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Multi-Layer Filter Material with a Superoleophobic Pore Size Gradient for the Coalescence Separation of Surfactant-Stabilized Oil-in-Water Emulsions

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Abstract: The performance of oil–water coalescence separation elements currently fails to meet the increasing demands of the oily wastewater treatment industry. To address this challenge, a series of fiber coalescing filters were developed through an underwater superoleophobic modification process using a simple impregnation technique. The effect of varying surface wettability on the separation efficiency of oil-in-water (O/W) emulsions stabilized with surfactants was investigated. The results demonstrate that, after undergoing underwater superoleophobic modification, the separation efficiency of the fiber filter material improved by 33.9%, the pressure drop was reduced by 46.1%, and the steady-state quality factor increased by 83.3%. Building upon these findings, an oil-repellent pore size gradient structure was introduced for the coalescence separation of surfactant-stabilized oil-in-water emulsions. This structure exhibited outstanding characteristics, including a low pressure drop and a high-quality factor. Furthermore, when processing emulsions stabilized with surfactants such as OP-10 (nonionic), CTAB (cationic), and SDS (anionic), the structure maintained high separation efficiencies of 93.6%, 96.4%, and 97.2%, respectively, after 10 cycles. Finally, based on experimental data and theoretical analysis, a separation mechanism for oil–water coalescence using superoleophobic pore size gradient filtration materials is proposed. This structure demonstrates significant potential for widespread application in liquid–liquid separation technologies.

Keywords: coalescence separation; surfactants; oil-in-water emulsions; superoleophobic modification; pore size gradient; separation efficiency



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1. Introduction

With the ongoing advancement of industrialization in China, large volumes of oil-containing wastewater are commonly generated in processes such as oil extraction and refining, metalworking, machinery cleaning, textile printing and dyeing, and leather treatment [1,2]. The oil phase in such wastewater typically exists in various forms, including free oil, dispersed oil, emulsified oil, and dissolved oil, often accompanied by pollutants such as surfactants, polymers, and oil sludge [3]. Improper treatment methods can lead to significant resource wastage, as well as causing equipment corrosion, environmental pollution, and posing health risks to humans [4]. Conventional oil-containing wastewater treatment methods include gravity sedimentation [5], flotation and vortex separation [6],

centrifugal separation [7], coalescence separation [8], membrane separation [9], electrostatic separation [10], and biodegradation [11]. Due to the high pollutant concentrations, complex compositions, and severe emulsification of oil-containing wastewater, conventional treatment methods often fail to meet the required treatment standards. Fiber coalescence separation technology has gained significant attention in the field of oil–water separation due to its efficiency, low energy consumption, and environmental benefits [12,13]. This technology utilizes both the fluid dynamics within the coalescing medium and the surface wettability of the materials to promote the coalescence of dispersed oil droplets, facilitating their separation by gravity. The coalescence process itself is complex, influenced by several factors that affect the performance of fiber-based separation systems [14].

Extensive research has been carried out globally on several aspects, including material surface modification [15], pore size regulation [16], solution properties [17], operating conditions [18], and models for pressure drop and efficiency calculations [19]. Among these, the effect of surface modification on coalescence separation performance has garnered significant attention. Wang et al. [20] introduced a straightforward modification method using a mixed solution of stearic acid and perfluorooctanoic acid, which proved crucial for achieving both super-hydrophobicity and high oleophobicity. Li et al. [21] proposed a theoretical model for the coexistence of superhydrophilicity and superoleophobicity and experimentally validated this model for the first time. Yang et al. [22] employed a spraying technique to create chitosan–perfluorooctane/silica nanoparticle surfaces (CTS-PFO/SiO₂) with superhydrophilic and superoleophobic properties, specifically designed for oil-contaminated wastewater treatment. Cui et al. [23] used a hydrothermal method to grow one-dimensional needle-like nanostructures of cobalt bicarbonate on nonwoven fabrics, combined with a polydimethylsiloxane (PDMS) coating to endow the material with underwater super-oil-repellent properties, which demonstrated a high separation efficiency. This study highlights the significant role of wettability in influencing the separation performance of materials.

Meanwhile, several scholars have also investigated the impact of the material pore size on coalescence separation performance. Kampa et al. [24] examined the performance of materials with five different pore sizes and wettability combinations. Their findings revealed that the increase in pressure drop primarily depends on the wettability and pore size of the medium, and confirmed that the filter’s behavior in terms of pressure drop, saturation, and oil transport closely align with the “jump and channel” semi-quantitative prediction model. Mino et al. [25] employed the lattice Boltzmann method (LBM) to study the effects of fiber wettability, separation porosity, and fiber diameter on oil–water coalescence behavior. Their simulation results indicated that separators with larger inter-pore distances are more likely to coalesce and form larger droplets. Swarona et al. [26] demonstrated that, in addition to emulsion properties and operating conditions, the separation performance is largely determined by the pore size, surface energy, and porosity of the separation medium.

Currently, research on the combined effects of oil-repellent modification and pore size gradient on the performance and coalescence mechanism of oil–water coalescence separation elements remains insufficient. Effectively leveraging the synergistic effects of both remains a critical issue in the design of oil–water coalescence separation materials. In this context, the present study focuses on analyzing the impact of super-hydrophobic modification and pore size gradient synergy on the coalescence and oil removal performance of fiber filter materials. Through experimental data and theoretical analysis, a novel multi-layer filter material structure with super-hydrophobic, pore size-increasing gradient for separating various surfactant-stabilized oil-in-water (O/W) emulsions is proposed. This innovative design provides valuable data support for the industrial application of oil–water

coalescence separation technologies and offers theoretical guidance for further research in related fields.

2. Materials and Methods

2.1. Materials

The polypropylene material was obtained from Changcheng Filter Materials Co., Ltd., based in Xinxiang City, Henan Province, China. Basic parameters were determined through three measurements using laboratory instruments, with average values recorded. These parameters are detailed in Table 1. Experimental reagents included 0# diesel (viscosity: 3.96 mPa·s, density: 844 kg/m³, surface tension: 32.6 mN/m), purchased from Sinopec Sales Co., Ltd., Beijing Petroleum Branch, Beijing, China. Deionized water (viscosity: 1.02 mPa·s, density: 998 kg/m³, surface tension: 70.6 mN/m) was sourced from Shanghai Titan Technology Co., Ltd., Shanghai, China. n-Hexane (AR, 97%) and surfactants, including octylphenol ethoxylate (OP-10, AR, 99%, non-ionic), cetyltrimethylammonium bromide (CTAB, cationic, powder form), and sodium dodecyl sulfate (SDS, 99%, anionic, powder form), were obtained from Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China. Sodium hydroxide (NaOH, 97%) was sourced from Tianjin Guangfu Chemical Reagent Co., Ltd., Tianjin, China. Fluorocarbon surfactant (FS-50, >99%) was supplied by DuPont, Wilmington, DE, USA. Chitosan quaternary ammonium salt (HCAA, 99%) and perfluorooctanoic acid (PFOA, 96%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. The densities, viscosities, and surface tensions of all liquids were measured using laboratory instruments. All reagents were used as received, without further purification.

