Analysis of Research Status of Modified PVDF Ultrafiltration Membrane

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Abstract. The current research status of PVDF ultrafiltration membranes is introduced, and the limitations of current PVDF membranes are described. In view of the existing problems such as easy pollution and clogging, low cleaning efficiency and low hydrophilic permeability, corresponding improvement measures have been found, the performance of the membrane has been greatly improved. In addition, the application prospects of ultrafiltration membranes are properly introduced.

1. Background
With the development of industry and economy, rivers and lakes have received too much sewage from factories and cities, and they have been seriously polluted, making water pollution more serious [1]. As an energy-efficient water treatment technology, membrane technology has been widely used in various fields [2-3]. Polyvinylidene fluoride (PVDF) membrane, as the most outstanding membrane, is widely used in many fields, such as industrial wastewater treatment, due to its excellent chemical resistance, high thermal stability, strong mechanical stress and good controllability, reverse osmosis pretreatment, etc [4-5]. However, traditional PVDF membranes still have some limitations, such as easy fouling and clogging, difficult to clean, easy to be contaminated, etc. Researchers have taken various modification measures to improve the PVDF ultrafiltration membrane, thereby further improving the performance of the membrane.

2. Current limitations
Under the current technical conditions, through the actual application and research of PVDF ultrafiltration membranes, it is found that the limitations of traditional unmodified PVDF membranes are mainly reflected in the following aspects.

2.1. Easy to contaminate and block
Although membrane technology is becoming more and more mature, membrane pollution is still one of the main factors limiting its promotion and application [6-8]. Membrane fouling refers to the adsorption and deposition of colloidal particles, sludge flocs, inorganic salts or dissolved organic matter in the filtrate due to physical and chemical or mechanical interaction with the membrane, or in the membrane pores. The internal adsorption causes the membrane pore size to become smaller or clogged, which increases the resistance of water to pass through the membrane and decreases the filterability, so that the membrane flux is continuously reduced or the transmembrane pressure difference increases [9-11].
In addition, membrane fouling will reduce membrane performance, reduce membrane service life, and increase application costs\cite{11-13}. If suitable membrane cleaning measures can be used, the dirt on the membrane surface can be effectively removed, and the performance of the membrane can be improved to a certain extent, so as to realize the long-term stable operation of the membrane system\cite{14}.

The pollution of membrane mainly includes organic pollution, inorganic pollution and microbial pollution\cite{15}. General experiments often use bovine albumin (BSA), sodium alginate (SA), humic acid (HA) and their mixed pollutants as simulated pollutants to conduct research on pollutant treatment. The formation mechanism of membrane fouling can be simply attributed to the following two aspects: One is concentration polarization\cite{16-17}. That is to say, larger substances are trapped by the membrane pores during the separation process and continuously accumulate on the membrane surface area, causing the concentration of the membrane surface to gradually be higher than the concentration of the main liquid. Driven by the concentration difference, the trapped substances will be removed from the membrane. Face the main body of the material and liquid for reverse diffusion. When equilibrium is reached, a solute concentration distribution boundary layer will be formed on the surface of the membrane, which has a blocking effect on the penetration of small molecules. In addition, the concentration polarization is so severe that a gel layer will be formed on the membrane surface. The second is the inevitable interaction between the separated pollutants and between the pollutants and the membrane surface, causing the pollutants to be adsorbed and deposited on the membrane surface or membrane pores, and in severe cases, a filter cake layer will be formed\cite{18}.

2.2. Low cleaning efficiency
The current membrane cleaning is mainly divided into two types of cleaning methods: physical cleaning and chemical cleaning. Physical cleaning is to flush and clean the membrane surface through high-speed fluid or a mixed fluid of air and water. Common methods include low-pressure high-speed flow cleaning, gas-liquid mixing and vibration cleaning, etc. This method is simple and easy to perform, with little damage to the membrane and not easy to introduce new pollutants, but for membrane modules with serious pollution, the treatment effect of this method is extremely weak. Chemical cleaning uses chemical cleaning agents to restore membrane flux. Common cleaning agents include alkaline cleaning agents, acidic cleaning agents, and surfactants\cite{18}.

