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Paper

Mussel and Fish Scale-Inspired Underwater Superoleophobic Kapok Membranes for Continuous and Simultaneous Removal of Insoluble Oils and Soluble Dyes in Water

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Bioinspired materials with special wettability towards water and oils have been proven very efficient in removal of insoluble organic pollutants in water. However, these materials cannot remove water-soluble organic contaminants, and often have some problems such as easily contaminated by oils, low water tolerance and complicated preparation methods. Herein, we present a simple approach for the fabrication of mussel and fish scale-inspired underwater superoleophobic kapok membranes via treatment of natural kapok fibers with sodium chlorite, surface modification with polydopamine, and then filtrated into membranes. SC treatment and PDA modification not only make the membrane underwater superoleophobic with high contact angles and low sliding angles for oils, but also introduce abundant *N*, *O*-containing groups. The kapok membranes feature excellent underwater superoleophobicity, high adsorption properties for water-soluble dyes, high stability and flexibility. Furthermore, continuous and simultaneous removal of many kinds of insoluble oils and soluble dyes in water was achieved with very high removal efficiencies in a short time by simply passing through the membrane. We believe that the underwater superoleophobic kapok membrane is very promising for removal of organic pollutants in water.

Introduction

Water pollution becomes a serious problem nowadays accompanying rapid population growth and development of economy.^[1] Water pollution has adverse effects on human health and ecosystem. Insoluble (e.g., oils and aromatic compounds) and soluble (e.g., dyes) organics are the main pollutants in water.^[2] The increased amount of oily wastewater owing to development of industry and frequent oil spills, e.g., flood of oil in the Gulf of Mexico in 2010, requires novel materials for efficient oil/water separation. In addition, the dye-containing wastewater produced by industries like textile and paper must be well purified before discharged into waters.^[3] So, great efforts have been paid in developing advanced materials and new approaches to decontaminate water efficiently, e.g., oil/water separation, adsorption and photocatalyzed decomposition.^[4]

Recently, lotus leaf-inspired superhydrophobic/superoleophilic materials including particles, membranes and sponges have been proven very efficient in removal of insoluble organic pollutants in water owing to their superior oil/water selectivity.^[5] The superior selectivity is attributed to their unique rough surfaces with low surface energy, and the difference in surface tension between water and most of oils.^[6] When an oil/water mixture contacted superhydrophobic/superoleophilic materials, oil quickly wetted the materials. The oils could be absorbed by or penetrated through the materials depending on their thickness and pore volume. Meanwhile, water was collected on the surface of the

materials like water on a lotus leaf. Although encouraging results have been obtained, superhydrophobic/superoleophilic materials can be easily contaminated by oils in the separation process due to their high affinity to oils, which will evidently reduce their performance and cause secondary pollution.

Fishes are well protected from contamination by oils in water, exhibiting self-cleaning property. The water trapped in the rough fish scales prevents the penetration of oils, yielding underwater low-adhesive superoleophobic surfaces.^[7] Different from superhydrophobic/superoleophilic materials, fish scale-inspired underwater superoleophobic materials remained clean in the oil/water separation process. The underwater superoleophobic materials can be fabricated by coating different metal meshes with various hydrophilic materials including hydrogels, graphene oxide and carbon nanotubes.^[8] Although the oil/water separation efficiency is high, underwater superoleophobic materials often have some problems such as low water tolerance of hydrogels, complicated preparation methods and high cost of the carbonaceous materials as well as low flexibility of metal meshes.

Moreover, both superhydrophobic/superoleophilic materials and underwater superoleophobic materials cannot remove water-soluble organic contaminants, e.g., the frequently encountered dyes. Until now, only a few studies have achieved removal of both insoluble oils and soluble dyes in water but in two steps via oil/water separation followed by photocatalyzed decomposition of dyes for a very long period of time.^[2]

Herein, we present a simple approach for the fabrication of mussel and fish scale-inspired underwater superoleophobic kapok membranes via treatment of kapok fibers (KFs) with sodium chlorite (SC), surface modification with polydopamine (PDA), and then filtrated into membranes. KFs, a kind of natural renewable resource, have a unique tubular structure.^[9] The kapok membranes feature excellent underwater superoleophobicity, high adsorption properties for soluble dyes, high stability and flexibility, which make them excellent materials for continuous and simultaneous removal of insoluble oils and soluble dyes in water.

