Progress in Preparation and Research of Hydrophilic Composite Nanofiltration Membrane

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Abstract: Most of the commercial nanofiltration membranes are composite nanofiltration membranes obtained by interfacial polymerization of polyamino and polyacid chloride on ultrafiltration membranes with non-woven fabrics. During the operation of the membrane, membrane fouling is caused by inorganic salt scale, colloid, organic matter and other factors in the environment, resulting in a decrease in water quality and water flux so that a significant reduction in membrane life and an increase in operating costs. Therefore, it is necessary to improve the pollution resistance of the film. The hydrophilic modification of the membrane can improve the anti-pollution performance of the membrane. This paper discusses the preparation and research progress of the hydrophilic composite nanofiltration membrane from three aspects: new monomer development, active layer modification and new base film development and the current research content is summarized and some of the contents that need urgent research are proposed.

1. Introduction
Nanofiltration is a membrane technology that was introduced in the 1970s. The preparation method of the nanofiltration membrane is very similar to that of the reverse osmosis membrane. Compared with the reverse osmosis membrane, the nanofiltration membrane has the characteristics of high flux and low working pressure so that nanofiltration membrane is mainly used for desalination and deep water treatment. As a pressure-driven membrane, the nanofiltration membrane is prone to membrane fouling during use, which affects the service life of the membrane. Therefore, the nanofiltration membrane is usually hydrophilically modified to improve the membrane's pollution resistance. [1-2].

2. Composition of composite nanofiltration membrane
The composite nanofiltration membrane is composed of a support layer, a base membrane and an active layer as shown in Figure 1. The support layer is usually a non-woven fabric, and the base membrane is composed of an ultrafiltration or microfiltration support membrane. The support membrane mainly serves as a mechanical support, but its structure also affects the structure of the selective separation layer and its effective filtration area.

The solute retention and solvent flux of the composite nanofiltration membrane is primarily dependent on the ultra-thin active layer. At present, most of the composite nanofiltration membranes are obtained by interfacial polymerization of polyamino and polyhydroxy compounds with polyacid...
chlorides on the surface of the base membrane. Interfacial polymerization refers to the different reactive monomers (usually polyamines and polyacid chlorides) dissolved in the aqueous phase and the organic phase (oil phase, alkanes), which are polymerized at the interface of the two phases to be an ultra-thin active layer in situ on the porous base membrane.

3. Preparation and modification of hydrophilic nanofiltration membrane

In recent years, research on new hydrophilic nanofiltration membranes has focused on the development of new monomers, modification of active layers and modification of base membranes.

Through the development of new monomer molecules, and thereby optimizing the functional layer materials, the hydrophilicity of the membrane is optimized to achieve the purpose of pollution resistance.

The active layer modification is to improve the hydrophilicity of the active layer of the membrane by introducing a hydrophilic group on the surface active layer of the membrane, and the main methods include surface coating, grafting, blending and the like to introduce a hydrophilic group.

The high performance base membrane is the basis for the preparation of an excellent hydrophilic nanofiltration membrane. The development of the base membrane is mainly to develop a new type of base membrane material or to modify the existing base membrane (including the modification of the base membrane material and the optimization of the base membrane structure). In this paper, the recent research on the development of new monomers, the modification of active layer or base membrane explores the recent progress of hydrophilic composite nanofiltration membranes.

3.1. New monomer development research

The composite nanofiltration membrane at this stage is usually obtained by interfacial polymerization of a polyamine and a polybasic acid chloride on the surface of a base membrane. Most of the previous studies were prepared by combining polyamines with polyacid chlorides. Moreover, most of the studies were shown that the composition and structure of the aqueous phase have a more important effect on the performance of the active layer than the organic phase. Therefore, most of the current new monomer developments are directed to aqueous monomers.

The new aqueous phase monomer is mainly obtained based on the modification of the previously used water phase monomer. Currently, the new type of aqueous phase monomer mainly includes bisphenol A type (TMBPA) and aliphatic amine (DETA, TETA, TEPA), PVAm[3], etc.), amino acids (silkin[4]), aromatic amines (DABSA[5]), piperazines (AEPPS), and so on. The improvement of the organic phase monomer is mainly a novel diamine monomer (PMIA [6]) or the introduction of inorganic nanoparticles (TiO$_2$, SiO$_2$, Al$_2$O$_3$, etc.) in the monomer.

Wang [6] et al. prepared PMIA hollow fiber nanofiltration membranes using PMIA combined with DMAC/LiCl/acetone/PVP K15 system, which was widely used in the fiber field, and studied its perfluorooctanesulfonyl compound (PFOS) in water. The removal rate of the PFOS is as high as 99.40%.

The method is not required for the experimental operation, and most of the monomers are modified on the original monomer, but the membrane prepared by using the modified monomer is generally not significantly improved compared with the membrane prepared by using the original monomer. Therefore, it is currently the focus of research to find new monomers with excellent hydrophilic properties suitable for use in nanofiltration membranes.

3.2. Active layer modification
3.2.1 Surface graft modification. The surface grafting method mainly involves grafting a specific group onto a base membrane having an active base treated by various energy sources (ultraviolet, plasma, gamma ray, electron beam, etc.).

For example, a hydrophilic and pollution-resistant substance such as methacryloyloxy-ethyl-trimethylammonium chloride (DMC) [8], 2-propenylamino-2-methylpropanesulfonic acid (AMPS) [7], acrylic acid [8], polyazo-isopropyl acrylamide (NIPAM) [9], PEI-g-SBMA [10] and the like.

