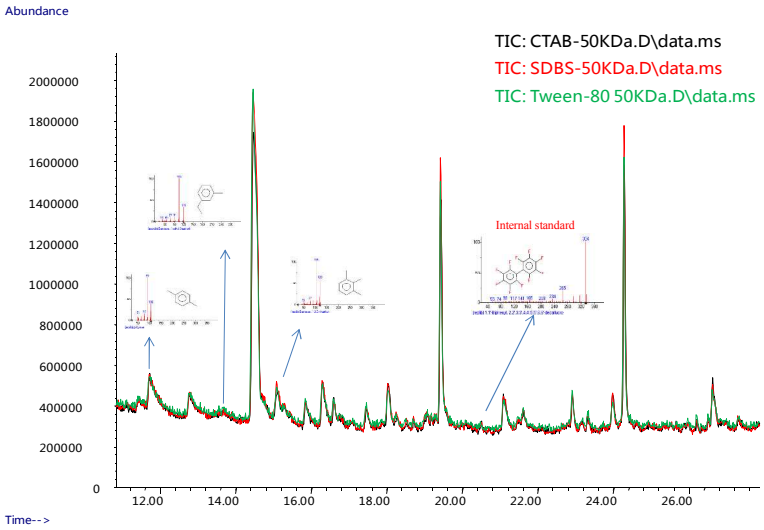


Figure S7. Aromatics identified in the feeds (after 0.45μm filter) with GC/MS.

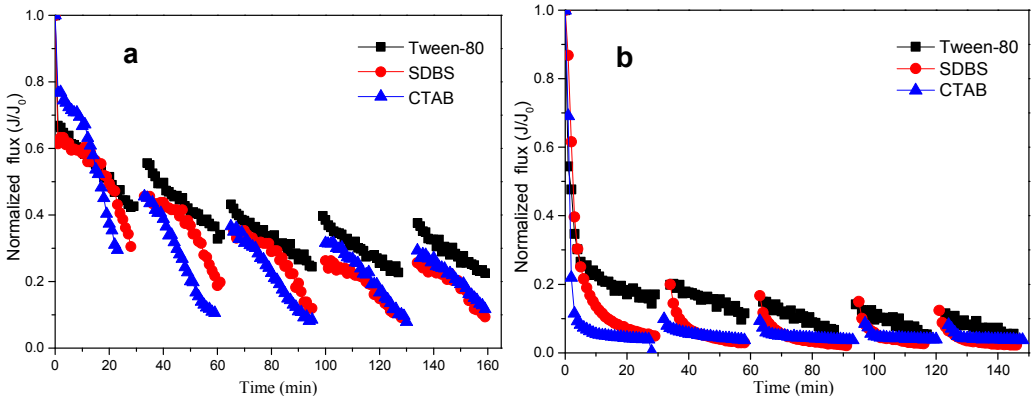


Figure S8. Normalized flux decline of 150 kDa (a) and 0.14 μm (b) ceramic membranes during the filtration of three crude oil/water emulsions prepared with different surfactants.

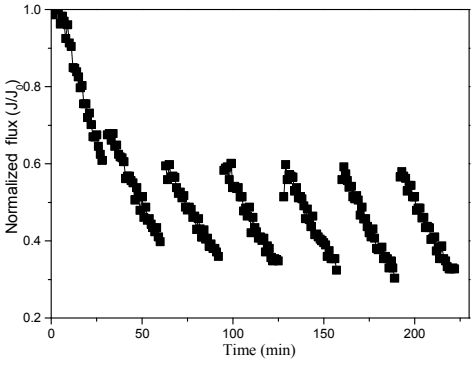


Figure S9. Normalized flux decline of the ceramic membrane during the treatment of SDBS/crude oil-prepared emulsion with larger average oil droplet size (427 nm).

1. Hermia, J., Constant Pressure Blocking Filtration Law Application to Power-Law Non-Newtonian Fluid. *Trans. Inst. Chem. Eng.* **1982,** *60*, 183-187.

2. Wei, C.-H.; Laborie, S.; Ben Aim, R.; Amy, G., Full utilization of silt density index (SDI) measurements for seawater pre-treatment. *J. Membr. Sci.* **2012,** *405-406*, 212-218.