Experimental Section

Materials

Raw KFs were purchased from Shanghai Panda Co., Ltd., China. Dopamine hydrochloride (98%) was purchased from Shanghai DEMO Medical Tech Co., China. SC, tris-(hydroxymethyl)amino methane hydrochloride (Tris-HCl), dichloromethane (DCM), methylene blue (MB), methyl violet (MV), toluene, 1, 2-dichlorobenzene, diphenyl oxide, acetic acid, hydrochloric acid, sodium hydroxide, Tween 80, *n*-hexane, CHCl₃ and anhydrous ethanol were purchased from China National Medicines Co., Ltd., China. Cationic red (CR) was provided by Binhai Torch Technology, Co., Ltd., China. Commercial petrol and diesel were purchased from Sinopec, Lanzhou, China. Deionized water was used throughout the experiment. All the chemicals used were analytical grade and were used as received without further purification. More information about the three model oils and the three model water-soluble organic dyes is summarized in Figs. S1 and S2, respectively.

Preparation of SC-KFs

The raw KFs were washed with copious amount of water and ethanol. SC (4.0 g) was dissolved in 400 mL of deionized water in a flask equipped with a mechanical stirrer and a thermometer. The pH of the SC solution was adjusted to 4.5 using 1.2 mL of acetic acid. Afterwards, 2.0 g of KFs was added and stirred at 600 rpm and 80 °C for 0, 1, 2 and 4 h. Finally, SC-KFs were washed with deionized water until pH 6, and then dispersed in deionized water.

Fabrication of SC-KFs@PDA membranes

Dopamine (1.5 mg/mL) was dissolved in a pH 8.5 10 mM Tris-HCl aqueous solution. SC-KFs were added to 400 mL of the above dopamine solution, and mechanically stirred for 0, 4, 12 and 24 h at room temperature. Then, SC-KFs@PDA were washed with deionized water until pH 6. Finally, SC-KFs@PDA were filtrated into membranes, and dried in an oven at 60 °C. The membranes with a PDA layer thickness of ~20 nm have a pore size of ~20 μm and a thickness of ~1 mm.

Removal of insoluble oils and soluble dyes in water

The water purification experiments using the kapok membranes were carried out with a setup composed of an automatic injector, a syringe with polluted water, a syringe filter with the as-prepared membrane and a vial. The as-prepared membrane (diameter = 2.5 cm) was fitted into the syringe filter (outer diameter = 2.9 cm, inner diameter = 2.4 cm) with a joint ring (outer diameter = 2.4

cm, inner diameter = 1.7 cm). When the wastewater containing emulsified oils and/or soluble dyes was filtrated through the membrane at a constant flux, oils and dyes were removed and the cleaned water was collected in the vial. The initial and residual concentrations of oils and dyes in water were measured using a UV-Vis spectrophotometer (Specord 200, Analytik Jena AG) at their maximum absorbance wavelengths according to the calibration curves (Fig. S3). Removal efficiencies (*REs*) of oils and dyes were calculated using the following equation:

$$RE = (c_0 - c_f) / c_0 \times 100 \quad (1)$$

where c_0 (vol% for oils or mg/L for dyes) is initial concentration of oils or dyes, c_f (vol% for oils or mg/L for dyes) is the concentration of oils or dyes in the filtrates.

The dye solutions were prepared by dissolving MB, MV and CR in deionized water. The surfactant-free emulsified oil solutions were prepared by mechanically stirring a mixture of a certain volume of oil (e.g., toluene, 1, 2-dichlorobenzene and diphenyl oxide) and deionized water at 1000 rpm for 0.5 h. The Tween 80 stabilized toluene-in-water emulsion was prepared by mechanically stirring a mixture of 5 mL of toluene and 95 mL of a 50 mg/L Tween 80 aqueous solution at 1000 rpm for 0.5 h. The model wastewater containing 5 vol% toluene and 5 ppm was prepared via a similar approach. The model wastewater containing 2 vol% toluene, 2 vol% 1, 2-dichlorobenzene, 2 vol% diphenyl oxide 2 ppm MB, 2 ppm MV and 2 ppm CR was also prepared via a similar approach. The model wastewater was freshly prepared before use.

Adsorption kinetics for MB

For kinetic study, 50 mg of SC-KFs@PDA was added into 500 mL of 5 ppm MB solution in a 1 L beaker and stirred at 150 rpm for predetermined time intervals. The adsorption capacity of SC-KFs@PDA for MB, q_t (mg/g), at time t , was calculated using the following equation:

$$q_t = (c_0 - c_t) \times V / m \quad (2)$$

where c_0 (mg/L) is initial MB concentration, c_t (mg/L) is the MB concentration at time t , V (L) is the volume of solution used, and m (g) is the mass of SC-KFs@PDA.

Desorption and regeneration of membranes

After removal of insoluble oils and soluble organic dyes in water, the SC-KFs@PDA membranes were washed with ethanol, regenerated using 50 mL of 0.1 M HCl aqueous solution for 60 min, and then washed with deionized water and ethanol for several times. Finally, the regenerated membranes were dried in an oven at 60 °C, and used for the subsequent water purification experiments.

