Preparation and characterization of phosphorylated Zr-doped hybrid silica/PSF composite membrane

Yuqing Zhang [a,b,*], Zhenhua Jin [a], Xing Shan [a], Jaka Sunarso [b], Ping Cui [a]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China
[b] ARC Centre of Excellence for Functional Nanomaterials, AIBN and School of Engineering, The University of Queensland, Brisbane 4072, Australia

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ABSTRACT

Polysulfone (PSF) membranes are broadly applied in many fields owing to good physicochemical stability, resistance to oxidation and chlorine. But when treated with wastewater containing oil, PSF membranes are easy to be contaminated for its hydrophobicity, which can result in the declining of flux and lifespan of the membrane and limit their application in large scale. To enhance the capability of PSF membrane in the above circumstances, phosphorylated Zr-doped hybrid silica particles (SZP particles) were firstly prepared. SZP particles have various point defects inside their structure and lots of hydroxide radicals on their surface. SZP particles were added to the porous matrix of PSF to prepare a novel composite membrane (SZP/PSF) through a phase inversion process. Finally, the optimum preparation conditions of SZP/PSF composite membranes were determined. The optimum conditions are: the mass ratio of PSF, PEG400 and SZP is 12:10:10; ultrasound 10 min inside each 30 min; the pre-evaporating time is 10 s. Optimized SZP/PSF composite membrane was characterized by scanning electron microscope (SEM) and ultrafiltration experiment. The results indicate that SZP particles can be uniformly dispersed in SZP/PSF composite membranes with excellent hydrophilic property, antifouling capability and tensile strength. Therefore, it can be concluded that the optimized SZP/PSF composite membrane is desirable in the treatment of wastewater containing oil and wastewater.

1. Introduction

Wastewater containing oil produced from industry not only pollutes the environment but also wastes crude oil and water resource. Moreover, emulsified and soluble oil in wastewater is difficult to be treated by traditional methods. Membrane technology has been widely used in water treatment, especially utilized in the treatment of wastewater containing oil [1]. This is because membrane separation technology is one of the most potential operation units of chemical engineering, for it has a lot of advantages such as easy operation, low cost, no phase transition, high efficiency and capability of reducing contaminants. But large-scale applications of the membrane separation technology (especially PSF membrane) for wastewater containing oil are limited because polymer membranes are easy to be contaminated by oil. Hence, the enhancement of the hydrophilic and anti-fouling property of PSF membranes captured a lot of attention of many researchers [2].

In recent years, lots of methods have been developed to enhance the properties (such as hydrophilic property, tensile strength and anti-fouling ability) of polymer membrane. The method of doping inorganic oxide particles to polymer to prepare organic–inorganic composite membranes is attractive, owing to its simple operating process and preparation technology. By adding ZrO_2 particles to PSF, Genné et al. [3] prepared a novel porous ZrO_2/PSF composite membrane to increase the permeability and reduce the resistance of composite membrane. By adding nanosilica to poly-4-methyl-2-pentine membrane, Merkel et al. [4] prepared a sort of composite membrane which had high permeability and selectivity. Yang et al. [5] added TiO_2 to PSF membrane to prepare a sort of composite membrane which had excellent water permeability, hydrophilic property, mechanical strength and good anti-fouling ability.

Though the capability of polymer membranes can be enhanced by adding inorganic oxide particles (ZrO_2, TiO_2, SiO_2, etc.), further enhancement of polymer membranes' properties is limited due to few Lewis acid sites and hydroxide radicals on the surface of stoichiometric monocomponent inorganic oxide particles [6]. Many researches [7,8] have been demonstrated that nonstoichiometric inorganic oxide particles have many point defects inside them and lots of exposed hydroxide radicals on their surface, which show stronger activity in the course of chemical bonding than stoichiometric monocomponent inorganic oxide particles. So when

nonstoichiometric inorganic oxide particles are dispersed in polymer membranes, the capability of polymer membranes is evidently improved. Recently, we have been committing to study on high active inorganic oxide particles for the membrane modification. In our previous works, we prepared Ce-doped nonstoichiometric nano-silica particles and sulfated Y-doped nonstoichiometric zirconia particles which were doped into PSF membranes to prepare composite membranes to enhance their hydrophilic property, tensile strength and anti-fouling ability [9–12]. In this paper, in order to enhance the capability of PSF membrane, phosphorylated Zr-doped hybrid silica particles (SZP particles) were firstly prepared. SZP particles have various point defects inside their structure and lots of hydroxide radicals on their surface. Then, SZP particles were then added to the porous matrix of PSF to prepare a novel composite membrane (SZP/PSF) through a phase inversion process. Finally, the optimum preparation conditions of SZP/PSF composite membranes were determined, and the properties of SZP/PSF as-prepared composite membrane were investigated.

