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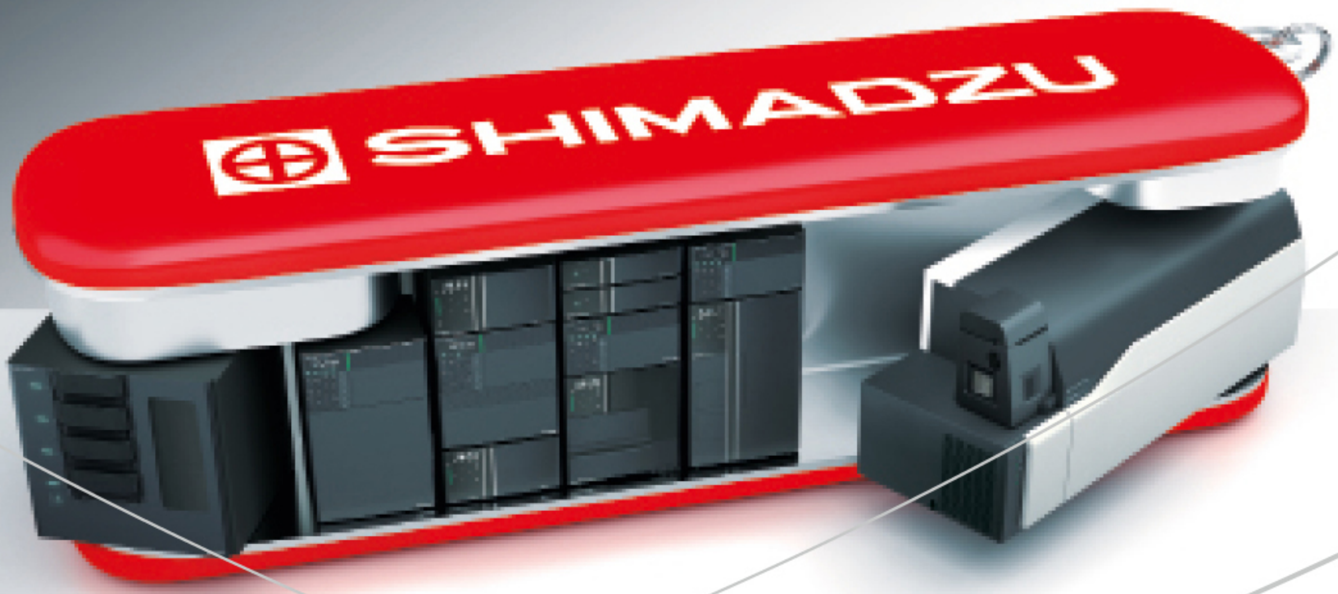
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RESEARCH ARTICLE

A simple and low-energy strategy for the separation of water and acetonitrile

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As acetonitrile is a widely used solvent for the chemical industry, the recovery of acetonitrile from acetonitrile wastewater is significant for both industrial cost reduction and environmental protection. In this article, a simple, low-energy, and low-cost strategy is proposed for the effective separation of acetonitrile from high-concentration acetonitrile wastewater. The approach is based on a sequential combination of two steps: salt-induced phase separation and hydrophobic filtration. The acetonitrile wastewater was first induced to split into two phases by salt, that is, the acetonitrile-rich phase and the water-rich phase, then the above two phases were poured into the hydrophobic filter paper funnel for the separation. It was shown that NaCl is a suitable salting-out reagent, and that hydrophobic filter papers—obtained from modification by butyltrichlorosilane and octyltrichlorosilane were the optimal choice for hydrophobic filtration. The salt-induced phase separation process is able to increase the volume fraction of acetonitrile in the acetonitrile-rich phase up to 92%. The acetonitrile-rich phase can pass through the hydrophobic filter paper, whereas the water-rich phase was intercepted. The hydrophobic filter paper retained strong hydrophobicity and high acetonitrile-separating capacity after 3 months storage, or upon immersion in acetonitrile-water mixtures for 12 h, or applied for 25 consecutive separations.

KEYWORDS

acetonitrile-water separation, azeotrope of acetonitrile-water, hydrophobic filtration, low-energy consumption, salt-induced phase separation

1 | INTRODUCTION

Acetonitrile is not only a fine solvent, extractant, and an important chemical raw material, but also a toxic chemical that is difficult to degrade. Acetonitrile has been widely used in the chemical industry, and this inevitably resulted in large volumes of highly concentrated and toxic industrial wastewater. As acetonitrile can cause great harm to

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Article Related Abbreviations: ACA, acetonitrile contact angle; ARP, acetonitrile-rich phase; C_1, methyltrichlorosilane; C_{12}, dodecyltrichlorosilane; C_{18}, octadecyltrichlorosilane; C_4, butyltrichlorosilane; C_8, octyltrichlorosilane; EDS, energy-dispersive X-ray spectroscopy; FID, flame ionization detector; HF, hydrophobic filtration; SIPS, salt-induced phase separation; WAS, water-acetonitrile-salt; WCA, water contact angle; WRP, water-rich phase; XPS, X-ray photoelectron spectroscopy.

humans, animals, and plants, high-concentration acetonitrile wastewater generally needs to be pretreated before it can enter the next level of process or meet the discharge standards [1–3].

As acetonitrile and water can form a mutually soluble binary azeotropic system (16% water, 84% acetonitrile, *v*/*v*), it is difficult to achieve complete separation for acetonitrile and water in acetonitrile-water mixed solution by common distillation methods [4]. Pervaporation is a membrane separation technology with the advantages of environmental protection and small footprint, which has been widely used in low-concentration acetonitrile separation [5–8]. To purify and recover acetonitrile from high-concentration acetonitrile wastewater, first distillation is used to obtain the 84% acetonitrile-water azeotrope. Next, high-purity acetonitrile is able to be obtained by adding dehydrating agents such as calcium chloride or sodium hydroxide into the azeotrope in a rectification separation process [9–11]. Although these technologies are relatively mature, there are some drawbacks such as large equipment investment, complex operation, and high energy consumption, resulting in large consumption of manpower and material resources and easy to cause secondary pollution [12].