Characterization

The micrographs of the samples were taken using a field emission scanning electron microscope (SEM, JSM- 6701F, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold (~7 nm). Digital micrographs of samples were taken using a Leica DM1000 microsystem (CMC GmbH, Germany). X-ray photoelectron spectra (XPS) were obtained using a VG ESCALAB 250 Xi spectrometer equipped with a monochromated Al K α X-ray radiation source and a hemispherical electron analyzer. Spectra were recorded in the

constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C 1s peak at 284.6 eV as the reference. FTIR spectra of the samples were recorded on a Nicolet NEXUS FTIR spectrometer using potassium bromide pellets. The CAs of water and DCM were measured by dropping 7 μL water or DCM droplets onto the surfaces of the membranes in air or underwater at ambient temperature. The reported CAs were acquired by averaging the data from the same sample at five different positions obtained using the Contact Angle System OCA 20 (Dataphysics, Germany). The zeta potentials of samples were measured on a Malvern Zetasizer Nano system with irradiation from a 633 nm He-Ne laser (ZEN3600). The high-speed video was taken using the Contact Angle System OCA 20 at 400 fps. All tests were carried out in triplicate.

Results and Discussion

Preparation of Underwater Superoleophobic Kapok Membranes

For the fabrication of the underwater superoleophobic kapok membranes, KFs were treated in a boiling SC aqueous solution in the presence of acetic acid, and then modified with a thin layer of PDA by polymerization of dopamine. Subsequently, the as-prepared brown SC-KFs@PDA fibers were filtrated into the underwater superoleophobic SC-KFs@PDA membranes (Fig. 1a). The light gray KFs became white after boiled in the SC solution. Like L-3,4-dihydroxyphenylalanine in the adhesive proteins of mussels, dopamine could spontaneous polymerize and deposit on the surface of SC-KFs in pH 8.5 Tris-HCl buffer solution.^{1,2} The PDA layer contains abundant *N*, *O*-containing groups such as catechol and amine groups,^[10] which not only help to make the membranes underwater superoleophobic, but also provide active sites for the adsorption of soluble dyes in water.

The SC treatment and the PDA layer have no influence on surface morphology and tubular structure of KFs (Figs. 1a, S4 and S5). Like the surface of KFs, the surfaces of SC-KFs and SC-KFs@PDA are very smooth, indicating that the PDA layer is very thin. FTIR spectra of KFs, SC-KFs and SC-KFs@PDA are shown in Fig. S6. The band of KFs at 3352 cm^{-1} (stretching vibration of O-H of cellulose) became broader after treated with SC. SC produced chlorine dioxide under acidic condition, which broke a part of hydrogen bonding and oxidated lignin in KFs.^[11] In addition, the bands at 1602 , 1509 and 1460 cm^{-1} (stretching vibration of C-C in different substituted aromatic rings of lignin) and 833 cm^{-1} (wagging vibration of C-H in 1, 4-disubstituted aromatic ring of lignin)^[12] almost disappeared after treated with SC, which further proved that lignin in KFs was decomposed. Also, the intensity of the band at 2910 cm^{-1} increases, which is concerned with the removal of wax on the surface of KFs.^[13] Thus, a part of cellulose is amorphous and there are a lot of O-H groups in SC-KFs. In the spectrum of SC-KFs@PDA, the appearance of the bands at 1625 cm^{-1} (stretching vibration of aromatic C=C groups), 3355 cm^{-1} (stretching vibrations of catechol O-H and N-H groups of PDA) and 1508 cm^{-1} (shearing vibration of N-H) indicates that SC-KFs were modified with PDA.^[14] The surface chemical composition of KFs, SC-KFs and SC-KFs@PDA was analyzed using XPS (Figs. S7-S8 and Table S1). The O/C atomic ratio increases from 0.12 to 0.31 after SC treatment, which further proves removal of wax on the surface of

KFs. For SC-KFs@PDA, the new N 1s peak further indicates that SC-KFs are covered with PDA.^[15] In the C 1s spectrum of KFs, the two peaks at 284.4 eV (C-C and -C-H) and 285.0 eV (C-O) (Fig. S8a) indicate that KFs mainly consist of cellulose and lignin.^[16] In the C 1s spectrum of SC-KFs, the new peak at 286.6 eV (O-C-O and C=O) (Fig. S8b) suggests that carbonyl species are formed by SC oxidation.^[17] The C 1s peak of SC-KFs@PDA can be curve-fitted into five peaks at 284.5 (C-C), 285.4 (C-N), 286.4 (C-O), 287.8 (C=O) and 288.9 eV (O-C=O), which are consistent with the O 1s spectrum (Fig. S8c).^[18] The N 1s peak is attributed to R-NH₂ (401.7 eV), R-NH-R or indolyl (399.8 eV), and R-N= (398.5 eV), which means dopamine was converted to indolic compounds during formation of the PDA layer.^[19] The weak peak of R-NH₂ is because of the self-assembled dopamine in the PDA layer.^[20]