Yang [11] used the Michael addition reaction between polydopamine and amine compounds to successfully construct a structurally stable positively charged nanofiltration separation cortex on the surface of ultrafiltration membrane by copoly precipitation of polyethyleneimine polydopamine, and through a series of regulation methods, the hydrophilic properties of the membrane are improved.

This method has higher requirements for porous base membranes. When the pore size distribution of the base membrane is not uniform, the large pores are hardly completely covered by the connected polymer, and thus the rejection rate of the nanofiltration membrane cannot be satisfied. If the pores of the membrane are to be completely grafted to the polymer, a large amount of grafting is required, which will result in a lower solvent flux of the nanofiltration membrane. Therefore, if a high-performance nanofiltration membrane is to be produced, it is preferable to use some ultrafiltration membranes having a relatively narrow pore size distribution as a base membrane, which limits the application of the method to some extent.

3.2.2 Surface coating modification. The coating method is to immerse the upper surface of the porous base membrane into the dilute solution of the polymer, and then pull the base membrane out of the solution and dry it out of the solution or scrape the polymer film liquid onto the base membrane, and then hydraulic the casting membrane into the micropore of the base membrane by external force. Then the film was prepared by L-S phase inversion (impregnated with cross-linking agent).

Lei [12] introduced a PEG-based hydrogel on the surface of Dow Membrane Tec NF270 nanofiltration membrane to prepare a modified nanofiltration membrane. The results showed that the introduction of PEG derivatives on the surface of nanofiltration membrane could compensate the surface defects of the polyamide functional layer and improve the salt rejection of the nanofiltration membrane. At the same time, the concentration polarization of the membrane surface was alleviated, and the pollution resistance of the nanofiltration membrane was obviously enhanced.

Surface coating is a relatively simple modification method that can effectively improve the hydrophilic properties of the nanofiltration membrane. However, in actual use, the coating layer is relatively weakly bonded to the surface of the membrane, and the use of high pressure outside the membrane often causes defects or even shedding of the surface coating functional layer, thereby affecting the use of the nanofiltration membrane, and the service life of the nanofiltration membrane is greatly reduced.

3.2.3 Blending modification. Two or more kinds of high-polymers are liquid-phase blended, and the blending modification can compensate the defects of the original materials while maintaining the performance of the original materials, and the excellent properties not possessed by the original materials can be obtained. The method can mix more polymers, including some new monomers and functional additives, and can use different additives according to different purposes, such as blending new aqueous monomer with traditional aqueous monomer to prepare new active layer (As described above, TMBPA, APEES, etc.), or blending some functional additives into conventional monomers to improve some of the properties of conventional monomers.

Mohammad [13] et al. used a sol-gel method to functionalize zinc oxide-modified graphene oxide and prepared a nanocomposite nanofiltration membrane by phase inversion technique. The membrane prepared after incorporation of nanoparticles (zinc oxide and functionalized graphene) has a significantly improved hydrophilicity and water flux compared to the polysulfone membrane. Through the E-coli antimicrobial test, it was found that the modified nanofiltration membrane had the least colony growth and water flux recovery rate.
Tan [14] et al. introduced hydrophilic macromolecular PVA into PIP aqueous phase solution and interfacial polymerization with TMC to prepare composite nanofiltration membrane. By adjusting the concentration of PVA, PIP, TMC and according to the reaction-diffusion principle, under certain experimental conditions, PVA delayed the diffusion rate of PIP in the interfacial polymerization reaction, thus successfully synthesized the Turing structure on the surface of the membrane for the first time. The water flux and hydrophilicity of the membrane were greatly improved.

The blending method is considered to be an effective and low-cost modification method, which can simultaneously modify the surface and the body of the membrane, thereby overcoming the disadvantages of surface coating and surface grafting. If a certain high-quality and economical modified polymer can be found, the method will be a viable membrane-forming method.

3.3. New base membrane
The composition of the composite nanofiltration membrane has been mentioned above, and is prepared by adhering an active layer having a selective separation function to a multi-empty support in a certain manner. The nanofiltration membrane is used as a pressure-driven membrane, and the pressure difference is used as the main driving force, so the membrane must have a certain mechanical strength. Generally, an ultrafiltration membrane or a composite membrane combined with a non-woven fabric and an ultrafiltration membrane is used as a multi-hollow support, and the structure of the base membrane has an important influence on the performance of the composite nanofiltration membrane. Therefore, the modification of the basement membrane structure or the development of the novel basement membrane has become an important direction of nanofiltration membrane research[15].

4. Conclusion
At present, significant progress has been made in the preparation and modification of composite nanofiltration membranes, but there are still problems that require further study.

- The membrane is modified to increase the hydrophilicity of the membrane, and the fouling resistance of the membrane is generally improved, but other properties such as salt rejection and mechanical properties tend to be lowered. Therefore, when developing new monomers or grafts, the balance between membrane fouling resistance and separation performance should be measured as much as possible.
- At present, the research on the membrane formation mechanism of nanofiltration membrane is not clear. In order to make nanofiltration membrane have better performance, it is necessary to have a deeper understanding of the reaction mechanism and microstructure of nanofiltration membrane.
- Some physical modification methods may affect the adhesion between the active layer and the base membrane, and some of the modifier may be detached from the membrane body during the operation of the membrane. It is therefore necessary to enhance the study of the adhesion between the modifier and the nanofiltration membrane body by this method.

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