2. Experimental

2.1. Materials and instruments

PSF was provided by Dalian Polysulfone Co., Ltd. and its MW and polydispersity were 84,400 Da and 1.37, respectively. SZP particles with the diameter from 1 to 3 μm were prepared in our laboratory. The SZP particles were characterized with SEM (X-650, Hitachi, Japan) and X-ray diffraction (XRD) with a PANalytical X'Pert HighScore (produced in Netherlands) using Co Kα radiation under 40 kV 40 mA. N,N-dimethylacetamide (DMAC) was purchased from Tianjin Damao Service of Chemical Instruments. Polyethylene glycol with average MW 400 Da (PEG400) was supplied by Tianjin Jinyu Fine Chemical Factory. The last two kinds of reagents were analytical grade and used as received.

2.2. SZP particles preparation

SZP particles with the diameter from 1 to 3 μm were prepared in our laboratory as an additive of composite membrane. The preparation process of SZP particles is similar to the literature [13], and the detailed procedure is as follows:

$ZrOCl_2 \cdot 8H_2O$ and TEOS were grinded fully in a mortar, and APTES (aminopropyltriethoxysilane) was then added to the mortar for mixing. Then the whole mixture was put in an ice water bath and stirred to form the gelatin form, and followed by being settled in room temperature for 24 h, then dried for 24 h in 100 °C. Then spread in the mixed solution of H_3PO_3 and HCHO, refluxed under the temperature of 80 °C for 6 h, then cooled down to room temperature, repeated centrifugal and washed. And then dried in 100 °C to constant weight, and finally samples of different diameters of SZP particles were obtained.

2.3. Composite membrane preparation

Dried PSF was firstly added to N,N-dimethylacetamide (DMAC), then stirred at 40–50 °C in a water bath to completely dissolve PSF. Then PEG400 was added as porogen to promote the yield of pores in a gelation process. After SZP particles were added to the mixture, vigorous stirring was needed until a homogenous solution was obtained. Finally, the solution was stilly kept for 24–48 h. The membranes (thickness ca. 0.3 mm) were cast and formed on a horizontal glass plate using a glass blade. After evaporated 10 s in the air, the membranes were leached by running water for 2 days. Finally, membranes were soaked in 30 wt.% glycerin aqueous solution for 5–12 h. To comparison, the pure PSF membranes were obtained by using the same procedure mentioned above. Finally membranes were stored in de-ionized water containing 1 wt.% formaldehyde to avoid the growth of bacteria. The influence of the concentration of PSF, content of SZP particles and content of PEG400 on the performance and morphology structure of the membranes were studied.

2.4. SEM studies

The composite membrane pieces were thoroughly rinsed by de-ionized water, and immersed in 30% glycerin aqueous solution and then dried in air for SEM analysis. Cross-section samples were obtained by being freeze-fractured in liquid nitrogen and sputtered with gold. Cross-section of the sample was observed under JEOL JSM-6400F scanning electron microscope (SEM).

2.5. Measurement of permeation flux

The flux (water permeation flux) was measured under pressure of 0.10 MPa at the temperature of 20 °C. The flux (F) is calculated as follows:

$$F = \frac{V}{At} \tag{1}$$

$$A = \frac{1}{4}\pi d^2 \tag{2}$$

where V is the volume of permeation (L), A is the effective membrane area (m^2), t is the operating time (s) and d is the diameter of membrane (m).

2.6. Measurement of retention

The retention of membrane can be measured by the solvent of Bovine Serum Albumin (BSA). Azocarmine and H_2SO_4 were used as color agent in this performance. The retention (R) of the membrane can be calculated by the following:

$$R = \left(1 - \frac{C}{C_0}\right) \times 100\% \tag{3}$$

where C is the concentration of BSA in the permeation (mg/L), C_0 is concentration of BSA in the feed (mg/L).

2.7. Measurement of hydrophilic property

Contact angles of membrane samples cast from different casting solutions were measured with a 1501 dynamic contact angle measuring instrument supplied by Micromeritics Corporation, America. The accuracy of measurements is ±0.1 °C.