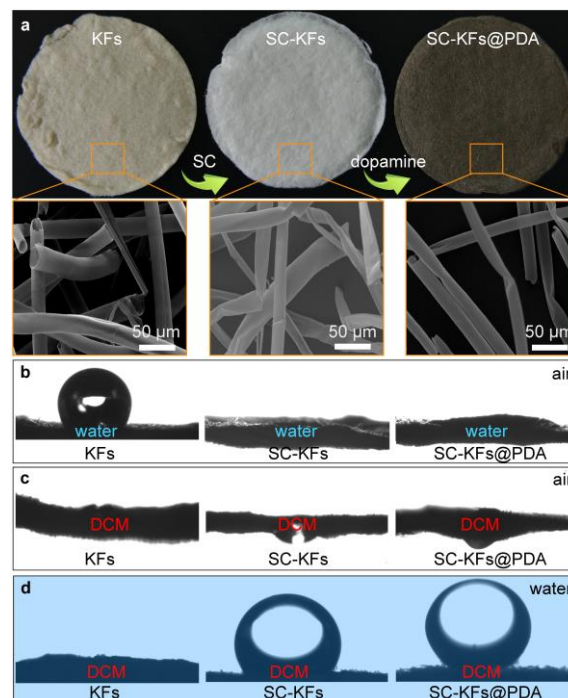


Fig. 1. (a) Synthesis of the underwater superoleophobic SC-KFs@PDA membranes and the corresponding digital and SEM images. Still images of 7 μL droplets of (b) water in air, (c) DCM in air and (d) DCM underwater on the KFs, SC-KFs and SC-KFs@PDA membranes. KFs were treated with SC for 4 h followed by modification with PDA for 24 h.

Wettability of Underwater Superoleophobic Kapok Membranes

Wettability of the KFs, SC-KFs and SC-KFs@PDA membranes towards water and DCM in air and underwater is shown in Figs. 1b-d and S9. In air, the KFs membrane is hydrophobic with a water contact angle ($\text{CA}_{\text{water}}^{\text{air}}$) of 142.4° owing to the waxy cutin on the surface of KFs. Thus, water cannot easily penetrate into the lumina of KFs driven by the capillary pressure.^[21] Water drops in air could completely penetrate the SC-KFs membrane in ~ 8 s and the SC-KFs@PDA membrane in less than 7 s, indicating that SC treatment and the PDA layer could improve hydrophilicity of the membrane. In air, DCM drops could wet and completely penetrate into all the three membranes in less than 2.5 ms because of its low surface tension compared to water. Different from in air, the membranes in water show obviously

different wettability towards DCM (Movie S1). The KFs membrane is underwater superoleophilic and DCM droplets spread out quickly in 50 ms once contacted the membrane in water. Whereas the SC-KFs membrane is underwater oleophobic (5 $CA_{DCM}^{water} = 134^\circ$). DCM droplets adhere firmly on the SC-KFs membrane in water and cannot roll off the tilted membrane. Large deformation of the DCM droplet was observed while moving it along the surface of the SC-KFs membrane (Movie S2, part 1), which means strong adhesion between them. Underwater superoleophobic SC-KFs@PDA membranes were formed after further modification with PDA. When the DCM droplet contacts with the SC-KFs@PDA membrane underwater, high content of water was trapped in the rough membrane, forming an oil/water/solid composite interface. The trapped water greatly reduced the contact area between the DCM droplet and the membrane, forming the underwater superoleophobic surface.^[7] In water, the DCM droplets are spherical in shape ($CA_{DCM}^{water} = 157^\circ$) on the SC-KFs@PDA membrane and could roll off the 10° tilted membrane without leaving a trace. No observable deformation of the DCM droplet was detected while moving it along the surface (Movie S2, part 2), which indicates very weak interaction between them.

Water Purification and Effects of SC Treatment and PDA Modification

Water purification experiments using the kapok membranes were carried out with a setup composed of an automatic injector, a syringe with wastewater, a syringe filter with the membrane and a vial (Fig. 2a). When wastewater containing emulsified oils and dyes contacted the membrane, the emulsion was broken by microfibers of the membrane. Subsequently, water wetted and passed through the membranes, whereas most of the insoluble oils were filtered out because of underwater superoleophobicity of the membrane. Meanwhile, the soluble dyes were adsorbed by the membrane in the wetting and penetration process, and the cleaned water was collected in the vial. Different from the previously reported materials, continuous and simultaneous removal of insoluble oils and soluble dyes in water was achieved

in a short time via a simple approach.