Table 1. Structure parameters of filter media.

Material Type	Thickness/mm	Weight/(g/m ²)	Average Pore Size/μm	Underwater Oil Contact Angle/°
PP1	0.72 ± 0.02	171.9 ± 0.9	9.82 ± 0.15	0
PP2	0.69 ± 0.01	148.8 ± 0.6	15.53 ± 0.13	0
PP3	0.63 ± 0.01	139.1 ± 0.5	21.09 ± 0.42	0

2.2. Preparation and Characterization of Modified Fibrous Filter Materials

The experimental materials include three types of polypropylene fiber filters with varying pore sizes, labeled PP1, PP2, and PP3.

The key parameters such as material thickness, grammage, pore size, and contact angle are summarized in Table 1. The modification process for these polypropylene fiber filters is depicted in Figure 1. The PP1 filters were repeatedly washed with deionized water and air-dried prior to use. The modification method, which combines hydrophilic and oleophobic treatments, follows the procedure outlined by the Pan [27] group. In a glass beaker containing 45 mL of deionized water, 0.5 g of APFO, 0.5 g of NaOH, 0.1 g of HCAA, and 5 mL of FS-50 were sequentially added and stirred at 60 °C for 6 h. After cooling to room temperature, the superoleophobic modification solution was prepared. The fluorine atoms in APFO impart excellent oleophobic properties, while NaOH facilitates hydrolysis or other reactions that expose hydrophilic groups. To achieve underwater superoleophobicity, HCAA and FS-50 were included. HCAA enhances the roughness of the fiber surface, while FS-50 integrates the perfluorocarbon chain into the coating, facilitating the desired underwater superoleophobic effect. To investigate the effect of the modifier concentration, various volumes of the modification solution were diluted with deionized water to create a series of concentration gradients for subsequent use. The pretreated PP1 fiber filters were immersed in these different concentration solutions for 5 min, followed by three rinses with distilled water to remove any residual reagents from the fiber surface. The

modified filters were then placed in a vacuum-drying oven (DZF-6020, Shanghai Hengyi, Shanghai, China) and cured at 120 °C for 6 h. Finally, the modified fiber filters—labeled PF, PF1, PF2, PF3, PF4, and PF5—were prepared using the same procedure, corresponding to modification solution concentrations of 0 wt%, 2 wt%, 4 wt%, 6 wt%, 8 wt%, and 10 wt%, respectively. The microstructures of the materials were characterized using a scanning electron microscope (Regulus 8230, Hitachi, Tokyo, Japan) coupled with energy dispersive spectroscopy (Quantax75, Hitachi, Tokyo, Japan). Material thickness was measured with a digital micrometer, while grammage was determined using an analytical balance (AL204-IC, Mettler Toledo, Zurich, Sweden). The pore size of the material was analyzed using a Porometer (3G, Quantachrome, USA), and the contact angle of the material was measured using an optical contact angle goniometer (Attension, BiolinScientific, Stockholm, Sweden).

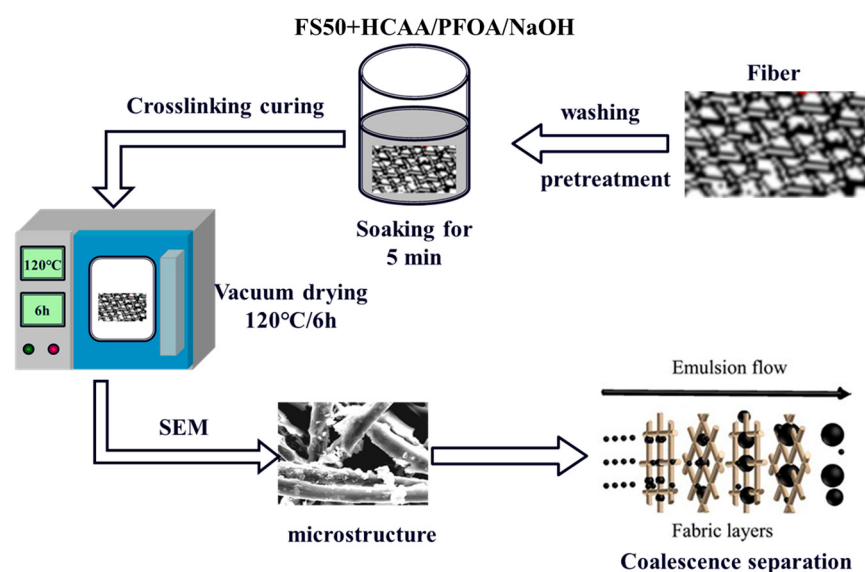


Figure 1. Preparation process of modified fibers for oil–water coalescence separation.

2.3. Preparation and Separation of Oil-in-Water Emulsion

The experimental setup is shown in Figure 2: (①) The storage tank contained a stirred, surfactant-stabilized oil-in-water emulsion, which was pumped horizontally via (②) a centrifugal pump (25SFBX-13, Shanghai Boyu Pump Co., Shanghai, China) into (③) a coalescing separator equipped with a disc-type filter material (effective filtration area: φ 78.5 cm²). After coalescence in the separator, the oil phase accumulated at the top of the coalescer, and the filtered liquid was collected in the (⑦) storage tank. The pressure drop across both ends of the filter material was monitored by (④) a differential pressure transmitter (3051D, Rosemount, Shakopee, MN, USA). (⑤) A control valve and (⑥) a turbine flow meter (LWGT-FMT-6C, Fimeet, Anhui, China) were used to regulate the system flow rate to 0.46 L/min (which corresponds to an apparent flow velocity of 0.001 m/s through the filter material). Real-time monitoring and recording were conducted. The oil concentration in water was detected by (⑧) an oil-in-water analyzer (TD560, Turner Designs, Fresno, CA, USA), while the particle size distribution was analyzed by (⑨) a particle size analyzer (AccuSizer2000, Particle Sizing Systems, USA). All data were processed and summarized on (⑩) a computer. Additionally, the liquid surface tension was measured using a surface/interfacial tensiometer (JYW-2008, Jinhe Instruments, Chengde, China), the liquid density was tested using an automatic densitometer (Digipol-D70, Shanghai Jiahang, Shanghai, China), and the viscosity was measured using a rotary viscometer (ND-J1, Shenzhen Puyun Electronics, Shenzhen, China).