Salt-induced phase separation (SIPS) is a simple process for separating homogeneous miscible solvents into two separated phases by adding salts as an inducer [13, 14]. For the separation of the components of an azeotropic mixture, the azeotropic point can be destroyed by adding salt. Then, the mixture is separated into two immiscible phases, and such a SIPS approach, with the advantages of simplicity, fast, low costs, and a low energy consumption, is widely used in industrial extraction and separation [15]. The phase behavior of the water-acetonitrile-salt (WAS) system has been systematically investigated, and the ternary phase diagrams of different salts in WAS system have been obtained [16–19]. The researches indicate that SIPS is able to achieve an efficient phase separation of acetonitrile-water mixed solution, and obtain the layered acetonitrile-water solution containing the upper acetonitrile-rich phase (ARP) and the lower water-rich phase (WRP).

The ARP and the WRP need to be further separated after being layered to achieve the cyclic utilization of water and acetonitrile. For the treatment of a small amount of layered acetonitrile–water solution in the laboratory, the separation of the WRP and the ARP can be simply carried out in the separating funnel. However, removing the ARP from the WRP in industrial production is challenging. Hydrophobic membranes, such as polymers of intrinsic microporosity [5], polydimethylsiloxane [7, 8, 22], and polypropylene [20, 21], are selective for the separation of the hydrophobic organic phase in permeation process. The hydrophobic organic phase can pass through the hydrophobic membranes, while the water phase cannot pass through the hydrophobic membranes. Thus, hydrophobic membranes are demonstrated to perform superiorly in removing volatile organic compounds from water and oil–water separation studies [22–26]. However, the used organic hydrophobic membranes are difficult to degrade and easy to cause secondary pollution. Compared with other substrates, modified filter paper is low-cost and environmental friendly, and has been used for sample treatment and water/oil separation [27, 28]. After being hydrophobically modified, filter paper is expected to substitute the hydrophobic membranes for oil–water separation.

In the present study, a simple two-step separation strategy, that is, rapid SIPS and hydrophobic filtration combined strategy (SIPS-HF) (Figure 1) was proposed. First, the hydrophobic filter paper was prepared by hydrophobic modification. Next, acetonitrile–water mixed solution was induced by inorganic salt to form a layered acetonitrile–water solution containing the ARP and the WRP. Finally, the hydrophobic filter paper was used to separate the ARP and the WRP, solely driven by gravity without any additional energy consumption. We outline the method in detail, display its efficiency for the recovery of acetonitrile from high-concentration acetonitrile wastewater and discuss potential applications and venues for further optimization.

2 | MATERIALS AND METHODS

2.1 | Materials

Analytical-grade ethanol, hexane, and inorganic salts (LiCl, NaCl, KCl, NH_4Cl, K_2CO_3, Na_2CO_3, Li_2SO_4, Na_2SO_4, and $MgSO_4$) were all obtained from National Drug Chemical Reagents Co., Ltd. Methanol and acetonitrile (HPLC grade) were purchased from Tiandi Co., Ltd. DMSO-D_6 (99.8%) was obtained from Shanghai Titan Scientific Co., Ltd. Organosilanes with different carbon chain lengths including methyltrichlorosilane (C_1) (98.5%), butyltrichlorosilane (C_4) (98%), octyltrichlorosilane (C_8) (97%), dodecyltrichlorosilane (C_{12}) (97%), and octadecyltrichlorosilane (C_{18}) (5–10% branched isomers) were purchased from Bailingwei Technology Co., Ltd. Sudan IV (analytical grade) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Quantitative filter papers (round, diameter: 90 mm) were purchased from Hangzhou Special Paper Industry Co., Ltd. Water was purified by using a Milli-Q purification system (Millipore Corporation). All reagents were not further purified before use.

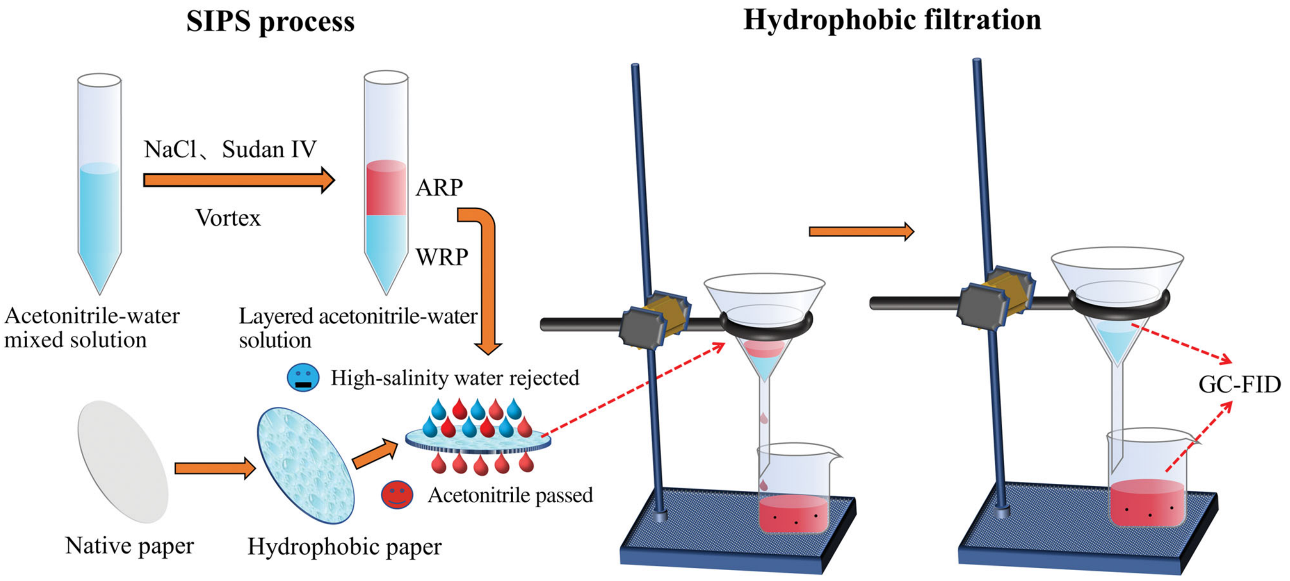

FIGURE 1 Schematic diagram of the SIPS-HF method.