The SC treatment time and dopamine polymerization time have great influences on performance of the SC-KFs@PDA membranes in removal of emulsified toluene (5 vol%, the model oil, without surfactant) and MB (8 ppm, the model soluble dye) in water (Fig. 2b-e). The performance of the KFs, SC_{4h}-KFs@PDA_{0h} (without PDA modification) and SC_{0h}-KFs@PDA_{24h} (without SC treatment) membranes were also studied for comparison. The concentrations of toluene and MB in water were determined by a UV-Vis spectrophotometer at 269 nm and 664 nm, respectively, and then the $RE_{toluene}$ and RE_{MB} could be obtained. For the KFs membrane, $RE_{toluene}$ is constant (97 ~ 98%), whereas RE_{MB} decreases evidently from 72.9% to 32.6% with increasing the permeation volume (PV) to 20 mL. After treated with SC for 4 h (SC_{4h}-KFs@PDA_{0h}), there was no change in $RE_{toluene}$, whereas RE_{MB} reached 80% and remained constant with increasing PV (Fig. 2b-c). For the SC-KFs@PDA_{24h} membranes, the increase in the SC treatment time from 0 to 4 h still has no influence on $RE_{toluene}$, but evidently improves durability of the membranes in removal of MB. After polymerization of dopamine for 24 h (SC_{0h}-KFs@PDA_{24h}), $RE_{toluene}$ reached above 99.5% and remained constant, and RE_{MB} reached 95.7% but decreased gradually to 67.7% with increasing PV to 20 mL. For the SC_{4h}-KFs@PDA membranes, $RE_{toluene}$ increased to 98 ~ 99% with increasing the polymerization time to 12 h, and then reached above 99.5% with further increasing the time to 24 h. Meanwhile, RE_{MB} increased from 80% to above 98% with increasing the polymerization time to 4 ~ 24 h. In addition, $RE_{toluene}$ and RE_{MB} remained constant with increasing PV for all the SC_{4h}-KFs@PDA membranes. The data in Fig. 2b-e indicate that there is a synergistic effect of SC treatment and the PDA layer on removal of toluene and MB in water. SC treatment and the PDA layer make the membrane underwater superoleophobic, which improves $RE_{toluene}$. Also, the functional groups of the PDA layer improve RE_{MB} . The SC_{4h}-KFs@PDA_{24h} membrane is very efficient in removal of both of them ($RE_{toluene} = 99.8\%$, $RE_{MB} = 98\%$).

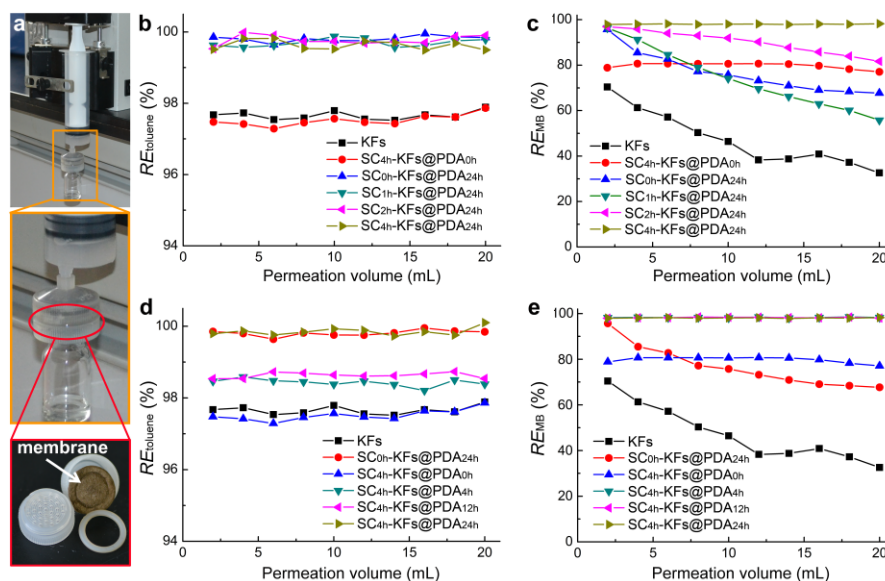


Fig. 2. (a) Experimental setup for removal of oils and dyes in water, variation of (b) $RE_{toluene}$ and (c) RE_{MB} with SC treatment time, and variation of (d) $RE_{toluene}$ and (e) RE_{MB} with dopamine polymerization time. The flux of the toluene-in-water emulsion and the MB aqueous solution is $0.6 \text{ mL}/(\text{cm}^2 \text{ min})$.