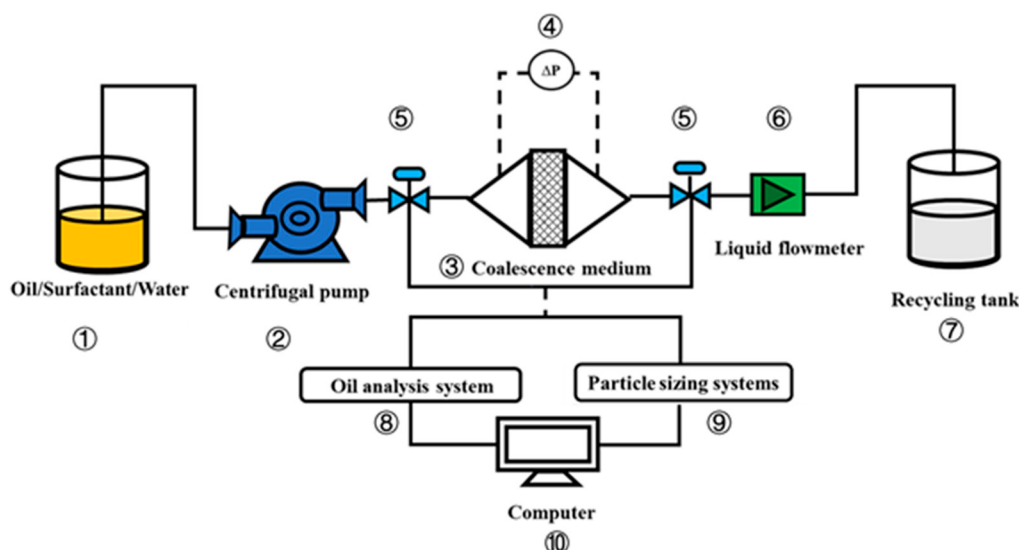


Figure 2. Experimental device for testing oil–water filtration performance. ①—Mixed fluid storage tank, ②—Centrifugal pump, ③—Coalescence medium, ④—Differential pressure transmitter, ⑤—Valve, ⑥—Liquid flowmeter, ⑦—Recycling tank, ⑧—Oil analysis system, ⑨—Particle size systems, ⑩—Computer.

The coalescing separation efficiency of fiber media is determined as follows [28]:

$$E = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (1)$$

where E is the separation efficiency, %; and C_{in} and C_{out} denote the oil concentrations at the inlet and in the filtrate, mg/L.

To evaluate the overall separation performance of the filtration material, this study introduced the concept of a quality factor [29]:

$$Q_f = -\frac{\ln(1 - E)}{\Delta P} \quad (2)$$

where Q_f is the quality factor, kPa^{-1} ; E is the separation efficiency, %; and ΔP is the pressure drop, kPa.

3. Results and Discussion

3.1. Characterization of Modified Materials

To investigate the impact of oleophobic properties on filtration performance, a modified polypropylene fiber filter (denoted as PP1) with the same pore size was used to ensure consistent pore structure parameters. Modified filters with varying concentrations, labeled PF, PF1, PF2, PF3, PF4, and PF5, were prepared using the modification method described in Section 2.2 for further experimental analysis. As shown in Figure 3, the surface morphology of the modified filters was examined using scanning electron microscopy (SEM) and compared with that of the original composite polypropylene fiber filter (PF). No significant changes in pore structure were observed following the oleophobic treatment. The oleophobic agent primarily adhered to the fiber surfaces and their intersections, reducing surface energy and enhancing the bonding strength between fibers. This modification consequently improved the mechanical strength of the polypropylene nonwoven fabric. The original polypropylene fiber filter consisted mainly of carbon (C) and oxygen (O), with trace amounts of fluorine (F), calcium (Ca), and other elements. In contrast, the surface of

the oleophobic-modified fiber filter showed a significant increase in the fluorine content, from 12.59% to 31.78%, compared to the untreated material.

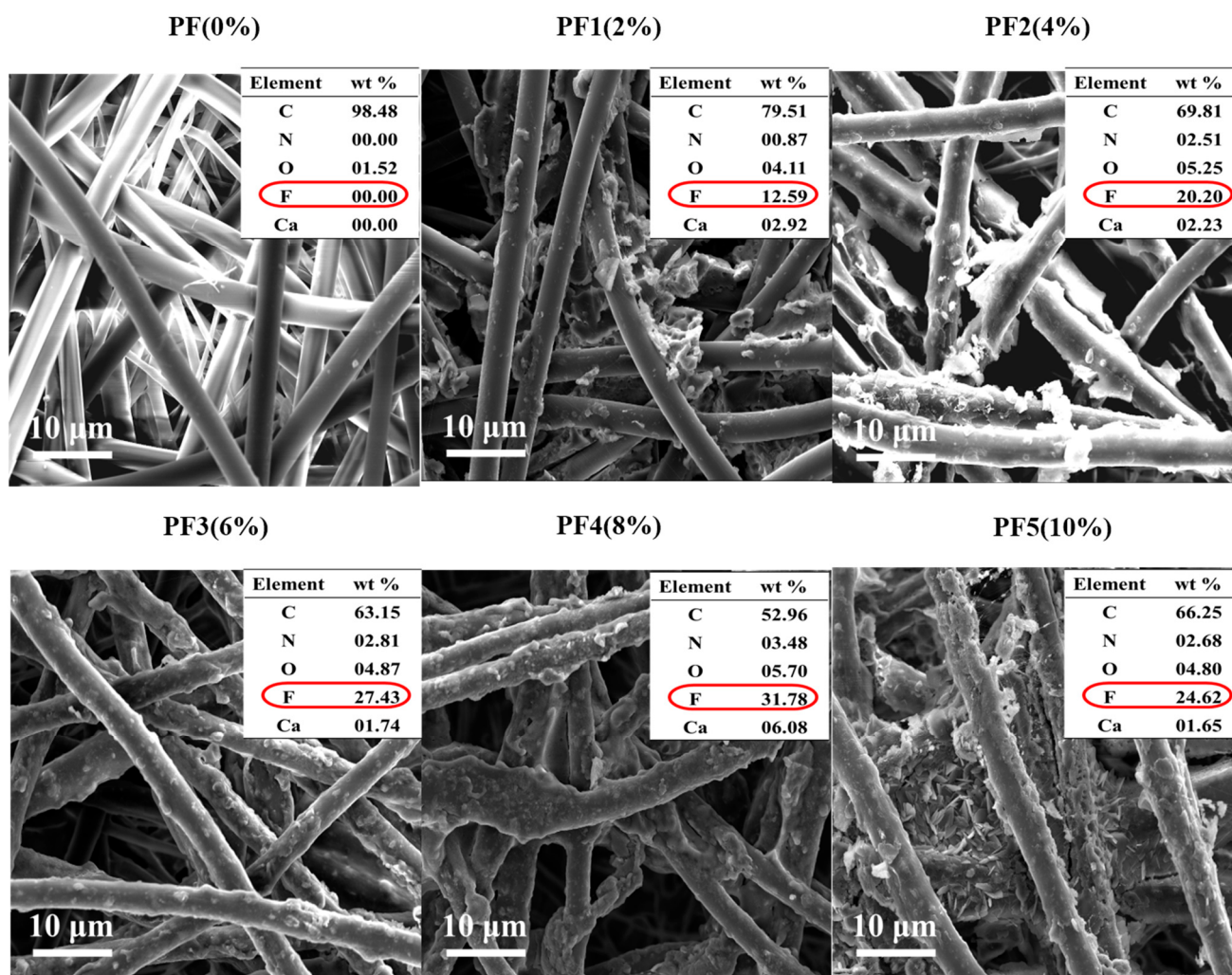


Figure 3. PF–PF5 surface morphology and energy spectrum element analysis. The red box shows the fluorine content.