2.2 | Preparation of solutions

Organosilanes were pipetted into a beaker containing *n*-hexane (50 mL), after which the mixture was placed in an ultrasound bath for 10 min to blend the solution evenly. And the volume fractions of different organosilanes in *n*-hexane are listed in Supporting Information Table S1.

A total of 1.0 mL of acetonitrile was added into a 100-mL glass volumetric flask, then 10 mL of water was added to dilute the acetonitrile. Finally, the above solution was diluted to the mark with water to form the acetonitrile solution with 1.0% of the volume fraction of acetonitrile. Subsequently, a series of working standard solutions with acetonitrile volume fraction of 0.01, 0.03, 0.05, 0.07, 0.09, and 0.10% were obtained by diluting the above acetonitrile solution. The calibration curve of acetonitrile volume fraction was obtained by plotting the peak areas of acetonitrile vs. the volume fraction of acetonitrile.

In the SIPS process, 0.1 mL of the ARP and 0.1 mL of the WRP were taken out by pipette after SIPS, and added into 100 mL volumetric flask, respectively, diluted to the mark with water and shaken up. The solutions prepared were used for the GC analysis. Then, the volume fractions of acetonitrile in the ARP and the WRP were calculated according to the calibration curve equation.

2.3 | Instrumental setups

The volume fractions of acetonitrile were determined by GC with flame ionization detector (FID). The GC (Shimadzu GC-2010) conditions were as follows: 30 m × 0.25 mm × 0.25 μm Omegawax250 capillary column (Sigma-Aldrich); inlet temperature, 220°C; FID temperature, 250°C; carrier gas (N_2) flow, 1 mL/min; injection volume, 1.0 μL; split ratio, 100:1; hydrogen flow, 40 mL/min; air flow, 400 mL/min; and make up flow, 30 mL/min. The column temperature program was as follows: 40°C for 12 min.

The molar ratio of acetonitrile/water in the ARP after SIPS was measured by nuclear magnetic resonance at 25°C (^{1}H NMR, DD2 400-MR, Agilent Technologies Inc.) using DMSO-D_6 as the solvent.

2.4 | Salt-induced phase separation

Acetonitrile and water in different volume ratios were placed into plastic centrifuge tubes separately and shaken for 30 s to form acetonitrile–water mixed solutions. After adding a saturated amount of inorganic salt, the WAS system was vortexed vigorously and then settled until sufficient phase separation was reached. The acetonitrile–water mixed solution was divided into two phases (the layered acetonitrile–water solution), that is, the upper phase of ARP and the lower phase of WRP. To facilitate observation, a hydrophobic dye (Sudan IV; see Supporting Information Figure S1 for its structure) was added to the upper ARP, which made the ARP appear red, while the WRP remained colorless. The recovery (R) of acetonitrile after SIPS was calculated by Equation (1):

$$R = \frac{n_a}{n_0}, \tag{1}$$

where n_a is the molar quantity of acetonitrile in the ARP after SIPS and n_0 is the molar quantity of acetonitrile in the acetonitrile–water mixed solution before SIPS.

2.5 | Preparation and characterization of the hydrophobic filter paper

The filter papers were immersed in the organosilane solutions (volume fractions are listed in Supporting Information Table S1) with ultrasonic mixing for 5 min for the surface silanization. Then, 5 mL of *n*-hexane, ethanol, and methanol were transferred sequentially with a plastic dropper to rinse the surface of the silanized filter paper. Finally, the filter papers were dried under ambient conditions for 12 h in a fume cupboard, and used as-is to separate the layered acetonitrile–water solution.

The filter paper was characterized before and after modification using the following three techniques: (1) Contact angles were measured using a TX500TM spinning drop interfacial tension meter (KinoChina). (2) Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses were conducted with a TESCAN MIRA4 (TESCAN Orsay Holding, a.s., Czech Republic). (3) The information on the surface chemical compositions of filter paper was obtained by determining the X-ray photoelectron spectroscopy (XPS) with a K-alpha machine (Thermo Fisher).

2.6 | Salt-induced phase separation and hydrophobic filtration method

The schematic diagram of the SIPS-HF method is shown in Figure 1. A hydrophobic filter paper was folded twice and placed in a triangular funnel to form a hydrophobic filter paper funnel. After SIPS, 10 mL of layered acetonitrile–water solution with 1:1 of ARP and WRP volume ratio was poured into the hydrophobic filter paper funnel. The WRP was intercepted by the hydrophobic filter paper in the lower part of the funnel. However, the upper ARP rapidly permeated through the filter paper to realize the rapid separation of the ARP and the WRP, as there was still a large contact area between the ARP and the hydrophobic filter paper.

