Effect of surface morphology on the mesoporous silicon modified nanofiltration membranes for high rejection performance

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Abstract: A new method to prepare composite nanofiltration membrane directly and efficiently by controlling the pore structure and surface morphology of the membrane is proposed in this paper. The fabrication of mesoporous silicon modified polysulfone blend membranes is via a phase inversion method. The structural morphology, surface functional group analysis, elemental analysis, hydrophilicity, chargeability, and nitrogen pollutant (ammonia nitrogen, nitrate nitrogen, total nitrogen) rejection properties of the modified membranes were found to be dependent on the amount of mesoporous silicon incorporated. The combination of the mesoporous silicon framework layer can not only effectively improve the surface structure of the modified membrane with a narrow pore size distribution but also increase the rejection of nitrogen pollutant compared with the pure NF membranes. The mesoporous material can absorb and storage the nitrogenous solution to facilitate the following interfacial polymerization, as well as induce the change of pore radius and surface structure. Compared to those pure NF composite membranes, the modified blend membranes exhibit increased water permeation flux as high as 29.09 L m⁻² h⁻¹ at 0.2 MPa. The results show that the optimum doping amount of mesoporous silicon is in the range of 0.5%-1.0%. Characterization studies demonstrated that the addition of the mesoporous silicon leads to decreased membrane pore size. Then, due to the enhanced hydrophilicity of carboxyl and hydroxyl groups on the surface, the electrostatic repulsion between the functional groups and nitrogen pollutant molecules in the membrane results in the enhanced rejection of nitrogen pollutants.

1. Introduction
Nanofiltration membrane, as a new membrane separation technology, has a wide application and far-reaching development potential in food industry, biomedical, seawater softening, chemical separation and other fields[1-3]. The NF membrane has the following characteristics: 1) there are obvious differences in the retention effect of monovalent salts and multivalent salts with ionic selectivity; 2) the interception molecular weight is between 200-1000 Da and some inorganic ions less than 200 Da can be trapped by the Donnan effect; 3) the operation pressure is under 0.5~2.0MPa [4,5].

However, there are still several limitations in commercial NF membranes including the low water flux, the high operation pressure and the low interception efficiency such as natural organic matter [6,7]. In recent studies, many inorganic nanoparticles such as TiO₂, ZnO and SiO₂ have been used to modify NF membranes to enhance its performance [8, 9]. On the other hand, it is very difficult to
control the structure and forming process of the membrane in the process of phase inversion. Therefore, it is very effective to modify the surface of the membrane to improve the water flux, retention efficiency and other properties of the membrane [10]. Mesoporous materials have attracted much attention due to their ordered pore structure, electrical and electrochemical properties [11]. Therefore, it still remains large room to further improve the NF membrane performances by optimizing the structures of both modified material and modified addition amount.

With the rapid development of mesoporous materials, mesoporous materials have been widely used in the field of membrane modification as a new type of functional materials [12]. The separation performance of small molecules of pollutant on NF membranes are relatively poor so we introduce mesoporous silicon for the modification of polyethersulfone (PES) composite NF membrane, thus the surface structure and the charge distribution of the film is improved and the efficient separation of nitrogen pollutant is achieved [13-14].

In this study, the commercial polyethersulfone nanofiltration membrane was modified by adding mesoporous silica and the surface structure, basic performance parameters and separation efficiency of the modified composite nanofiltration membrane were determined. In this paper, the amount of modified material is discussed and the influence of the addition of mesoporous material on the properties of the films is analyzed by means of characterization methods. And the difference in performance index of PES composite NF membrane was compared with NF270 (commercial NF membranes).

2. Methods

2.1 Synthesis of mesoporous silicon modified PES membranes

The modified PES commercial NF membranes were prepared in our previous papers [15, 16]. The different compositions of modified PES membranes are named as 0.0% Si/PES, 0.5% Si/PES, 1.0% Si/PES, 5.0% Si/PES. The different compositions of modified PES membranes are shown in Table 1.

| Membrane type   | PES (wt %) | Mesoporous silicon content (wt %) | DMAc |
|-----------------|------------|----------------------------------|------|
| NF270           | 0          | 0.0                              | 0    |
| 0.0% Si/PES     | 25         | 0.0                              | 75   |
| 0.5% Si/PES     | 25         | 0.5                              | 75   |
| 1.0% Si/PES     | 25         | 1.0                              | 75   |
| 5.0% Si/PES     | 25         | 5.0                              | 75   |

2.2 Performance testing

The laboratory prepared water (NO\textsuperscript{3}\textsuperscript{-} 1.0 mg/L, NH\textsuperscript{4}+ 0.5 mg/L, HA 3 mg/L) was used to carry out the filtration experiment with ultrafiltration cup.