3. Results and discussion

3.1. Characterization of SZP particles

It can be seen from Fig. 1 that SZP particles with the diameter from 1 to 3 μm are spherical shape. The schematic of structure of SZP particle is shown in Fig. 2. The phosphorus hydroxyls are grafted to the surface of hybrid silica [14]. At the same time, Si–Zr composite oxide also has lots of strong Lewis acid sites and Brönsted acid sites. Thus, SZP particles theoretically perform the good hydrophilic property.

3.2. Effect of concentration of PSF on performance of composite membrane

At first, the content of PEG400 and SZP particles were both fixed at 10 wt.% [11]. As could be seen in Fig. 3, when the concentration of PSF changes from 10 to 18 wt.%, the flux (water permeation flux) of
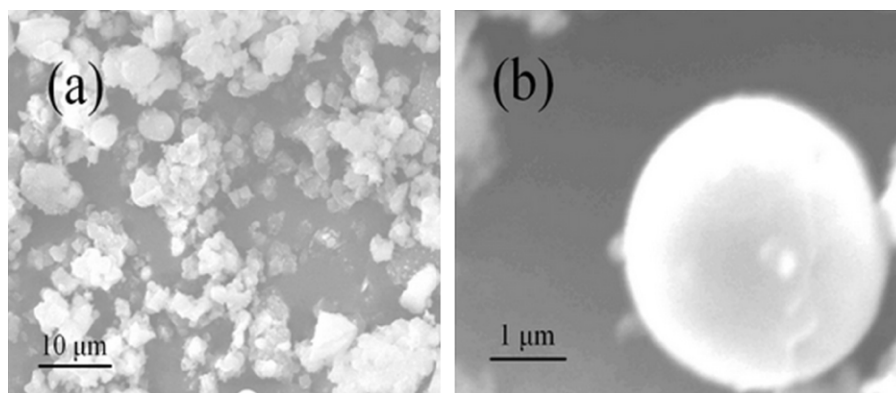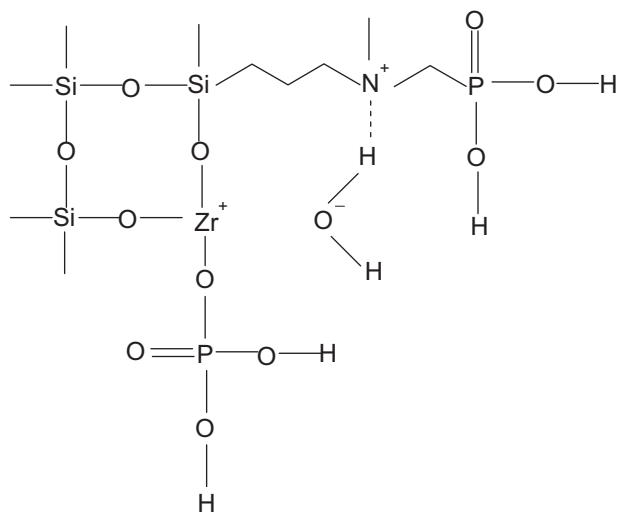
Fig. 1. SEM view of SZP samples.

Fig. 2. Sketch of structure of SZP particles.

Table 1
Effect of SZP particles on membrane porosity.

Membrane code number	Content of particles (wt.% PSF)	Porosity (%)
P0	0	30
P1	5	42
P2	10	60
P3	15	58
P4	20	56

Remarks: P0, pure PSF membrane; PS, silica/PSF membrane; P1–P4, SZP/PSF membrane.

the porosity of composite membrane declines, owing to the conglomerations between SZP particles destroy the network structure in the composite membrane.

When the flux and retention are investigated together, the composite membrane with 12 wt.% PSF has a higher retention and lower flux. Therefore, in this paper the fitting concentration of PSF is 12 wt.%.

