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ZrO_2 solid superacid porous shell/void/TiO_2 core particles (ZVT)/polyvinylidene fluoride (PVDF) composite membranes with anti-fouling performance for sewage treatment

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HIGHLIGHTS

- ZrO_2 solid superacid porous shell/void/TiO_2 core particles (ZVT) and ZVT/PVDF composite membranes are successfully prepared.
- Micro reaction locations (MRLs) are formed inside channels and surface of PVDF membranes.
- ZVT can interact with PVDF chains by hydrogen bonds.
- ZVT/PVDF composite membranes have good anti-fouling, anti-compaction and hydrophilic properties.

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ABSTRACT

To enhance the capabilities of anti-fouling, anti-compaction and hydrophilicity of PVDF membranes, ZrO_2 solid superacid porous shell/void/TiO_2 core particles (ZVT) were firstly prepared and then doped them to PVDF to prepare a novel composite membrane (ZVT/PVDF composite membrane) through a phase inversion process. ZVT and ZVT/PVDF composite membranes were characterized through scanning electron microscope (SEM), transmission electron microscope (TEM), Brunauer–Emmett–Teller (BET) and Fourier transform infrared (FT-IR), respectively. The results indicate that ZVT with the diameter of around 500 nm are uniformly dispersed in PVDF membranes, the pore size of ZrO_2 shell is about 3 nm, a solid superacid ZrO_2 shell on the TiO_2 core is formed due to a stretching vibration peak of S=O double bond at 1460 cm^{-1} in FT-IR spectra. The results of anti-compaction, contact angle and tensile strength measurements show that ZVT/PVDF composite membranes have anti-compaction, hydrophilicity properties and mechanical strength. Ultrafiltration experiment indicates ZVT/PVDF composite membranes show fine oil retention property and its oil retention ratio reaches 93.82%. And chemical cleaning and photocatalytic activity tests indicate that ZVT/PVDF composite membranes have anti-fouling property. Therefore, ZVT/PVDF composite membranes with anti-fouling, anti-compaction and hydrophilic properties are desirable for sewage treatment.

1. Introduction

Sewage needs to be treated effectively before it is released to the environment. However, soluble oil in sewage cannot be entirely eliminated by conventional treatment methods such as flocculating precipitation, activated sludge process and fiber adsorption, etc [1]. Membrane technology, especially ultrafiltration membrane, has been widely used in the advanced treatment of sewage containing oil because it offers an efficient solution for the problem mentioned above [2]. However, ultrafiltration membranes are not only vulnerable to be contaminated by oil, but also easy to be compacted when treating with sewage containing oil [3]. These defects result in a dramatic loss of membrane permeation flux and seriously hamper the widespread application of membrane technology [4,5]. Therefore, the enhancement of hydrophilicity, anti-fouling and anti-compaction properties by modifying membranes is a key to solve above problems.

Membrane fouling is mainly caused by three classes of pollutants such as organic pollutants, microbes and inorganic pollutants in the sewage [6]. In the process of sewage treatment, organic pollutants (hydrocarbon and soluble oil, etc.) and microbes contribute to form the gel layer on the surface of membranes, which can

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Abbreviation: PVDF, polyvinylidene fluoride; PSF, polysulfone.

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gradually increase the membrane resistance, declining the membrane permeation flux; inorganic pollutants (metal oxide, etc) can be adsorbed and deposited on the surface of membranes and channels, also causing the decline of the permeation flux of membranes. Therefore, it has been being an important task for researchers how to settle the fouling of membranes mentioned above [7].

Nowadays a large number of strategies have been reported to settle the fouling of membranes. Among these methods, the strategy of doping inorganic oxide particles to polymer to prepare organic–inorganic composite membranes is promising, owing to its simple operating process and preparation technology [8]. Liu et al. [9] added γ-Al_2O_3 particles into PVDF membranes to improve their hydrophilicity and anti-fouling properties. Liao et al. [10] prepared a novel M-SiO_2/PVDF (P–M) composite membrane with M-SiO_2 nano-dispersed in PVDF, the mechanical stability and hydrophilicity of the composite membrane have been increased to some extent. Hong et al. [11] tended to modify PVDF membranes by addition of Nano ZnO, the improved hydrophilicity of the composite membrane enhances its anti-fouling performance. Zhang et al. prepared phosphorylated Zr-doped hybrid silicas (SZP)/PSF composite membranes [12,13] and sulfated Y-doped nonstoichiometric zirconia (ZD)/PSF composite membranes [14] by taking the advantages of nonstoichiometric inorganic oxide particles with various point defects on the inside and numerous exposed hydroxide radicals on the surface, the properties of two classes of PSF composite membranes have been evidently improved. Furthermore, to enhance the compatibility between inorganic particles and polymers, Zhang et al. [15] also prepared phosphorylated silica nanotubes (PSNTs) with specific high ratios of length to diameter as a better filling material to modify polymer membranes.