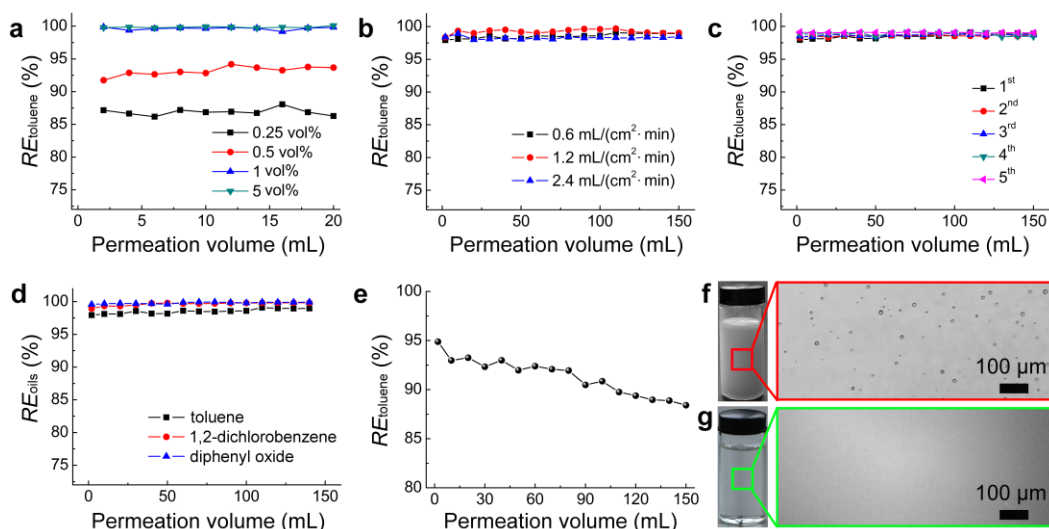


Fig. 3. Variation of RE_{toluene} with (a) toluene concentration (0.6 mL/(cm² min)), (b) flux (5 vol%) and (c) recycle times (5 vol%, 0.6 mL/(cm² min)), (d) RE_{oils} for different oils (5 vol%, 0.6 mL/(cm² min)), (e) RE_{toluene} for the tween 80 (50 mg/L) stabilized toluene-in-water emulsion (5 vol%, 0.6 mL/(cm² min)), and digital images and micrographs of (f) the tween 80 stabilized emulsion and (g) the 150th filtrate.

Selective Removal of Oils

The performance of the SC_{4h}-KFs@PDA_{24h} membrane for the selective removal of oils in water is shown in Fig. 3. RE_{toluene} is above 99.8% at a toluene concentration of 5 vol%. RE_{toluene} gradually decreases with decreasing the toluene concentration, but is still above 86.7% even at a very low concentration of 0.25 vol% (Fig. 3a). The SC-KFs@PDA membrane maintains its high RE_{toluene} with increasing the flux from 0.6 to 2.4 mL/(cm² min) even at a PV of 150 mL (Fig. 3b). In addition, the SC-KFs@PDA membrane can be repeatedly used for removal of toluene in water in high efficiency, indicating excellent recyclability (Fig. 3c). 1, 2-Dichlorobenzene and diphenyl oxide have long-term adverse effects on the aquatic environment. In spite of the difference in the substituent or the number of benzene rings compared to toluene, RE_{oils} of the SC-KFs@PDA membrane for them are all above 98% (Fig. 3d). The SC-KFs@PDA membrane can also remove other insoluble oils such as petrol, diesel and CHCl₃ with similar RE_{oils} . Moreover, the SC-KFs@PDA membrane is also effective in removal of toluene from the tween 80 stabilized toluene-in-water emulsion (Fig. 3e). The uniform emulsion became clear after simply filtered using the SC-KFs@PDA membrane (Fig. 3f-g). RE_{toluene} gradually decreases from 94.9% with increasing PV, but is still above 88.4% even at a PV of 150 mL. RE_{toluene} for the tween 80 stabilized emulsion is slightly lower than that for the surfactant-free emulsion. This is because the size of the emulsion droplets in the tween 80 stabilized emulsion is smaller (Fig. S10).

Adsorption of water-soluble dyes

The performance of the SC_{4h}-KFs@PDA_{24h} membrane for the adsorption of organic dyes in water is shown in Fig. 4. The MB solutions became colorless after filtered by the membrane. RE_{MB} is above 93% for the MB solutions with an initial concentration of 3 ~ 10 ppm (Fig. 4a). The adsorption of MB by the SC-KFs@PDA membrane is rapid and the adsorption equilibrium can be achieved within 10 min following the pseudo-second-order model (Figs. 4b and S11). This is attributed to