3.3. Effect of content of PEG400 on performance of composite membrane

Porogen utilized in this work is a non-solvent swelling chemical which may not react with PSF and DMAC, but it can dissolve in a solvent and coagulation bath. In this paper, when the concentration of PSF and content of SZP were fixed at 12% and 10 wt.%, respectively, the content of PEG400 (porogen in this study) was changed from 5 to 12 wt.%. And then the flux (water permeation flux) and retention of composite membrane were tested, the results are shown in Fig. 4.

composite membrane decreases from 350 to 260 ($L\,m^{-2}\,h^{-1}$) while the retention of composite membrane for oil increases from 82% to 99%. This is because the flux and retention of composite membrane are controlled by porosity and pore size in the composite membrane. And porosity of composite membrane is also affected by the adding amount of SZP particles, the results are also shown in Table 1. The porosity of the composite membrane increases with the adding amount of particles increases, which can form a network structure through interaction between particles and PSF chains. However, when the content of SZP particles is bigger than 10 wt.%,
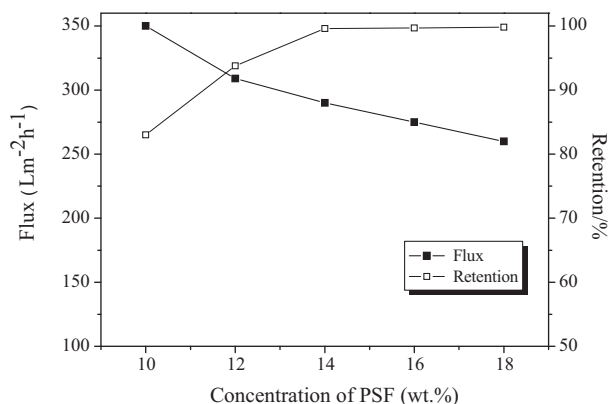

Fig. 3. Effect of concentration of PSF on membrane flux and retention.

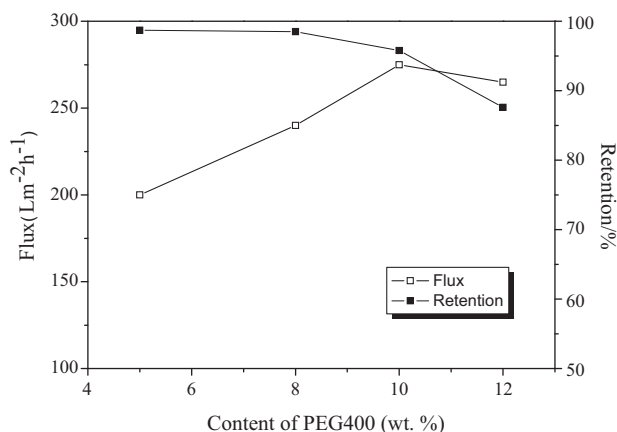**Fig. 4.** Effect of content of PEG400 on membrane flux and retention.
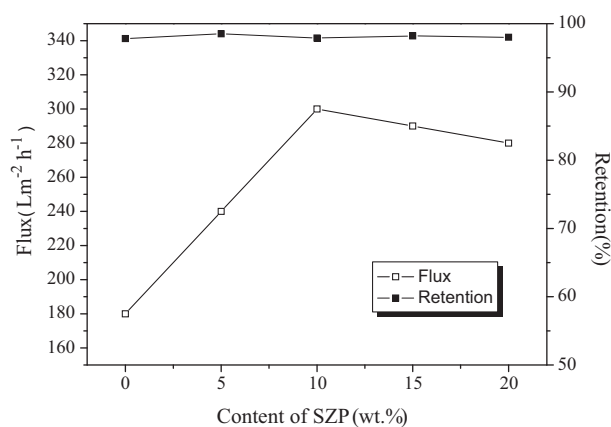
Fig. 5. Effect of content of SZP on membrane flux and retention.

Table 2
Effect of ultrasound condition on casting solution.

Membrane code number	State of the casting solution
P1	Particles have settled, light gray
P2	Particle settled after standing for some time, gray
P3	Particles dispersed uniformly, gray
P4	Particles dispersed uniformly and transparent, gray

Table 3
Effect of pre-evaporating time on membrane properties.

	Pre-evaporating time (s)				
	0	5	10	15	20
Flux ($L\,m^{-2}\,h^{-1}$)	280	294	310	315	320
Porosity (%)	62	61	65	63	64
Rejection (%)	96	95	97	98	98

It can be observed from Fig. 4 that at the initial stage of experiment, the flux of composite membrane increases with content of PEG400 increases, and its retention keeps a constant value. However, when the content of PEG400 is more than 10 wt.%, the flux and retention of composite membrane indeed decrease at the same time. This is because excessive porogen reduces the deliquescent capacity of PSF in DMAC, which result in forming small pore diameters and low porosity of composite membrane, thereby the flux of composite membrane declines. From the results it can be determined that the fitting content of PEG400 is 10 wt.%.