2.7 | Calculation of the separation efficiency and the flux of the acetonitrile-rich phase passing through the hydrophobic filter paper

After adding the WRP and the ARP into the hydrophobic filter paper funnel, only the upper ARP passed through the hydrophobic filter paper funnel, while the WRP was intercepted by the hydrophobic filter paper and left in the funnel. The separation efficiency (E) of the ARP is calculated as Equation (2):

$$E = \frac{V}{V_0}, \tag{2}$$

where V is the volume of the ARP passed through the hydrophobic filter paper and V_0 is the volume of the original ARP. The flux of the ARP is defined by Equation (3):

$$\text{Flux} = \frac{V_0}{S_0 \cdot t}, \tag{3}$$

where S_0 is the area of the ARP contact with the hydrophobic filter paper, and t is the separation time for the ARP to pass through the hydrophobic filter paper. In general, when a semicircle is folded into a cone with a cone angle of 60°, the relation between the area of the semicircle (S') and the volume of the folded cone (V') is defined by Equation (4) [27]:

$$S' = \left(\frac{24\pi}{V'^2}\right)^{\frac{1}{3}}, \tag{4}$$

We define the contact area of the ARP and that of the WRP with the hydrophobic filter paper as S_0 and S_1, and the volume of the ARP and the volume of the WRP in the hydrophobic filter paper funnel as V_0 and V_1, respectively. The flux of the upper ARP can be calculated from Equations (3) and (4) and expressed as:

$$\text{Flux} = \frac{V_0}{\left({V_2}^{2/3} - {V_1}^{2/3}\right) \cdot (24\pi)^{1/3}} \cdot \frac{1}{t}, \tag{5}$$

where V_2 is the sum volumes of the WRP and the ARP, that is, $V_2 = V_0 + V_1$. For the separation test with precise volumes of the WRP and the ARP, t, V_0, and V_1 are easily recorded and measured, and the flux is, thus, routinely calculated.

2.8 | Energy efficiency of distillation

A thermostatic magnetic stirrer (model HWCL-1, 300 W, Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd.) and a set of glass distillation apparatus were used to separate acetonitrile–water mixed solution. A total of 100 mL of a 50/50 (*v*/*v*) acetonitrile–water mixed solution, and 100 mL of acetonitrile water azeotrope (84/16. *v*/*v*) were added to the distillation apparatus, respectively, both of which were distilled at 80°C and atmospheric pressure. The time that the thermostatic magnetic stirrer was used during distillation was recorded for calculating energy consumption.

The energy consumption is calculated by Equation (6):

$$W = P \cdot t, \tag{6}$$

where P is the power rating of the thermostatic magnetic stirrer integrating heating and stirring during normal operation, and t is the total time required for the distillation, from the time the thermostatic magnetic stirrer is turned on until the final drop of distillate flows out.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of silanized filter paper

SEM was used to observe the surface microstructure change of the filter paper before and after silanization modification. As shown in Supporting Information Figure S2A,B, the fiber structure has no distinguished difference after silanization modification. However, a thin film is observed on the surface of silanized filter paper, and the surface of the silanized filter paper is smoother than that of the native filter paper (see Supporting Information Figure S2D,E). EDS elemental mappings of the native filter paper and the silanized filter paper are displayed in Supporting Information Figure S2C,F, respectively. The element composition of the native filter paper is mainly C and O (H cannot be detected). After modification, the Si peak shows an increased intensity for the silanized filter paper as shown in Supporting Information Figure S2F, demonstrating that the silanization of the filter paper surface was effective.

XPS analytical results of the native filter paper and the silanized filter paper surface are shown in Supporting Information Figure S3 and Table S2. From Supporting Information Figure S3A, for the native filter paper, only two peaks, of C 1s at 286.5 eV and O 1s at 532.8 eV, are observed. However, the peak of Si 2s at 153.8 eV and the peak of Si 2p at 102.5 eV are also observed for the silanized filter paper. High-resolution XPS spectra of the native paper and the silanized filter paper are further deconvolved, and their spectra are carefully compared for C 1s (Supporting Information Figure S3B), O 1s (Supporting Information Figure S3C) and Si 2p (Supporting Information Figure S3D). On C 1s spectra of native filter paper, three peaks are observed at 284.8, 286.5, and 288.0 eV, belonging to the C–C, C–OH, and O–C–O bonds, respectively. The peak at 286.5 eV (C–OH) decreased and the peak at 284.8 eV (C–C) increased due to silanization.

Generally, both water and acetonitrile can pass through the native filter paper. To achieve the purpose of acetonitrile permeating through the filter paper and water intercepted by the filter paper, it is essential to endow filter paper with hydrophobicity and acetonitrile affinity. The affinities of filter paper to water and acetonitrile are expressed by water contact angle (WCA) and acetonitrile contact angle (ACA), respectively. In order to obtain the hydrophobicity and acetonitrile affinity filter paper, five different organosilanes (C_1, C_4, C_8, C_{12}, and C_{18}) were used to modify the filter paper separately. The effects of the kind and the volume fractions of the organosilanes (listed in Supporting Information Table S1) on the WCA and ACA were investigated. The results are shown in Figure 2. Figure 2 indicates that the filter papers modified by the above five kinds of organosilanes under the explored volume fractions exhibit good hydrophobicity with more than 120° of WCA. For the identical organosilane, the WCA of the silanized filter paper increases gradually with the increase of the organosilane volume fraction. Silanized filter papers modified with long carbon chain organosilane can obtain larger WCAs than those modified with short carbon chain organosilane under the same volume fraction of organosilane. When the volume fraction of C_8, C_{12}, and C_{18} is greater than 0.5, 0.2, and 0.02%, the WCAs of the as-silanized filter papers are all greater than 140°, exhibiting excellent water repellency. Figure 2 indicates that whether C_1, C_4, or C_8 is used as modification reagent, the ACAs of the silanized filter papers are all close to 0°, exhibiting excellent wettability to acetonitrile. However, when C_{12} and C_{18} are used as the modification reagents, the ACAs of the silanized filter papers rapidly increase from 0 to 50° and 70°, with the increase in the volume fraction of the modification reagents from 0.05 to 0.1% for C_{12} and 0.01 to 0.02% for C_{18}, respectively. Unfortunately, the ACAs are also close to 60° and 70° when the WCAs reach 140° with C_{12} and C_{18} as the modification reagents. The results demonstrate that the silanized filter papers modified with much long-chain organosilanes, such as C_{12} and C_{18} as the modification reagents, also appear to cause certain repellency to acetonitrile. In summary, using C_4 or C_8 as the modification reagent enables obtaining a hydrophobic filter paper with both hydrophobicity and acetonitrile affinity, which is expected to demonstrate satisfactory separation performance for acetonitrile–water solutions.