Although the anti-fouling property of these membranes can be improved using the above methods, further enhancement of the anti-fouling property of these membranes is limited. This is because these methods just dope functional materials with small size into polymer membranes to enhance their hydrophilic and anti-fouling properties by physical interaction on the interface between aqueous solution and composite membranes, but without any chemical reaction. Therefore, if the anti-fouling property of these membranes is further enhanced, the membranes should be modified by doping novel functional materials, making membranes have good integrative capabilities such as micro reaction locations (MRLs) inside channels and surface of membranes, hydrophilicity and anti-compaction. It is reported that TiO_2 photocatalytic particles with high photocatalytic activity [16,17] can effectively degrade organic pollutants and microbes, delaying or eliminating the formation of gel layer on the surface of membranes [18]; SO_4^{2-}/ZrO_2 solid superacid particle is a sort of typical oxide with 10,000 times Hammett acidity of 100% pure H_2SO_4 [19,20], which can decompose inorganic pollutants such as metal oxides or restrain their formation inside channels and surface of membranes. The strategy with MRLs will further enhance the anti-fouling capability of membranes.

Therefore, in this paper, to enhance the anti-fouling, anti-compaction and hydrophilic properties of PVDF membranes, TiO_2 photocatalytic particles and SO_4^{2-}/ZrO_2 solid superacid were firstly integrated to fabricate ZrO_2 solid superacid porous shell/void/TiO_2 core particles (ZVT) Then ZVT were doped into PVDF to prepare ZVT/PVDF composite membranes through a phase inversion process, making ZVT/PVDF composite membranes have a lot of MRLs inside channels and surface of membranes. Therefore, when treating sewage using ZVT/PVDF composite membranes, ZVT/PVDF composite membranes perform good anti-fouling, anti-compaction and hydrophilic properties, which are desirable for sewage treatment.

2. Experimental

2.1. Materials

PVDF (1015) was obtained from Solvay Co., Ltd (USA) and its density was 1.78 g/cm^3. Tetraethyl orthosilicate (TEOS) was provided by Tianjin Jiangtian Chemical Technology Co., Ltd. Zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$) and cetyltrimethylammonium bromide (CTAB) were offered by Tianjin Guangfu Fine Chemical Institute, Anhydrous ethanol and aqueous ammonia were bought from Tianjin Guangfu Science and Technology Development Co., Ltd. Sodium hydroxide was supplied by Tianjin North Glass Procurement Center. Polyvinylpyrrolidone (PVP-K30) and N,N-dimethyl acetamide (DMAC) were obtained from Tianjin Tiantai Fine Chemicals Co., Ltd and Tianjin Damao Service of Chemical Instruments, respectively. All reagents and chemicals were used as received.

2.2. Synthesis of ZVT

ZVT with the diameter of around 500 nm were prepared in our laboratory. The synthesis approach is schematically showed in Fig. 1. The preparation process of TiO_2 particles is similar to literature [21], and the other detailed procedures are as follows:

TiO_2 particles were transferred into deionized water after predispersed in anhydrous ethanol, and then ultrasound was conducted for 30 min. TEOS was added dropwise into the mixture whose pH had been adjusted to 9–10 with aqueous ammonia

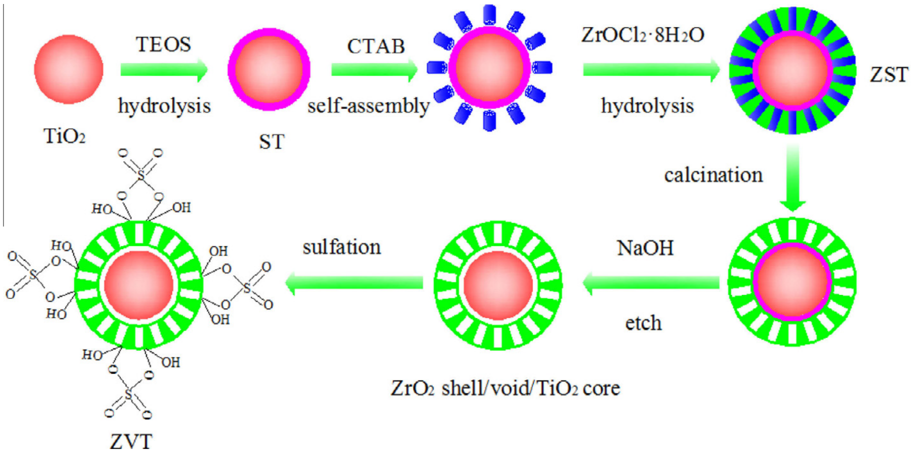

Fig. 1. Scheme of synthesis process of ZVT.