3.4. Effect of content of SZP particles on performance of composite membrane

In this paper, in order to investigate the effect of the content of SZP particles on the performance of composite membrane, the concentration of PSF and content of PEG400 was fixed at constant values (12 wt.% and 10 wt.%, respectively). As could be seen in Fig. 5, the flux (water permeation flux) of composite membrane increases with the increasing of content of SZP particles (the adding amount), before the content of SZP reaches to 10 wt.%. This result can be attributed to lots of hydroxyl groups on the surface of particles filled in PSF can improve and enhance the hydrophilic property of PSF membrane. As a result, the hydrophilic layer formed on the surface of composite membrane could effectively prevent the pollution of composite membrane. In contrast, when the content of SZP particles is bigger than 10 wt.%, the flux of composite membrane indeed declines; this is because conglomeration between SZP particles reduces the amount of hydroxyl groups on the surface of composite membrane. It also can be easily observed that the retention of composite membrane has a little change with the adding amount of SZP particles increases. Therefore, the fitting content of SZP is 10 wt.%.

3.5. Effect of ultrasound condition

To study the effect of ultrasound on casting solution, four different ultrasound conditions were used and investigated in this study. The samples of different ultrasound conditions were labeled P1, P2, P3 and P4, respectively. P1: without ultrasound; P2: just ultrasound 30 min in initial stage after starting the experiment; P3: ultrasound 10 min inside each 30 min; P4: always ultrasound during the experiment. The results under different ultrasound conditions are shown in Table 2. From Table 2 it can be seen that a uniform and stable casting solution can be obtained by using an intermittent ultrasonic system (P3) when the SZP particles can be uniformly dispersed in casting solution. However, other ultrasound conditions (P1, P2, and P4) cannot give a good result of uniformly dispersing SZP particles in casting solution. This is because cavitations of ultrasound can promote SZP particles uniformly disperse in casting solution. Therefore, to save electricity and assure the quality of casting solution the chosen fitting ultrasound condition is P3 (ultrasound 10 min inside each 30 min).

3.6. Effect of pre-evaporation time on composite membrane properties

Pre-evaporation can significantly affect the properties of the membrane, especially pore diameter and porosity. Table 3 indicates that with pre-evaporation time extends, the flux of composite membranes increases, but porosity changes a little. When pre-evaporation time is 10 s, the water flux of composite membranes is $310\,L\,m^{-2}\,h^{-1}$ (bigger), porosity is 65% (biggest). Therefore, to save preparation time and enhance yield efficiency, 10 s is chosen as a fitting pre-evaporation time.

3.7. Membrane characterization

The SZP/PSF composite membranes prepared under the fitting preparation conditions mentioned above were characterized and tested by SEM, tensile strength and hydrophilic property. The results of characterization and test of composite membranes are as follows.
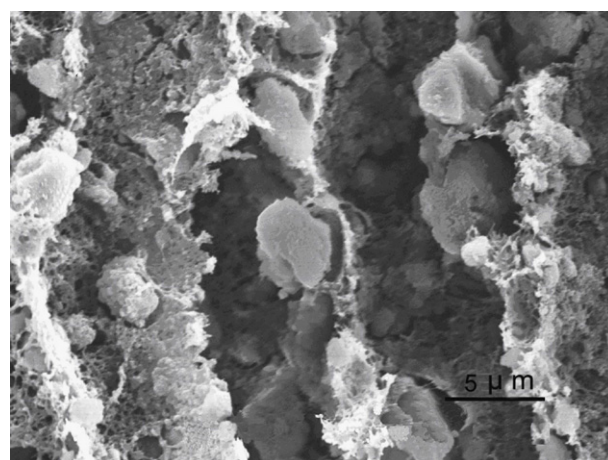

Fig. 6. SEM of the cross section of the composite membrane.

Table 4
Tensile strength of membranes with different casting solutions.

Content of particles (wt.% PSF)	Tensile strength (MPa)
0	1.837
10[a]	2.095
5[b]	2.764
10[b]	3.310
15[b]	2.987
20[b]	2.896

[a] Adding silica particles.
[b] Adding SZP particles.