3.2 | Salt-induced phase separation

In SIPS process, selecting suitable inducer is vital for inducing phase separation [16–18]. Nine different salts, that is, LiCl, NaCl, KCl, NH_4Cl, K_2CO_3, Na_2CO_3, Li_2SO_4,

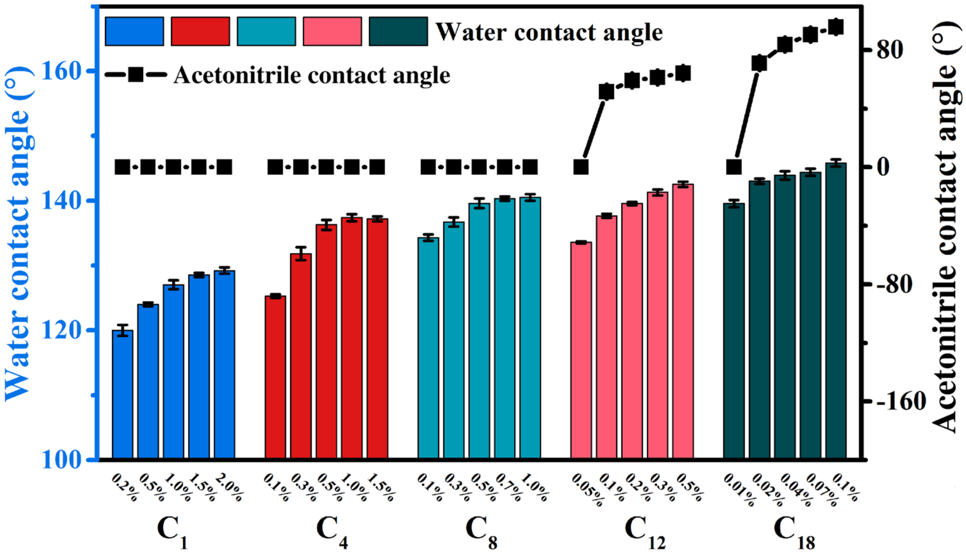

FIGURE 2 Effect of organosilanes type and concentration on WCA and ACA of hydrophobic filter paper.

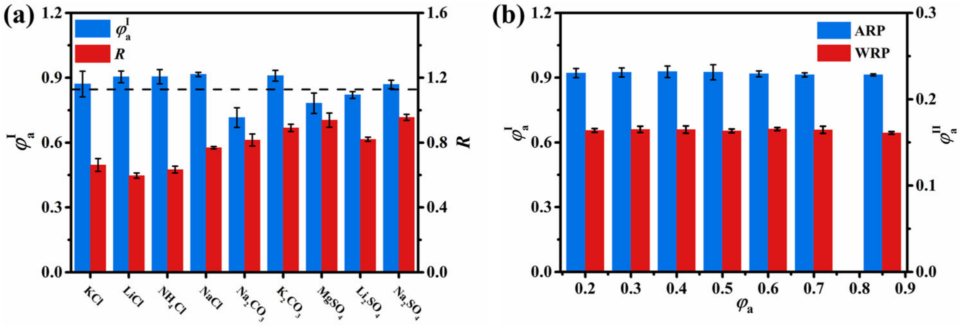

FIGURE 3 Effect of the inorganic salts and the volume fraction of acetonitrile in the acetonitrile–water mixed solutions on the SIPS. (A) The effect of the inorganic salts on φ_a^I and R (the dashed line in the figure is $\varphi_a^I = 0.84$). (B) The effect of the volume fraction of acetonitrile in the acetonitrile-water mixed solutions on φ_a^I and φ_a^{II}.

Na_2SO_4, and $MgSO_4$, were investigated for phase separation efficiency. The volume fractions of acetonitrile in the ARP and the WRP were determined by GC-FID and were denoted by φ_a^I and φ_a^{II}, respectively. The recovery of acetonitrile after SIPS was calculated according to Equation (1). The effects of different inorganic salts on φ_a^I and R after SIPS of acetonitrile–water mixed solutions are shown in Figure 3A. As shown in Figure 3A, all of the salts studied are capable of promoting the phase separation of the acetonitrile–water mixed solutions to form the layered ARP and WRP. The volume fractions of acetonitrile in the ARP with chlorine salt (KCl, LiCl, NH_4Cl, NaCl), K_2CO_3, and Na_2SO_4 as the inducer are greater than 0.84 (volume fraction of acetonitrile in acetonitrile water azeotrope, the dashed line in Figure 3A). Figure 3A also indicates that higher acetonitrile recoveries are obtained with NaCl, Na_2CO_3, K_2CO_3, $MgSO_4$, Li_2SO_4, or Na_2SO_4 as the inducers. However, a large amount of heat was released when K_2CO_3 was dissolved, which is not conducive to the application of the actual process. The volume fraction of acetonitrile in the ARP with Na_2SO_4 as the inducer is only 0.86, and the wastewater containing Na_2SO_4 will cause environmental contamination. In addition, the volume fractions of acetonitrile in the ARP with Na_2CO_3, $MgSO_4$, or Li_2SO_4 as the inducer are all lower than 0.84. Therefore, considering the environmental friendliness and the cost, NaCl is preferred as the inducer to ensure better phase separation capacity as well as higher acetonitrile recovery.