This study examined the changes in the water contact angle (WCA) and underwater oil contact angle (UWOCA) of fiber filters before and after modification. The tests were performed using deionized water and diesel, as outlined in Section 2.1, at room temperature (20 ± 5 °C). As shown in Figure 4a, the unmodified PF material exhibited a WCA of 114.1° . Following modification, the WCA values decreased as the modifier concentration increased, transitioning from hydrophobic to superhydrophilic. Specifically, the WCA values for PF1, PF2, PF3, PF4, and PF5 were 23.3° , 10.9° , 0° , 0° , and 0° , respectively. This behavior is attributed to the hydrophilic groups in the FS-50 modifier, which cause water droplets to spread and penetrate the fibers upon contact.

Figure 4b shows the UWOCA values for PF, PF1, PF2, PF3, PF4, and PF5, which are 0° , 107.7° , 131.8° , 155.8° , 153.9° , and 149.0° , respectively. Notably, the UWOCA of PF3 reached 155.8° , surpassing the superoleophobicity threshold of $>150^\circ$. In summary, after treatment with the appropriate modifier concentration, the fiber filter material transitioned from hydrophobic/underwater oleophilic properties to superhydrophilic/underwater superoleophobic characteristics.

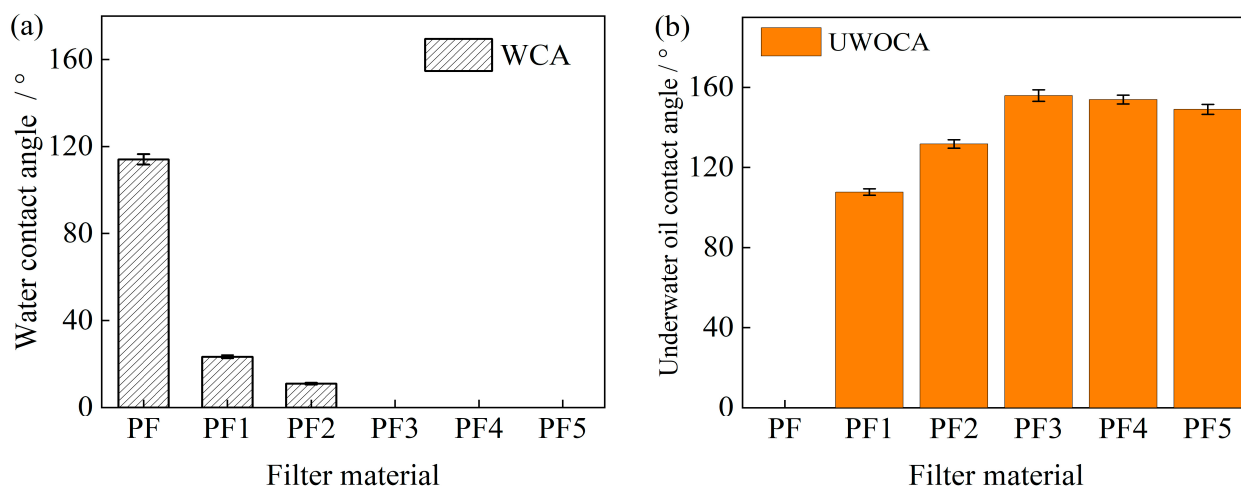


Figure 4. (a) Water contact angle (WCA) in air. (b) Underwater oil contact angle (UWOCA).

3.2. Effect of Oleophobic Modification on Separation Performance

To simulate the real operating conditions, the experimental setup was configured with an inlet oil concentration of 100 mg/L, a system flow rate of 0.46 L/min, a pressure of 1 atm, a water temperature of 20 ± 5 °C, and 10 mg/L of the non-ionic surfactant OP-10. Figure 5a shows the separation efficiency of the filter material before and after oleophobic modification. Compared to unmodified filter materials, the separation efficiency of the superoleophobic-modified filter material was significantly improved. For instance, the separation efficiency of the modified PF3 filter material increased from 26.0% to 59.9%, while the average oil concentration in the effluent decreased from 82.0 mg/L to 41.4 mg/L. This improvement can be attributed to the reduced surface energy of the oleophobic filter material, which leads to a better interaction with the oil droplets. According to the Gibbs free energy principle, oil droplets tend to spontaneously shrink into a spherical shape, increasing the separation area and enhancing the likelihood of intercepting and breaking oil-in-water droplets. Figure 5b shows the relative change in droplet size of the effluent compared to the inlet. less than 0 indicates that the effluent droplet size is smaller than that of the inlet [30]. After oleophobic modification, the average droplet size of the effluent from the PF3 filter material decreased by approximately 39.5%, whereas the unmodified PF filter material exhibited only a 15.2% reduction. This suggests that oleophobic modification enhances the demulsification and interception of oil-in-water emulsions, thereby improving the separation efficiency.

Figure 5c presents a comparison of pressure drops before and after the modification of the filter material. Compared to the unmodified PF filter material, the steady-state pressure drop of the modified PF1–PF5 filters is reduced by 28.6% to 46.1%. According to the capillary theory proposed by Washburn [31], the increase in pressure drop is linked to the capillary forces that the liquid must overcome when entering or exiting the fiber surface. After modification, the adhesion of filter fibers to droplets is reduced, particularly for PF3, which has the largest underwater oil contact angle, as shown in Figure 4b. This results in lower capillary resistance, enabling oil droplets to be expelled more easily. Consequently, PF3 exhibits the smallest steady-state pressure drop.

As shown in Figure 5c, this study analyzes the variation in pressure drop during separation before and after the modification, using the unmodified PF and oil-repellent-modified PF3 filter materials as examples. Based on the “jump-channel” pressure drop variation model proposed by Kampa et al. [24], the pressure drop process of the unmodified oleophilic PF and the oil-repellent-modified PF3 filter materials is divided into three stages. Compared to the PF filter material, the pressure drop increase in the second stage is

effectively suppressed in the oil-repellent-modified PF3, resulting in a 46.1% reduction in its steady-state pressure drop. Therefore, although the structural parameters of PF and PF3 are identical, the oil-repellent modification significantly reduces the steady-state pressure drop, indicating a notable improvement in the performance of the filter material.