3.7.1. SEM analysis of SZP/PSF composite membrane

Fig. 6 shows SEM micrograph of cross-section of SZP/PSF composite membrane (the amount of adding SZP particles is 10 wt.%). It is observed that particles are uniformly dispersed inside PSF membrane. The SZP particles, which have abundant hydrophilic radicals on the surface and strong chemical bonding capability with PSF, can effectively improve the intensity, tenacity and hydrophilic property of the composite membrane. A hydrophilic layer formed on the surface of the membrane plays an important role in removing the gel layer; this is because the SZP particles added in composite membrane have a stronger hydrophilic property. Even though a gel layer of contamination was formed on the surface of membrane, it could be easily eliminated by the feed fluid. Therefore, SZP/PSF composite membrane has a stronger anti-fouling capability.

3.7.2. Analysis of tensile strength

As indicated in Table 4, the tensile strength of the membrane increases as the addition amount of SZP particles increases. It is explained that the SZP particles with small size and large curvature can effectively decentralize the stress and impact from outside and make the composite membranes have a good capability of anti-impact and tensile strength. The maximum tensile strength of SZP/PSF composite membrane prepared by the solution containing 10 wt.% SZP particles reaches to 3.31 MPa. In contrast, the tensile strength of SZP/PSF composite membrane decreases as the adding amount of SZP particles increases consecutively (the adding amount of SZP particles is more than 10 wt.%), which is caused by aggregation between particles.

3.7.3. Analysis of hydrophilic property

As is known the lower the contact angles between water droplets and the surface of membrane, the better the hydrophilic property of SZP/PSF composite membrane [15]. The contact angles between water droplets and SZP/PSF composite membranes with different adding amount of SZP particles were tested, and the results were shown in Table 5. It indicates that the hydrophilic property of composite membrane containing SZP particles increases with increase of the amount of adding SZP particles. And its hydrophilic property is also better than that of composite membrane filled by SiO_2 particles. This is because SZP particles with nonstoichiometric structure have lots of point defects and exposed hydroxide radicals on their structure. Thereby, when SZP

Table 5
Effect of particles on membrane hydrophilicity.

Membrane code number	Content of particles (wt.% PSF)	Contact angle (°)
P0	0	80.1
PS	10	67.5
P1	5	49.8
P2	10	42.6
P3	15	43.8
P4	20	45.7

Remarks: P0, pure PSF membrane; PS, silica/PSF membrane; P1–P4, SZP/PSF membrane.

Table 6
Analysis results of water samples.

Membrane	Oil concentration in permeation (mg/L)	Oil retention rate (%)
Oil concentration in feed	80.00	
PSF	5.10	93.63
5 wt.% SZP/PSF	1.25	98.70
10 wt.% SZP/PSF	0.84	98.95
15 wt.% SZP/PSF	0.83	98.96
20 wt.% SZP/PSF	0.82	98.98

particles were filled in PSF membrane, hydrophilic property of the membrane was evidently improved.

From Table 5, it can be observed that the contact angle between water droplets and SZP/PSF composite membrane reaches 42.6° (minimum) when the amount of adding SZP particles is 10 wt.%. However, the hydrophilic property of SZP/PSF composite membrane declines when the adding amount of SZP particles is more than 10 wt.%. This is because the amount of hydroxide radicals on the surface of SZP particles decreases owing to aggregation between particles.

3.8. Retention of oil

The effect of membrane separation can be learned by the retention of oil. The membrane experiment was carried out with SZP/PSF composite membrane (with different amount of adding SZP particles), treating with wastewater containing oil at the condition of room temperature and operating pressure of 0.20 MPa. Table 6 shows that the oil retention rate increases with the amount of adding SZP particles increases. However, the oil retention rates change a little when the amount of adding SZP particles exceed 10 wt.%, i.e. the oil retention rates are a constant. Therefore, under considering other preparation conditions of SZP/PSF composite membrane and preventing SZP particles' aggregation, the fitting amount of adding SZP particles is 10 wt.%. Thereby, the content of the SZP have a limit, namely 10 wt.%. The qualities of permeate with oil contamination (0.84 mg/L) meet the environment standard for wastewater discharge (<10 mg/L). The results indicate that SZP/PSF membrane has a potential application in treatment of wastewater containing oil.

4. Conclusions

SZP particles with mean diameter between 1 and 3 μm are spherical state. The optimum preparation conditions of SZP/PSF composite membrane are: concentration of PSF is 12 wt.%; content of PEG400 is 10 wt.%; content of SZP is 10 wt.%.; ultrasound 10 min inside each 30 min; the pre-evaporating time is 10 s. With SZP particles were filled to polysulfone, the hydrophilicity and tensile strength of the composite membrane were effectively improved, and hence the composite membrane could be applied in water and wastewater treatment.

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