3. Results and discussion

3.1 XPS analysis of mesoporous silicon/PES Composite Membranes

The chemical structure of the membrane surface was characterized by XPS. The typical spectrum of XPS is shown in Figure 1. It can be seen that both pure and modified membranes contain S, C, N, O and Si elements. It can be seen from Fig. 1 (b) that with the different content of the modified film, the silicon peaks of the modified film and NF270 show obvious differences. The data shows that there is a linear relationship between the content of silicon and the response of absorption peak when the doping content is below 0.5wt%. However, when the doping amount of mesoporous silicon is higher than
0.5wt%, the linear relationship disappeared which is caused by agglomeration of mesoporous silicon at the bottom of casting solution. Compared with the standard XPS spectra, silicon atoms have characteristic absorption peak at 99.3 eV and the tetravalent silicon have absorption peak near 103.3 eV. From Fig. 2 can be seen, a strong absorption peak at 102 eV appeared of the Si/PES membrane, while the characteristic absorption peak did not appear at 99.3 eV, indicating the mesoporous silicon modified on the surface of film is in the tetravalent forms rather than atomic state. The synthesis of mesoporous silica is the hydrolysis of silicic acid to form silica sol, which is formed by self-assembly with template and crystallized. So the mesoporous silicon is mainly in the form of tetravalent bonding.

3.2 Water flux of mesoporous silicon/PES Composite Membranes
Through the water flux test results, we can see that the maximum water flux of 0.5%Si/PES membrane is 29.09 L/m² h, which is nearly 73.88% higher than 16.73 L/m² h of the pure PES membrane NF270 in the mesoporous silicon modified NF membrane. This is due to different properties such as pore size and surface hydrophilicity for the membranes. The water flux of other modified membrane such as 1.0% Si/PES membrane is 56.16% which is higher than NF270 and the water flux of 5.0%Si/PES film decreases because of excessive mesoporous silicon doping on the surface which damaged the structure of the membrane then it is difficult to form a uniform structure of NF membranes. The 0.0% Si/PES membrane had the lowest flux (9.09 L/m² h) due to its low hydrophilicity. In general, the fluxes for all the composite modified membranes containing mesoporous silicon were larger than those of pure PES membrane. Consequently, the excessive dose in mesoporous silicon mass ratio into PES composite membrane led to the formation of less porous membranes, which led to flux decline.

3.3 Pore size analysis of mesoporous silicon/PES Composite Membranes
The results show that the structure of the membrane is related to the pore size of the membrane. The pore size of the synthetic membrane was determined by the rejection of polyvinyl alcohol (PEG) (Fig. 2). With the increase of PEG molecular weight, the rejection rate of NF membrane to peg increased. When the rejection of PEG is more than 90%, the molecular weight of the rejection is the molecular weight of the membrane. The rejection rate of 0.5% Si/PES modified membrane for 600Da PEG was more than 90%, while that for 400 Da PEG was less than 90%. After calculation, the pore radius of 0.5%Si/PES modified membrane was 0.581 nm. Compared with NF270, nanofiltration membrane is more conducive to the retention of inorganic matter with the decrease of pore size. This data shows
that mesoporous silicon doping can effectively reduce the pore radius of PES composite nanofiltration membrane, and the pore size of PES composite nanofiltration membrane can be effectively controlled by changing the amount of mesoporous silicon, so as to improve the pore structure of the membrane [17].

![Figure 2: Rejection of the PEG solutions with different molecular weights (400, 600, 1000, 2000 Da) for NF membrane and mesoporous silicon modified PES membranes.](image)

3.4 Nanofiltration performances of the PES membranes

From Fig. 3, the retention rates of NH$_3^+$, NO$_2^-$ and TN on the mesoporous silicon modified polyethersulfone composite nanofiltration membrane are 18.0% - 36.1%, 66.7% - 76.5% and 53.2% - 62.9% respectively in the concentrated solution.

The results show that higher nitrate rejection rate is conducive to the retention of nitrogen-containing pollutants. However, due to the electrostatic effect on the membrane surface, the rejection rate of NH$_3^+$ is lower than that of nitrate. Therefore, the addition of mesoporous silicon on the membrane is conducive to the rejection of ammonia nitrogen and improves the separation effect of inorganic nitrogen [18]. The rejection rate of nitrate in the mixture was 66.7% on NF270 nanofiltration membrane and 73.4% on modified PES composite NF membrane. From Fig. 3, the trend of high retention rate of TDN is consistent with the trend of effective retention rate of HA. At the same time, the high retention rate is due to the high retention rate of nitrate nitrogen. The retention rate of TDN on NF270 membrane was 53.2%, while the retention rate of 0.5% Si / PES modified membrane with the highest retention rate of TDN was 62.9%. Compared with NF270 nanofiltration membrane, mesoporous silicon modified membrane is more conducive to the retention of TDN on the membrane surface.
Fig. 3 NF separation treatment for nitrogen pollutant with pure PES membrane and mesoporous silicon modified PES membranes.

4. Conclusions
In this study, mesoporous silicon was used to change the pore size distribution and electrostatic distribution in the membrane matrix. The modified membrane shows better results for separation of nitrogen pollutants especially HA due to membrane structure, pore size between hydrogen bonding and permeability balance. Among all prepared membrane, 0.5% Si/PES membrane shows an enhanced anti-fouling capability with the highest water flux of 29.09 L/m² h as well as the lowest pore radius of 0.581 nm. This work provides a novel protocol to design high-performance modified PES composite NF membrane for water treatment.

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