superhydrophilicity of the SC-KFs@PDA membrane in air with abundant *N*, *O*-containing groups. The SC-KFs@PDA membrane maintains its RE_{MB} of above 95.8% with increasing PV at a flux of 0.6 mL/(cm² min) (Fig. 4c). The increase in the flux to 1.2 and 2.4 mL/(cm² min) results in decrease in RE_{MB} , but is still as high as 85.4% even at a flux of 2.4 mL/(cm² min) and a PV of 70 mL. This is because a higher flux decreases residence time of the MB aqueous solution in the SC-KFs@PDA membrane. In addition, the SC-KFs@PDA membrane exhibits good recyclability for the removal of MB by using 0.1 M HCl as the desorption agent (Fig. 4d). The morphology of the SC-KFs@PDA membrane has no obvious change after five adsorption-desorption cycles (Fig. S12), which is attributed to tight binding of the PDA layer and excellent stability of the layer itself. Besides MB, the SC-KFs@PDA membrane can also be used to efficiently adsorb other cationic dyes such as MV and CR (Fig. 4e). The absorbance of the 70th filtrates of the 5 ppm MB, MV and CR solutions is zero (insets in Figs. 4e and S13).

After adsorbed by the SC-KFs@PDA membrane, the absorption band of MB at 1600 cm⁻¹ (stretching vibration of aromatic C-C) shifted to 1595 cm⁻¹, the band at 1339 cm⁻¹ (stretching vibration of C-N) shifted to 1333 cm⁻¹, and the band at 1355 cm⁻¹ (stretching vibration of C-N) disappeared (Fig. S14).^[22] Meanwhile, the bands of the SC-KFs@PDA membrane at 3355 cm⁻¹ (stretching vibrations of catechol O-H and N-H groups of PDA) and 1318 cm⁻¹ shifted to 3376 and 1333 cm⁻¹, respectively. The zeta potential of KFs decreased from -30.5 mV to -44.3 mV after SC treatment and PDA modification (Table S2). This is because of the abundant *N*, *O*-containing groups of SC-KFs@PDA, which provides a strong affinity for the positively charged MB.^[3, 23] Thus, the zeta potential of SC-KFs@PDA increased to -17.9 mV after adsorption of MB. The changes in the FTIR spectra and the zeta potentials indicate that hydrogen bonding and electrostatic interaction between SC-KFs@PDA and MB are the main driven forces for the removal of MB in water (Fig. 4f).^[24]

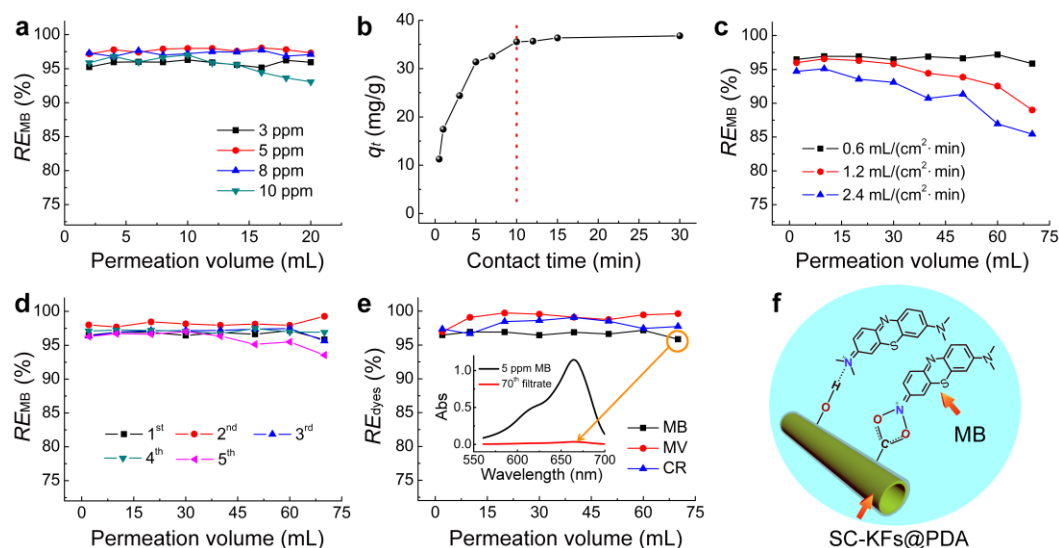


Fig. 4. Variations of (a) RE_{MB} with MB concentration (0.6 mL/(cm² min)), (b) adsorption capacity (q_t) with contact time (5 ppm), (c) RE_{MB} with flux (5 ppm), (d) RE_{MB} with recycle times (5 ppm, 0.6 mL/(cm² min)) and (e) RE_{dyes} for different dyes (5 ppm, 0.6 mL/(cm² min)), and (f) adsorption mechanism of SC-KFs@PDA for MB. The inset in (e) is the UV-Vis spectra of the 5 ppm MB solution and the 70th filtrate.