In industrial production and laboratory research, the amount of acetonitrile in the acetonitrile–water mixed solution is generally unknown. To investigate the phase separation behavior of different volume ratios of acetonitrile–water mixed solutions with NaCl as the inducer, a saturated amount of NaCl was added in the same volume of acetonitrile–water mixed solutions with initial acetonitrile volume fraction φ_a of 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.85, respectively. The associated separation behaviors are exhibited in Figure 3B. From Figure 3B, we find interestingly that under the studied initial volume fractions of acetonitrile, nearly identical φ_a^{I} or φ_a^{II} are obtained no matter how the initial volume fractions of acetonitrile vary. The volume fractions of acetonitrile in the ARP (φ_a^{I}) are all approximately 0.92, while the volume fractions of acetonitrile in the WRP (φ_a^{II}) are all approximately 0.16. The results demonstrate that the initial volume fraction of acetonitrile does not affect the SIPS ability with NaCl as the inducer in separating the acetonitrile–water mixed solutions. The φ_a^{I} in obtained ARP is as high as 0.92, which is essential for the efficient recovery of acetonitrile from acetonitrile wastewater. The results further prove that NaCl is an excellent inducer.

3.3 | Intercepted concentration of the hydrophobic filter paper

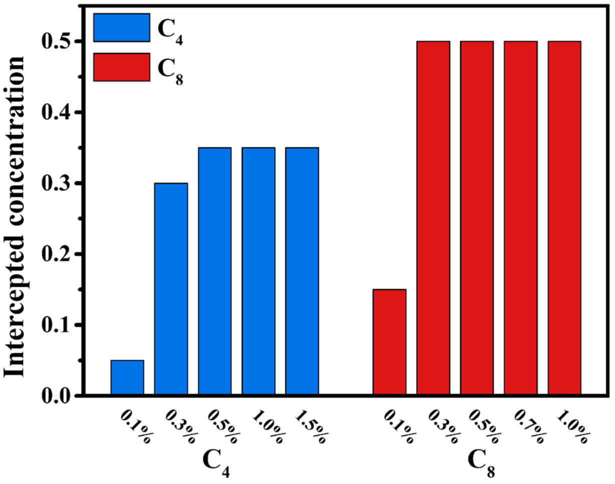

FIGURE 4 Effect of organosilanes type and concentration on the intercepted concentration of the hydrophobic filter paper.

For the separation of layered acetonitrile–water solutions, a suitable hydrophobic filter paper should allow the ARP to penetrate and the WRP intercepted. However, both the ARP and the WRP inevitably contain a certain volume fraction of acetonitrile. When the volume fraction of acetonitrile in the ARP is too tiny, the ARP may not penetrate through the hydrophobic filter paper, and will be intercepted. At the same time, when the volume fraction of acetonitrile in the WRP is sufficiently large, the WRP may also penetrate through the hydrophobic filter paper. For the convenience of expression, the "*intercepted concentration*" of hydrophobic filter paper is used to define the intercepted ability of different hydrophobic filter papers to acetonitrile–water mixed solutions. The *intercepted concentration* is the maximum volume fraction of acetonitrile that does not penetrate through the hydrophobic filter paper. That is to say that the acetonitrile–water mixed solution can penetrate through the hydrophobic filter paper only when the volume fraction of acetonitrile in the acetonitrile–water mixed solution is greater than the intercepted concentration. When the volume fraction of acetonitrile in the acetonitrile–water mixed solution is less than the intercepted concentration, the acetonitrile–water mixed solution will be intercepted.

From Figure 3B, it can be observed that using NaCl as the inducer, the volume fractions of acetonitrile in the ARP and the WRP after SIPS are all approximately 0.92 and 0.16, respectively, no matter how large the initial volume fractions of acetonitrile in the acetonitrile–water mixed solution are. To ensure that the ARP penetrates through the hydrophobic filter paper while the WRP is intercepted with NaCl as the inducer, the intercepted concentration of the hydrophobic filter paper should be higher than 0.16. For this purpose, the intercepted concentrations of the hydrophobic filter paper modified with different concentrations of C_4 or C_8 were investigated. A series of acetonitrile–water mixed solutions with different volume fractions of acetonitrile (φ_a in the order of 1.0, 0.95, 0.9, 0.85, 0.8, 0.75, 0.7, 0.65, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, 0.3, 0.25, 0.2, 0.15, 0.1, 0.05, 0.0) were prepared and poured into the hydrophobic filter paper funnel, respectively, to explore the intercepted concentration of the hydrophobic filter paper modified by C_4 or C_8. When the acetonitrile–water mixed solution is poured into the hydrophobic filter paper funnel to remain for 10 min and cannot penetrate through the hydrophobic filter paper, the corresponding volume fraction of acetonitrile in this acetonitrile–water mixed solution is defined as the intercepted concentration of the hydrophobic filter paper. The results are shown in Figure 4. As shown in Figure 4, the intercepted concentration of hydrophobic filter paper modified with both C_4 and C_8 shows the same increase tendency with the increase in the concentration of C_4 and C_8 initially, and then the plateaus are reached with the further increase in the concentration of C_4 and C_8. The intercepted concentration of the hydrophobic filter paper modified with C_8 is more significant than that of hydrophobic filter paper modified with C_4 at the same modification concentration. The intercepted concentrations of the hydrophobic filter papers modified with 0.3–1.5% C_4 and 0.3–1.0% C_8 are in the range of 0.16–0.92, which are higher than 0.16. This result suggests that after SIPS with NaCl as the inducer, the ARP will be able to smoothly penetrate through the hydrophobic filter paper modified with 0.3–1.5% C_4 and 0.3–1.0% C_8 and the WRP will be intercepted. In other words, 0.3–1.5% C_4 and 0.3–1.0% C_8 may be both suitable to modify the filter papers to satisfy the requirements.