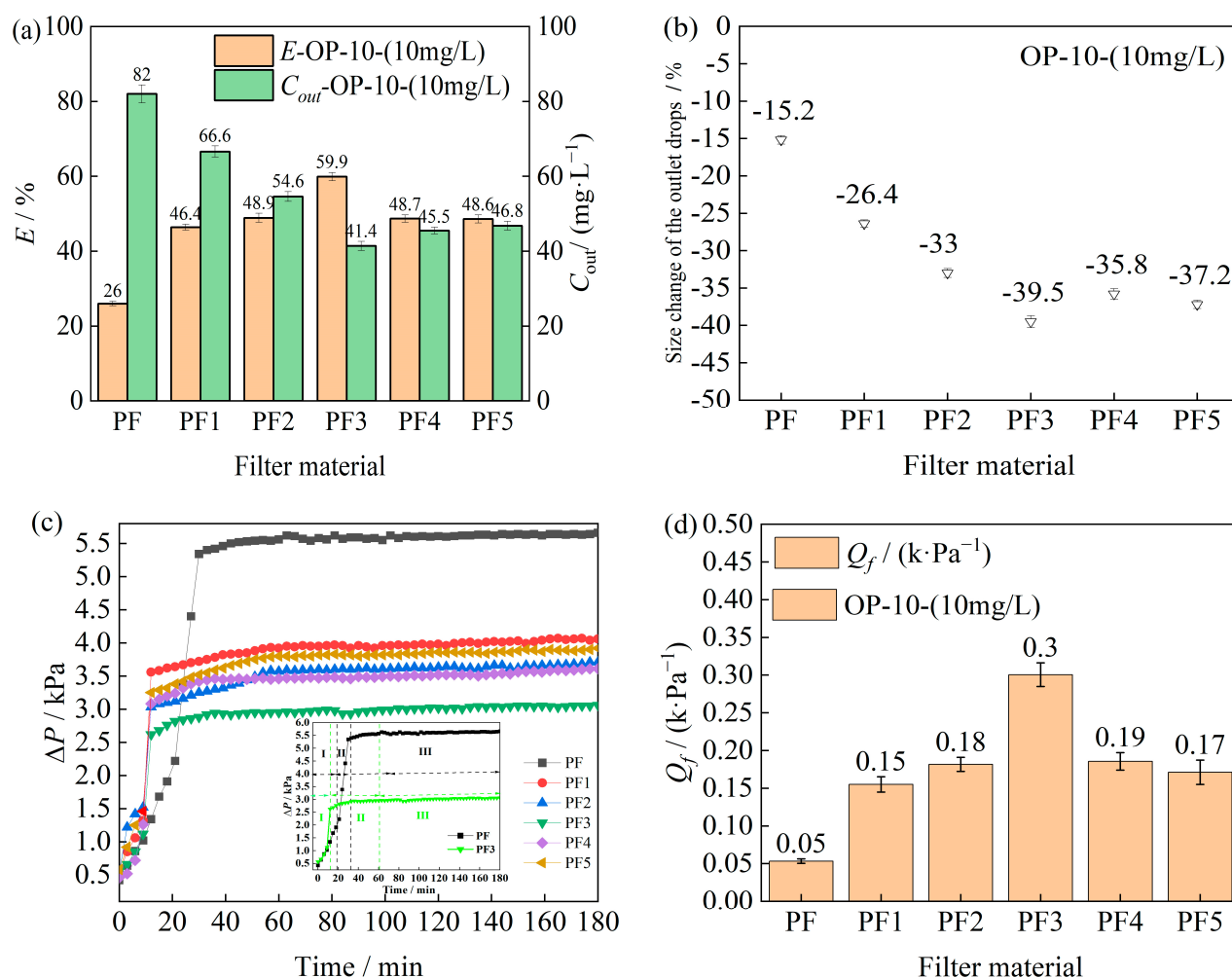


Figure 5. Effect of oleophobic modification. (a) Filter material oil removal efficiency, (b) droplet size change, (c) PF-PF5 filter material pressure drop, and (d) comparison of steady-state factor Q_f .

To comprehensively evaluate the impact of oil-repellent modification on the coalescence separation performance of the filter material, the steady-state quality factor of the filter material before and after modification was compared, as shown in Figure 5d. The unmodified PF has a quality factor of only 0.05, while the modified filter materials show an improvement in the quality factor, with PF3 reaching 0.30. In conclusion, after treatment with a 6 wt% oil-repellent modifier, the steady-state quality factor of the PF3 filter material increases by 83.3%, demonstrating the best overall separation performance.

3.3. Effect of Pore Size Distribution on Coalescence Separation Performance

Based on the findings from Section 3.1, the specific parameters of three polypropylene fibrous filtration materials with different pore sizes, PP1, PP2, and PP3, are presented in Table 1. These materials were immersed in a 6 wt% oleophobic modification solution and, after drying, the corresponding modified filtration materials, labeled NP1, NP2, and NP3, have their physical properties listed in Table 2. Compared to the original mate-

rials, the modifications led to negligible changes in the thickness and pore size of the superoleophobic filters.

Table 2. Summary of structure parameters of superoleophobic modified filters.

Material Type	Thickness/mm	Weight/(g/m ²)	Average Pore Size/ μ m	Underwater Oil Contact Angle/ $^{\circ}$
NP1	0.75 ± 0.04	214.9 ± 2	8.16 ± 0.28	155.8 ± 2.2
NP2	0.72 ± 0.02	190.2 ± 1.2	14.62 ± 0.60	151.2 ± 1.3
NP3	0.66 ± 0.01	188.4 ± 0.8	19.27 ± 0.72	149.6 ± 1.8

To evaluate the impact of pore size distribution on the pressure drop during the oleophilic filtration process, the experimental conditions from Section 3.2 were employed, with the emulsified oil at the inlet maintaining an average particle size of approximately 20 μ m. Based on the dissection of the oil–water coalescence filter, the filter consists of three fixed layers. Samples of filter materials with varying pore size distributions were designed, as detailed in Table 3.

Table 3. Summary of filter structure parameters.

Filter Material Combination	NP123	NP321	NP111	NP222	NP333
1st layer (inlet liquid level)	NP1	NP3	NP1	NP2	NP3
2nd layer (middle layer)	NP2	NP2	NP1	NP2	NP3
3rd layer (liquid outlet)	NP3	NP1	NP1	NP2	NP3

As shown in Figure 6a, the separation efficiency of the NP123 filter combination is 73.7%, slightly higher than the 68.2% of the NP321 filter, indicating that the pore structure of the filter material plays a significant role in the coalescence separation process. The comparison of demulsification performance in Figure 6b reveals that, after filtration with the NP123 combination, the droplet size decreases by 46.0%, whereas the NP321 combination results in a 36.8% reduction in droplet size change. This demonstrates that the NP123 filter combination performs better in intercepting oil droplets compared to the NP321. Among the NP111 to NP333 filter combinations with the same pore size per layer, the separation efficiency of NP111 is 80.0%, significantly higher than the 32.3% achieved by NP333. This difference arises because the NP111 filter has smaller, more uniform pores, allowing most of the oil droplets with surfactant on their surface to be intercepted by the first layer with small pores. A small portion of the droplets is broken during migration, significantly increasing the surface tension of the oil–water interface in the effluent (an increase of 4.84 mN/m), while also leading to a rise in the jump pressure drop. In contrast, the NP333 filter, with larger pore sizes, has bigger equivalent pore channels, resulting in only a 16.4% change in droplet volume in the effluent, with a surface tension change of less than 1.2%. Therefore, the underwater super-hydrophobic, pore-size-increasing structure of the NP123 combination exhibits a higher separation efficiency compared to the pore-size-decreasing NP321 combination.