2.3. Low hydrophilic permeability
Polyvinylidene chloride (PVDF) has excellent chemical stability, thermal stability and easy film formation. It is widely used to prepare membrane materials, but the material itself has low surface energy and strong hydrophobicity, and the prepared membranes are poor hydrophilic\cite{19}. First, the water flux in the water treatment process is low, which requires a higher water pressure to increase the water flux of the membrane, which increases the operating cost; secondly, in the oil-water separation process, organic pollutants will be adsorbed on the surface of the membrane or in the membrane pores, it is easier to produce pollution, which shortens the service life of the membrane\cite{20}.

3. Ultrafiltration membrane modification measures
In view of the various problems mentioned above, modification has become a mainstream solution to improve the anti-fouling performance and water treatment effect of the membrane. It mainly modifies the membrane pore size, hydrophilic and hydrophobic properties, and membrane surface smoothness. Commonly used modification methods mainly include surface coating, film surface graft modification, chemical treatment, high-energy radiation, and low temperature. The research direction of modification is mainly the use of nanomaterials such as TiO$_2$, ZnO, Ag, and TiO$_2$ or biological processes such as MVIR. In the current technical environment, there is still a lot of room for improvement of the catalytic effect of TiO$_2$ on PVDF. At present, adopting different methods to improve the modified materials is the main research topic.
3.1. TiO$_2$ is used for membrane improvement

3.1.1. Doping TiO$_2$ with Fe
At present, the most widely studied photocatalyst is the ultraviolet-responsive TiO$_2$ catalyst, but the use of sustainable luminous energy such as visible light or sunlight is finite [21-23]. Photocatalytic technology is an effective means to remove persistent organic pollutants in water. In contrast to the visible spectrum ultraviolet display, the absorption of Fe-doped TiO$_2$ (Fe-TiO$_2$) extends to the visible region, and the scanning electron microscope image shows a significant change in the cross-sectional shape of the composite film. That is, the addition of photocatalyst makes the composite membrane have both visible light catalytic and ultrafiltration properties. The research results show that under visible light irradiation, the mechanical ability and self-cleaning ability of the composite film are enhanced [24].

3.1.2. Add TiO$_2$/graphene oxide for modification
In order to improve the water flux and antifouling performance of the PVDF ultrafiltration membrane, the titanium dioxide-graphene oxide ultrafiltration membrane was prepared by the immersion precipitation phase inversion method for the first time. After that, a new type of polyvinylidene fluoride hybrid membrane was prepared with TiO$_2$-GO nanocomposites grafted with different polyethylene glycols as additives. The structure and surface properties of the composite membrane were characterized by FTIR spectrometer, SEM, zeta potentiometer and static contact angle analyzer, and the membrane performance was evaluated by ultrafiltration method. The results show that the interaction of graphene oxide and TiO$_2$ makes the titanium oxide-graphene oxide distributed well in the polymer membrane, improves the polarity and porosity of the composite membrane, thereby improving the water flux and antifouling performance of the composite membrane. The grafted polyethylene glycol on the titanium oxide-graphene oxide nanocomposite not only played a role in pore formation, but also enhanced the distribution and surface polarity of the titanium oxide-graphene oxide, and improved the hydrophilicity of the hybrid membrane. Therefore, the flux and antifouling performance of PVDF modified membrane containing TiO$_2$-GO are significantly higher than that of unmodified PVDF membrane [25].

3.2. Other modification measures

3.2.1. Modification of grafted zwitterionic polymer hydrogel
In recent years, the reuse of drinking water has attracted attention from all sectors of society. The safety of microorganisms in drinking water, especially with regard to pathogenic viruses, is an issue that people attach great importance to. Membrane technology can fully filter and remove pathogenic viruses without producing disinfection by-products, but it requires a lot of energy. Ruiqing Lu et al. studied the modification of grafted zwitterionic polymer hydrogels by grafting zwitterions onto ultrafiltration polyethersulfone membranes and found that they can significantly filter out viruses. In the experiment, both the original membrane and the grafted membrane used the soluble microbial product (SMP) extracted from the membrane bioreactor (MBR), and the grafted membrane had a higher filtration rate for viruses than the ungrafted membrane. The functionalization of graft polymerization of commercial membranes can improve the efficiency of virus filtration, which reflects the prospect of membrane filtration technology for pathogen control in drinking water applications [26].