TABLE 1 The separation efficiencies of ARP and the fluxes of ARP penetrating through the hydrophobic filter papers after SIPS of the acetonitrile–water mixed solutions.

Concentration of organosilane	Intercepted concentration	Flux (L/m^2/h)	Separation efficiency (%)
0.3% C_4	0.30	485	96
0.5% C_4	0.35	480	96
1.0% C_4	0.35	420	96
1.5% C_4	0.35	420	96
0.3% C_8	0.50	415	95
0.5% C_8	0.50	350	96
0.7% C_8	0.50	350	95
1.0% C_8	0.50	345	95

3.4 | Separation of the acetonitrile-rich phase and the water-rich phase

Ten milliliter of layered acetonitrile–water solution (the volume ratio of the ARP and the WRP is 1:1) was used as a model solution for testing the separation performance of the ARP and the WRP. The separation efficiencies of ARP and the fluxes of ARP penetrating through the hydrophobic filter papers modified with 0.3–1.5% C_4 and 0.3–1.0% C_8 after SIPS of the acetonitrile-water mixed solutions were investigated. The results are listed in Table 1. Table 1 indicates that the hydrophobic filter papers modified with C_4 and C_8 exhibit high flux from 420 to 485 L/m^2/h and from 345 to 415 L/m^2/h, respectively. Accordingly, the separation efficiency remains relatively high; the maximum separation efficiency of 96% is attained. All these results indicate that the hydrophobic filter papers exhibit high efficiency for separating the ARP and the WRP with high flux significantly. The fluxes of the hydrophobic filter papers modified with C_4 are higher than that of the hydrophobic filter papers modified with C_8, which may be due to the decrease in porosity and pore size of hydrophobic filter paper surface with the increase in carbon chain length of the organosilanes, resulting in the decrease of the flux. The fluxes of the hydrophobic filter papers modified by different concentrations of C_4 and C_8 are affected by the modification concentration, and their fluxes show an overall tendency to decrease with the increasing concentration of the organosilanes.

Durable separation performance is important for treating the WAS system in practice. Therefore, the hydrophobic stability of the filter paper modified with 0.5%C_8 was investigated. As shown in Figure 5A, when the hydrophobic filter paper is stored at room temperature for 15 days, the WCA of the hydrophobic filter paper changes very little, and the intercepted concentration does not change significantly. The WCA of the filter paper modified with 0.5%C_8 are maintained above 137° even after 3 months of storage, only dropping 1.0%. Though the

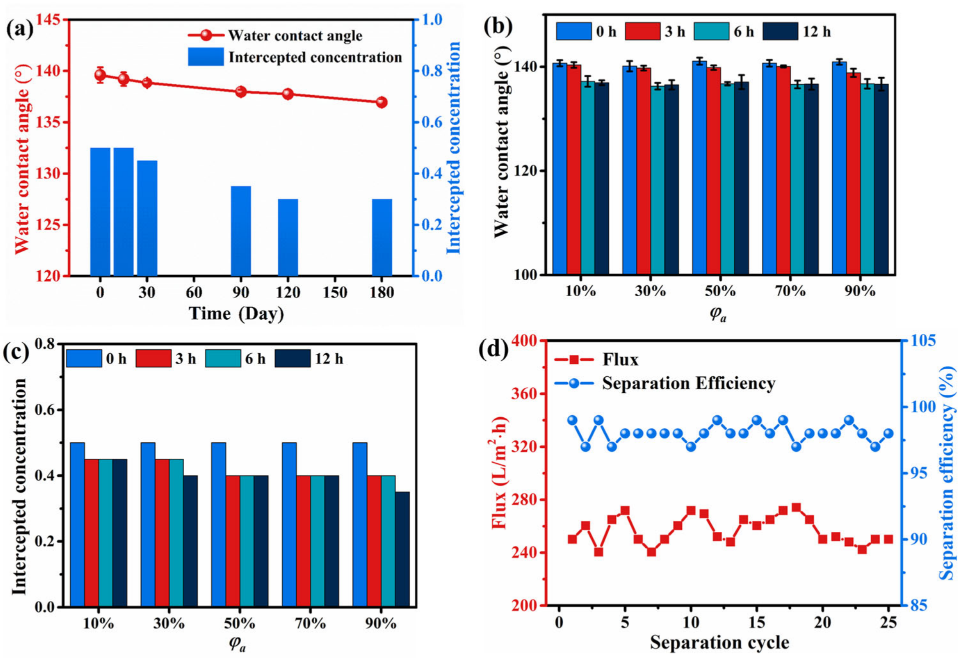

FIGURE 5 Stability of the hydrophobic filter paper modified with 0.5%C_8. (A) Effect of the storage time on the WCA and the intercepted concentration of the hydrophobic filter paper. (B) Effect of the storage environment and the storage time on the WCA of the hydrophobic filter paper. (C) Effect of the storage environment and the storage time on the intercepted concentration of the hydrophobic filter paper. (D) Effect of the separation cycle on the flux and the separation efficiency of the hydrophobic filter paper.

TABLE 2 Comparison of separation performance between distillation and SIPS-HF.