As shown in Figure 6c, the separation pressure drop of the NP123 filter can be divided into three stages. In the first stage, due to the inherent oil-repellent properties of the filter material, oil droplets are retained in the fiber pores (as shown in Figure 6e), and the pressure drop increases linearly. The trend of the average droplet size in the effluent, shown in Figure 6b, indicates that the median droplet size is smaller, suggesting that a large number of droplets are retained on the surface of the oil-repellent first layer of small-pore filters, which leads to a rapid increase in pressure drop. In the second stage, the slope of the pressure drop curve is significantly lower than the sharp rise in the first stage.

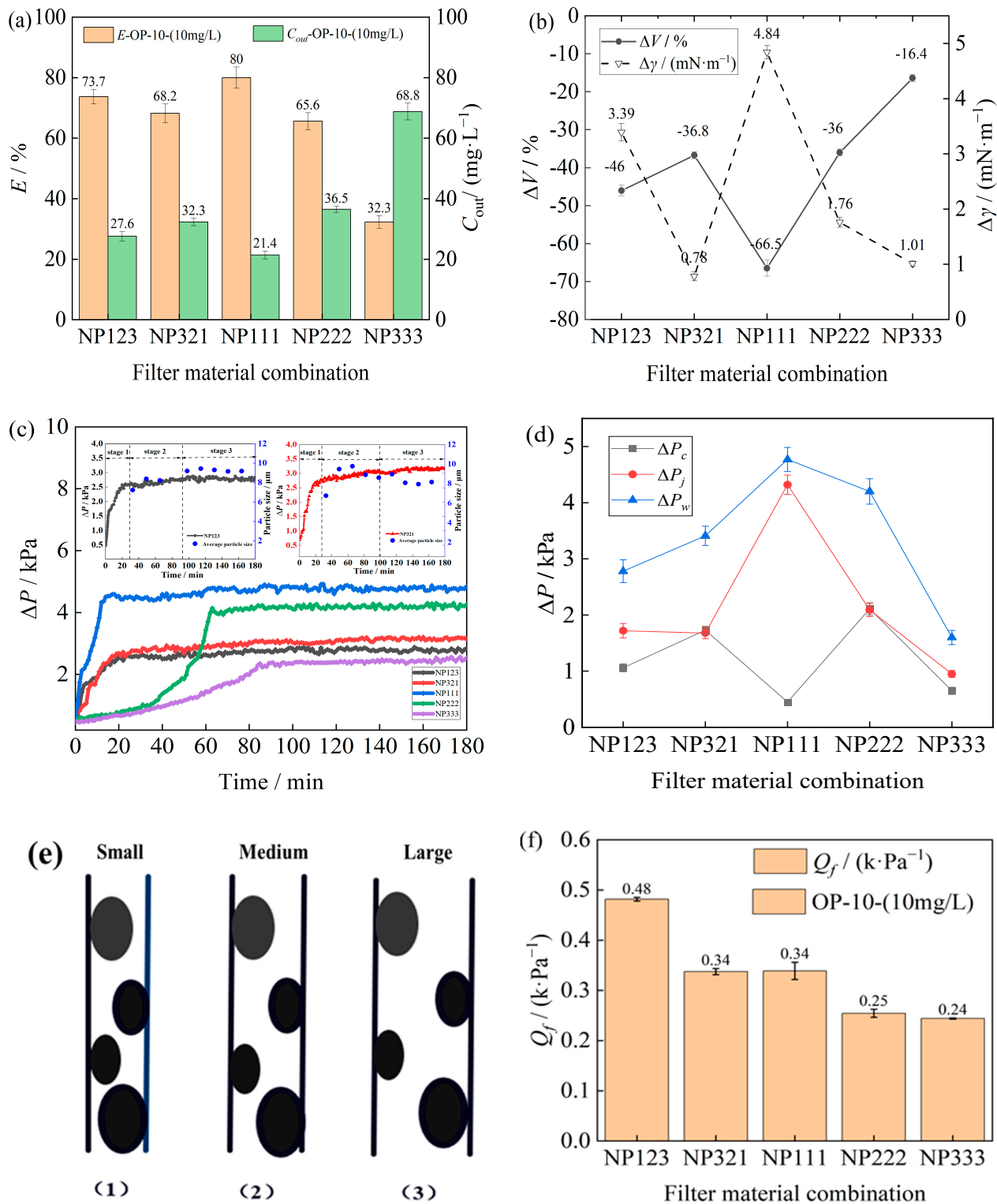


Figure 6. Effect of pore size. (a) Oil removal efficiency, (b) Changes in droplet size (ΔV) and tension ($\Delta \gamma$) before and after filtration, (c) process pressure drop curve, (d) pressure drop comparison, (e) presence of oil droplets in fiber capillary tubes, and (f) steady-state quality factor Q_f .

According to capillary theory [31], the surface energy of oil-repellent filters is lower, making it easier for oil droplets to coalesce into larger droplets on the back of the filter material. These larger droplets then detach from the fiber surface under the influence of gravity and are eventually expelled through the drainage layer. In the third stage, the pressure drop stabilizes. For the pore-size-decreasing gradient NP321 filter combination,

the separation pressure drop also shows three stages (see Figure 6c), but no obvious stratification is observed. In comparison to the NP111-NP333 filter combinations with the same pore sizes, the first-stage pressure drop of the small-pore combination (NP111) is higher than that of the larger-pore combination (NP333). As shown in Figure 6e, the minimum equivalent pore size of the fibers in the NP111 combination is approximately 8.16 μm , while the equivalent pore diameter between fibers in the large-pore combination is approximately 19.27 μm , with the inlet particle size distribution remaining unchanged. This indicates that the droplets occupy more volume in the NP111 pore channels, leading to narrower and more tortuous fluid pathways, which increases the resistance to fluid flow through the channels.

The steady-state quality factors for various filter material combinations were calculated using Equation (2), with the results presented in Figure 6f. The steady-state quality factor of NP123 is 0.48, approximately 1.4 times that of NP321. This discrepancy arises despite using the same filter material combination, as the separation efficiency of NP123 is only 5.5 percentage points higher than that of NP321. Regarding the steady-state pressure drop, NP123, with an increasing pore size combination, exhibits larger outlet pores, leading to a lower pressure drop during transitions. This ultimately results in a lower overall steady-state pressure drop compared to NP321, which shows the opposite trend. Based on the analysis, the steady-state quality factors are ranked from highest to lowest as follows: NP123 > NP111 > NP321 > NP222 > NP333.