Continuous and Simultaneous Removal of Oils and Water-Soluble Dyes

The SC-KFs@PDA membrane can be used for continuous and simultaneous removal of insoluble oils and soluble dyes in water. Once the wastewater containing 5 vol% toluene and 5 ppm MB passed through the membrane, both toluene and MB were efficiently removed (Fig. 5a). $RE_{toluene}$ is above 98.5% and RE_{MB} is above 94.3% event at a PV of 150 mL. The wastewater showed strong absorption bands at 269 nm (toluene) and 664 nm (MB) in the UV-Vis spectrum (Fig. 5b). After passed through the membrane, the band for MB disappeared and the band for toluene

became very weak even for the last part of the filtrate (the 150th filtrate highlighted in Fig. 5a). We also tested performance of the SC-KFs@PDA membrane in purifying wastewater containing many kinds of organic pollutants. The wastewater containing 2 vol% toluene, 2 vol% 1, 2-dichlorobenzene, 2 vol% diphenyl oxide, 2 ppm MB, 2 ppm MV and 2 ppm CR was used as the model wastewater. After simply passed through the membrane, the purple-blue disgusting wastewater became very clean as proved by the UV-Vis spectra and the digital images (Fig. 5c-d). This result indicates that the SC-KFs@PDA membrane is very promising for practical water purification.

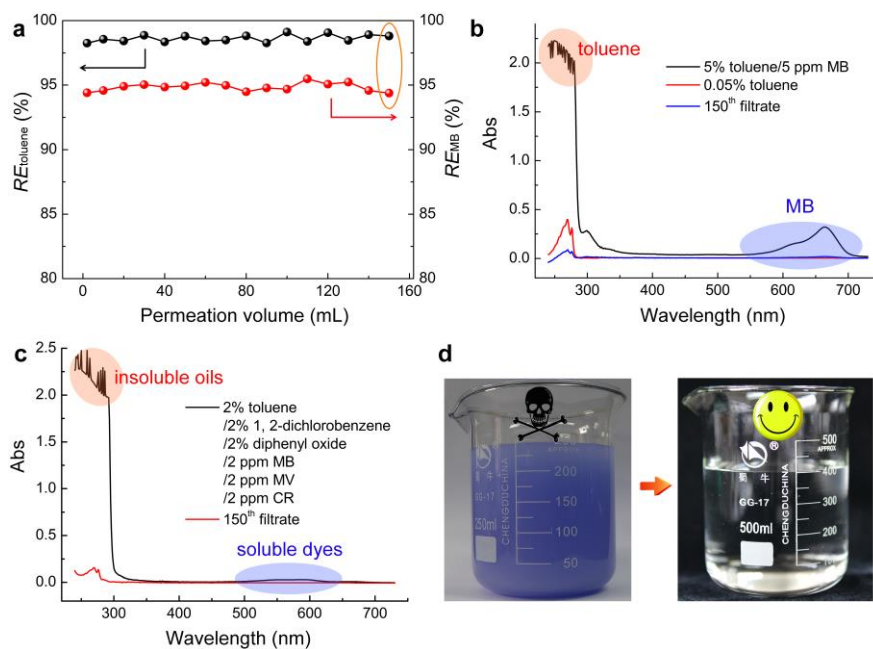


Fig. 5. (a) $RE_{toluene}$ and RE_{MB} for the 5 vol% toluene/5 ppm MB solution, (b) UV-Vis spectra of the 5 vol% toluene/5 ppm MB solution, 0.05 vol% toluene and the 150th filtrate, (c) UV-Vis spectra of the wastewater containing many kinds of organic pollutants and the 150th filtrate, and (d) images of the wastewater and the filtrate.

Conclusions

In summary, we have successfully fabricated mussel and fish scale-inspired underwater superoleophobic SC-KFs@PDA membranes with a high CA and a low SA for oil by the combination of SC treatment and PDA modification followed by filtrating into membranes. SC treatment and PDA modification not only make the membrane underwater superoleophobic, but also introduce abundant *N*, *O*-containing groups. Furthermore, continuous and simultaneous removal of insoluble oils and soluble dyes in water was achieved with very high *REs* in a short time by simply passing through the membrane. We believe that this underwater superoleophobic kapok membrane is very promising for wastewater purification as the membrane prepared by a very simple procedure can continuously and simultaneously remove many kinds of insoluble oils and soluble dyes in water.

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Notes and references

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†Electronic Supplementary Information (ESI) available: [digital images, FTIR spectra, XPS, SEM images and videos]. See DOI: 10.1039/b000000x/

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Table of Contents artwork

Kapok membranes with excellent underwater superoleophobicity, high adsorption properties for water-soluble dyes, high stability and flexibility are fabricated.