Solution composition $V_{\mathrm{acetonitrile}}:V_{\mathrm{H2O}}$	Approaches	Time (min)	Energy consumption (kJ)	Price of the apparatus (CNY)	Volume fraction of acetonitrile	
					Outflow/ ARP (%) ($n = 3$)	Residue/ WRP (%) ($n = 3$)
84:16	Distillation	180.0	3.24×10^3	1800.0	83.2 ± 0.5	20.9 ± 0.1
	SIPS-HF	30.0	[a]	40.0	91.3 ± 0.5	16.1 ± 0.2
50:50	Distillation	100.0	1.80×10^3	1800.0	80.8 ± 1.1	9.6 ± 0.1
	SIPS-HF	20.0	[a]	40.0	92.5 ± 1.5	16.3 ± 0.2

[a] The energy consumption of the SIPS-HF method was almost zero.

intercepted concentration dropped from 0.5 to 0.35 after 3 months, it is still within the acceptable range (>0.16) according to the abovementioned study. After 180 days of storage, the WCA of the hydrophobic filter paper modified with 0.5%C_8 are still maintained above 127°, and the intercepted concentration is about 0.30, which could still be used to separate the ARP and the WRP.

The hydrophobic filter paper was also immersed in a series of acetonitrile–water mixed solutions with different volume fractions of acetonitrile for a while to simulate the application in the actual separation process. As shown in Figure 5B, the WCA of the hydrophobic filter paper modified with 0.5% C_8 only decreased slightly about 0.3–1.5% when the hydrophobic filter paper is soaked in acetonitrile–water mixed solutions with acetonitrile volume fractions increase from 10 to 90% for 3 h, respectively. And when the immersion time increases from 0 to 12 h, the WCA decreases only about 2.0–3.0%, indicating that the hydrophobic filter paper has superior stability to the acetonitrile–water mixed solutions with acetonitrile volume fractions ranging from 10 to 90%. In addition, after being immersed in the acetonitrile–water mixed solutions for 12 h, the intercepted concentrations of the hydrophobic filter paper decrease about 0.05–0.15, and the intercepted concentrations decrease gradually with the increment of acetonitrile volume fractions, but they are still within the applicable range (see Figure 5C).

The hydrophobic filter paper, with a diameter of 90 mm can hold a maximum volume of approximately 20 mL of solution when folded into a cone. Thus, 20 mL of layered acetonitrile–water solution with a volume ratio of 1:1 of the ARP and WRP was used as a model solution for the separation study. The effect of the separation cycle on the flux and the separation efficiency of the hydrophobic filter paper modified with 0.5%C_8 are exhibited in Figure 5D. Figure 5D shows that after continuous 25 repeatable separation cycles, the fluxes fluctuated between 240 to 280 L/m^2/h with the separation efficiency remaining above 95%, and no WRP is observed to pass through the hydrophobic filter paper. The results demonstrated that the prepared hydrophobic filter paper possesses good stability during the separation process. Meanwhile, the stability of other hydrophobic filter papers studied previously in this article is comparable to that of this 0.5%C_8 modified filter paper.

3.5 | Comparison with distillation separation

To investigate the separation performance of the SIPS-HF method, a distillation method was selected to compare with the SIPS-HF strategy. A total of 100 mL of the acetonitrile-water mixed solution with the volume ratio of 1:1 of the acetonitrile and water and 100 mL of acetonitrile–water azeotrope (acetonitrile with a volume fraction of 84%, and water with a volume fraction of 16%) were used as the test samples. The time spent on each separation process was recorded and the energy consumption was calculated using Equation (6). The separated sample solutions were also collected, diluted, and analyzed by GC-FID. The results are shown in Table 2. The distillation of 100 mL of the acetonitrile–water mixed solution with the volume ratio of 1:1 of the acetonitrile and water took 100 min (from the time the thermostatic magnetic stirrer is turned on until the final drop of distillate flows out). In contrast, the separation of the same acetonitrile–water mixed solution by the SIPS-HF took only 20 min (including the time of the SIPS process and the time of separation of the ARP and the WRP by hydrophobic filter paper), which is one-fifth of the distillation time. The price of the apparatus required in the distillation process is almost 50 times higher than that in the SIPS-HF. And the distillation process is accompanied by a lot of energy and water waste. As acetonitrile and water can form an infinitely miscible solution, the conventional distillation procedure only obtained an acetonitrile–water mixed solution with a volume fraction of acetonitrile of 84%. However, SIPS can wreck the azeotropic point of the acetonitrile–water mixed solution, enabling to obtained the ARP with acetonitrile volume fraction greater than 90%.

Furthermore, the molar ratio of acetonitrile/water in the ARP after SIPS-HF was determined by nuclear magnetic resonance. The volume fractions of acetonitrile and water in the ARP obtained after unit conversion were 0.93 and 0.07 (70 mg/mL), respectively, which were consistent with the results of GC detection.

4 | CONCLUSIONS

In summary, a SIPS-HF method with low energy consumption to separate and recover acetonitrile from acetonitrile wastewater was developed. The effects of nine inorganic salts and five organosilanes on the separation were investigated. The optimized inducer is NaCl. The most suitable organosilanes are C_4 and C_8. The hydrophobic filter papers modified with C_4 and C_8 exhibited strong hydrophobicity and acetonitrile affinity. The volume fractions of acetonitrile in the ARP and the WRP after SIPS process of acetonitrile–water mixed solutions with different volume ratios of acetonitrile and water with NaCl as the inducer are all 0.92 and 0.16, respectively. The developed method is simple, rapid, and low-energy with excellent separation efficiency of over 95% while maintaining high flux. The hydrophobic filter paper retained strong hydrophobicity and high acetonitrile intercepted concentration even after being stored for 3 months and soaked in acetonitrile-water mixed solution for 12 h, or after repeating the separation 25 times, which also demonstrates its promising durability in the separation process. The used hydrophobic filter paper can be removed by incineration without causing secondary contamination. The established method provides a green, low-cost, and sustainable paper-based separation device for high-efficiency acetonitrile wastewater treatment.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

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SUPPORTING INFORMATION

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