3.4. Analysis of Superoleophobic Gradient Properties and Demulsification Mechanism

To investigate the separation performance and stability of the super-hydrophobic pore-size-increasing gradient structure under varying oil concentrations and surfactant types, the experimental system was set with a flow rate of 0.46 L/min, a pressure of 1 atm, and a water temperature of 20 ± 5 °C. The surfactant concentration (OP-10) was maintained at 10 mg/L, and the oil concentration ranged from 100 mg/L to 1000 mg/L. Figure 7a illustrates the effect of oil concentration on the separation efficiency and steady-state quality factor of the filter material. As the oil concentration in the inlet water increased from 100 mg/L to 1000 mg/L, the separation efficiency improved from 63.9% to 93.9%, and the steady-state quality factor (Q_f) increased by approximately 1.3 times. Figure 7b shows the change in droplet size distribution at the inlet and outlet, revealing that the droplet size in the outlet filtrate decreased by 54.2% to 62.3% compared to that in the inlet. This change indicates that the oil-repellent gradient filter combination effectively demulsified and intercepted most of the emulsified oil droplets. Additionally, the study evaluated the impact of different surfactants (OP-10, CTAB, and SDS) on the separation performance of the filter combination. In all experiments, the concentration of each surfactant was maintained at 10 mg/L.

Figure 7c illustrates the impact of different surfactants on the separation stability of oil-in-water emulsions using oleophobic gradient composite filter materials. The separation efficiencies of the filter materials with OP-10, CTAB, and SDS as surfactants were 93.9%, 96.4%, and 97.2%, respectively. Figure 7d presents images and particle size distributions of the samples before and after separation. Prior to separation, all three emulsions appeared milky white; after filtration, the liquid became clear and transparent, indicating that the oleophobic gradient composite filter material effectively reduced the volume of oil droplets by intercepting and coalescing them. The volume of oil droplets in emulsions containing OP-10, CTAB, and SDS decreased by 56%, 83%, and 89%, respectively. To evaluate the stability of the oleophobic gradient structure material, the impact of repeated use on separation efficiency was assessed, as shown in Figure 7e. Under fixed testing conditions, with each test lasting 3 h, the separation efficiency showed only a slight decline after

10 cycles, remaining generally stable. This demonstrates that the oleophobic gradient structure material retains good stability and consistent oil removal performance over extended use.

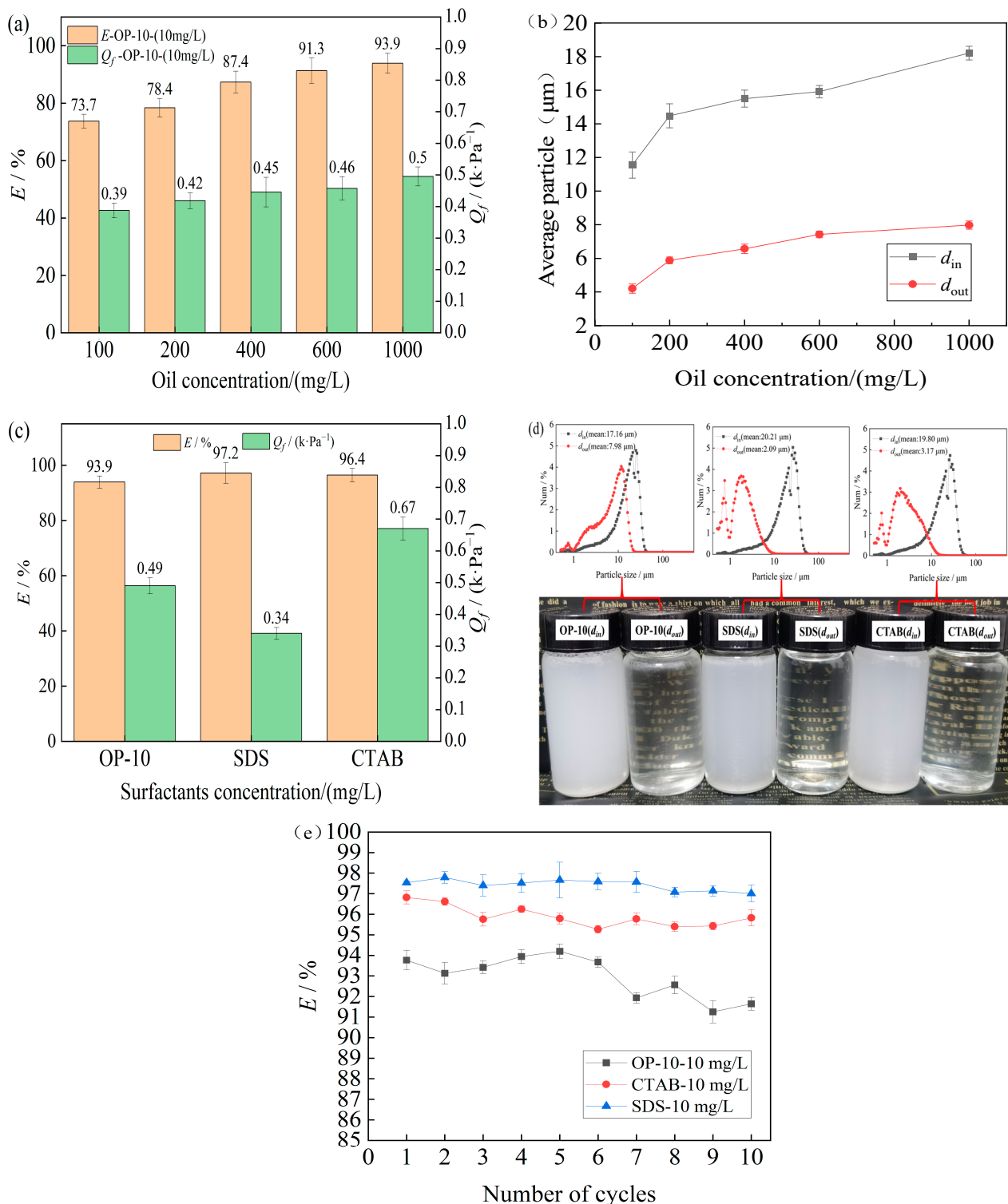


Figure 7. Analysis of the comprehensive performance of superoleophobic gradient structure. (a) The influence of the oil content, (b) inlet and outlet oil droplet size, (c) influence of surfactants, (d) sample and oil droplet size before and after filtration, and (e) influence of cycle times.

Table 4 summarizes the performance of the super-hydrophobic, pore-gradient structured filter material in water-in-oil emulsion separation and compares it with other oil-

removal materials from similar studies. Compared with the traditional single-pore materials listed in Table 4, the filter material demonstrates significant advantages, particularly in terms of lower filtration resistance and broader surfactant separation capabilities. First, the resistance of this material ranges from 4.9 to 10.5 kPa, which is significantly lower than that of other single-pore materials in the table. The low pressure not only reduces energy consumption but also minimizes the risk of membrane fouling. In traditional single-pore membrane materials, smaller pore sizes often lead to oil film blockage, which reduces the separation efficiency. In contrast, the pore-gradient design in this study optimizes the filtration process by enhancing coalescence while effectively reducing oil film blockage, ensuring long-term stable performance. Second, while many traditional filtering materials target the separation of a single surfactant, the material developed in this study is capable of effectively separating three different surfactants, thereby demonstrating broader applicability. By infiltrating the substrate, a super-hydrophobic underwater surface was created, achieving an oil contact angle of 155.8° underwater. This imparts a strong resistance to oil and surfactant fouling in the material.