3.2.2. Quaternary ammonium salt modified MWNTs
Yan Xi et al. used tertiary ammonium salt 2-dimethylaminochloroethane hydrochloride (DCH) as the precursor of the quaternary ammonium salt, and grafted epichlorohydrin to oxidized multi-walled carbon nanotubes (O-MWNTs). The obtained quaternary ammonium salt modified multi-walled carbon nanotubes (MWNTs) (namely N$^+$-MWNTs) are added as an additive to the casting solution to prepare polyvinylidene fluoride (PVDF) ultrafiltration membranes (PVDF/N$^+$-MWNTs membranes). The surface roughness of the prepared PVDF/N$^+$-MWNTs composite membrane is obviously reduced, and
the hydrophilicity is obviously improved. In the pollution-cleaning cycle experiment of bovine serum albumin (BSA), the PVDF/N+–MWNTs composite membrane compared with the pure PVDF membrane, the pure water flux and its flux recovery rate have been significantly improved. In addition, the retention performance of the composite membrane for BSA did not decrease, and the antibacterial rate remained at a high level[27].

The anti-fouling ability of the membrane is closely related to the roughness of its surface. According to the four sets of M-0, M-0.2, M-0.4, and M-0.6, the roughness parameters of the membrane with different N+–MWNTs added amounts are measured, as shown in Figure 1 below.

![Roughness parameters of films with different addition amounts of N+-MWNTs](image)

Figure 1 Roughness parameters of films with different addition amounts of N+-MWNTs

It can be seen from the figure that the addition of N+–MWNTs reduces the surface’s roughness of the membrane, thereby enhancing the antifouling ability of the membrane.

4. Application

4.1. Application of modified PVDF membrane in dye wastewater treatment

The dyes in wastewater can absorb light, reduce the visibility of water bodies, consume a large amount of oxygen in the water, cause severe hypoxia in the water body, affect the growth of aquatic organisms and microorganisms, destroy the self-purification ability of water bodies, and easily cause visual pollution. At the same time, dye wastewater contains heavy metals such as chromium, lead, mercury, arsenic, and zinc, which are difficult to biodegrade. Direct discharge of dye wastewater is extremely harmful to human health and can cause serious pollution to the natural ecological environment[28]. Dye wastewater is mainly composed of dyes and heavy metals. The separation of solid and liquid in wastewater can be achieved by using functional modified membranes, and the heavy metals in the water body can be absorbed at the same time to realize the harmless treatment of dye wastewater[29].

4.2. Application of sulftaine type PVDF membrane in oil-water separation

The sulftaine type PVDF membrane is a highly hydrophilic blend membrane, which can effectively remove the oil components in the oil-water emulsion, and the oil content of the filtrate obtained by one filtration is only 1.2ppm. And this zwitterionic membrane has excellent pollution resistance. After simple washing, the water flux recovery rate of the membrane is as high as 94%[30].

4.3. Application of PVDF membrane modification in copper hydrometallurgy

The addition of HDPE improves the strength of the PVDF ultrafiltration membrane. The experimental results show that when the concentration of HDPE is 2 wt%, the concentration of PVDF is 20 wt%, and
the concentration of PVP is 3 wt%, the tensile strength of the membrane reaches the best value. It is 2.48 MPa. At the same time, the addition of PMMA improves the hydrophilicity of the PVDF ultrafiltration membrane. The results show that the membrane performance reaches the best when the PVDF:PMMA ratio is 6:4 and the polymer concentration is 20 wt%[31].

5. Conclusion
At present, the global water pollution problem cannot be delayed. PVDF ultrafiltration membrane provides a good purification tool for environmental engineering water pollution treatment. However, traditional PVDF membranes inevitably have problems such as low cleaning efficiency, low hydrophilic permeability, and easy fouling and clogging. PVDF modification is undoubtedly a mainstream and effective way to solve these problems, which can greatly improve the hydrophilicity of the membrane, the separation effect of pollutants and the antifouling ability.

PVDF membrane has a large number of applications and researches in the field of environmental engineering water treatment technology. How to improve PVDF membrane to obtain different performance characteristics, so as to better adapt to different use needs, and at the same time promote it with high-performance and economical improvement measures to put into practical application is an important forward direction of scientific research.

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