Table 4. Comparison of oil removal performance with other similar materials reported in the literature.

Material Type	Emulsifier Type	Test Conditions	$C_{out}/(\text{mg}\cdot\text{L}^{-1})$	$\Delta P/\text{kPa}$	References
Polypropylene fiber	SPAN20	Cross flow	95	25	Yue et al. [32]
metal and polymer	/	Cross flow	96–97.5	30	Lu et al. [33]
Polydopamine–polyethyleneimine	TWEEN80	Dead end filtering	<96	/	Gao et al. [34]
Polyester	SDS	Cross flow	97.2	16	Zhang et al. [18]
Stainless steel fiber	SPAN80	Cross flow	95.5	20	Hao et al. [35]
Glass fiber	OP-10	Cross flow	>95	/	Zuo et al. [36]
Polypropylene fiber	OP-10	Cross flow	93.9	5.6	This work
Polypropylene fiber	CTAB	Cross flow	96.4	4.9	This work
Polypropylene fiber	SDS	Cross flow	97.2	10.5	This work

Even after multiple cycles of use, the material maintains a separation efficiency between 93.9% and 97.2%, demonstrating exceptional durability and stability. In conclusion, the improvements in the pore-gradient super-hydrophobic multi-layer filter material lie primarily in the optimized pore design, reduced filtration resistance, and enhanced fouling resistance. These advancements enhance separation efficiency, extend the material's lifespan, and broaden its potential applications in complex oil-water separation environments.

The model features a gradient structure with increasing pore sizes, as illustrated in Figure 8. The green arrow indicates the direction of liquid flow. The green arrow on the left side of the figure marks the inlet liquid level, while the arrow on the right side indicates the outlet liquid level. During the oil–water separation process, when the surface-active agent-stabilized oil-in-water emulsion approaches the fiber surface on the inlet side of the first filter layer, the oil droplets encapsulated in the emulsion are released due to the small pore size and superhydrophilic properties of the first filter layer. The filter material exhibits superoleophobic behavior in water, as shown in Figure 4b. According to capillary theory, a larger contact angle corresponds to a lower surface energy, making it difficult for the released oil droplets to spread on the backside of the filter material. This increases the likelihood of collisions and coalescence with neighboring oil droplets, leading to the interception or extrusion of most oil droplets larger than the pore size, thereby forming an oil film on the surface of the first layer. As the emulsified oil droplets pass into the second and third layers of medium- and large-pore filter materials, their droplet size increases further, a process driven by capillary forces and liquid film formation [32]. Additionally, due to the incremental increase in the pore size across the layers, the re-

dispersion of the emulsified oil droplets is minimized. Ultimately, large oil droplets, formed through successive coalescence, move and grow on the oleophobic surface and, under the influence of gravity, detach from the fibers, completing the de-emulsification and coalescence process. In conclusion, the multi-layer fiber filter with a superoleophobic pore size gradient structure offers significant advantages in the de-emulsification and separation of oil-in-water emulsions stabilized by various surfactants. The low surface energy of the oleophobic filter material facilitates the coalescence of oil droplets on the backside of the filter into larger droplets, which then detach from the fiber surface under gravity, effectively separating the oil-in-water emulsion.

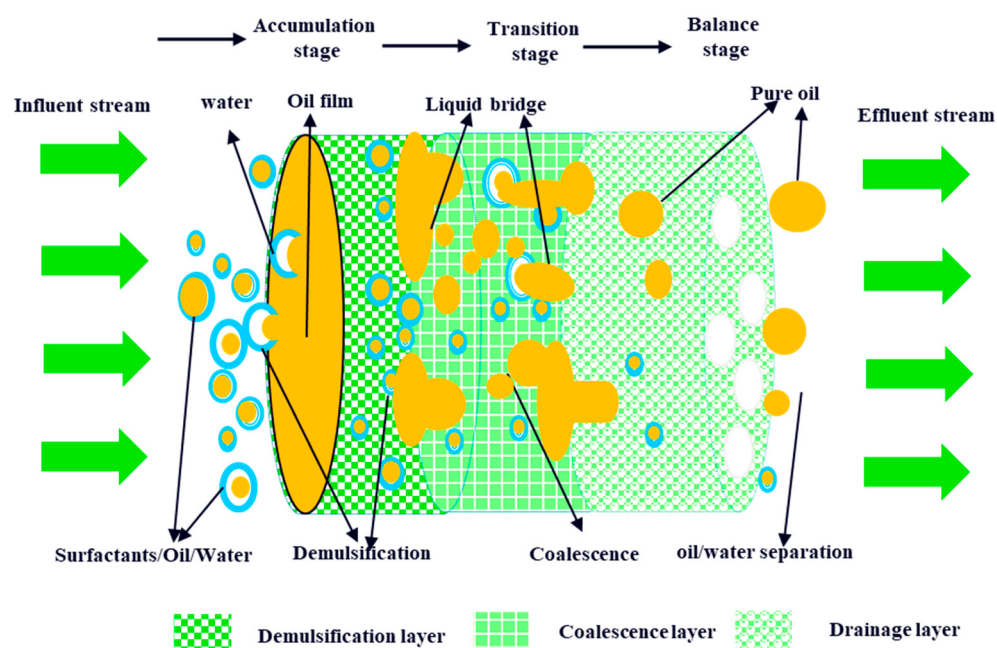


Figure 8. Mechanism of coalescence and separation in a superhydrophobic structure with an increasing pore size.

4. Conclusions

In summary, this study systematically investigates the combined effects of filter material wettability and pore size on the separation performance of oil-in-water emulsions stabilized by the non-ionic surfactant OP-10. A novel strategy is proposed—a multi-layer structure with an oil-repellent, gradient-increasing pore size—for the efficient separation of oil-in-water emulsions stabilized by various surfactants. The experimental results show that, compared to other pore size combinations, the increasing-pore-size gradient significantly enhances the oil removal efficiency, doubling its overall quality factor. Further studies confirm the sustained high oil-removal capacity of this oil-repellent, increasing-pore-size gradient filter material combination when processing emulsions stabilized by three common surfactants. After 10 cycles, the separation efficiencies were 93.6% (OP-10), 96.4% (CTAB), and 97.2% (SDS), with the structure maintaining a high separation efficiency. Additionally, based on experimental data and capillary theory analysis, a new emulsification and coalescence mechanism is proposed, offering a novel solution for treating high-concentration emulsified oil–water mixtures. The proposed oil-repellent, increasing-pore-size gradient multi-layer structure strategy is not only applicable to fiber filters but also has broad application potential for the research and application of other membrane materials. The results further demonstrate that the precise control of wettability and pore size significantly affects demulsification efficiency and overall performance metrics. By

optimizing the pore size and wettability design for each layer, the material's filtering performance can be significantly enhanced, thus improving the overall separation effect.

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