Characteristics and Preparation of PVDF Catalytic Membrane Modified by Nano-TiO$_2$/Fe$^{3+}$

Xi Lijun$^1$, Zhang Li$^1$, Li Li$^1$, Chi Jingyuan$^1$, Lu Junchi$^1$, Tian Ye$^1$ and Zhang Yingjie$^{*,1,2}$

$^1$School of Chemical Engineering, Northeast Dianli University, P. O. Box 81, JiLin 132012, PR, China
$^2$National Engineering Research Center of Urban Water Resources, State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, P.O. Box 2627, Harbin 150090, PR, China

**Abstract:** The polyvinylidene fluoride (PVDF)/Fe$^{3+}$-TiO$_2$ catalytic membrane was prepared by sol-gel method. It was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), FT-IR spectrum (FT-IR), mechanics capability, water flux, pepsin retention, porosity and contact angle etc. The catalytic activity of PVDF/Fe$^{3+}$-TiO$_2$ catalytic membrane was evaluated by the degradation of refractory dye Orange IV in the presence of H$_2$O$_2$. The results show that the addition of appropriate nano-sized TiO$_2$ sol in the preparation of PVDF membrane has greatly improved some properties of the membrane such as microstructure, hydrophilic ability, mechanics intensity and water flux etc. The addition of Fe$^{3+}$ ion in the preparation of PVDF membrane has greatly improved its catalytic activity to decompose H$_2$O$_2$. The catalytic activity of PVDF/Fe$^{3+}$-TiO$_2$ is increased with the increase of the content of Fe$^{3+}$ ion. When the content of Fe$^{3+}$-TiO$_2$ sol is 21%, the content of Fe$^{3+}$ ion is from 0.02% to 0.12%, the discolorization rate of Orange IV in this Fenton-like oxidation is from 61.2% to 90.5%. The catalytic activity of PVDF/Fe$^{3+}$-TiO$_2$ is not changed with the increase of the content of nano-sized TiO$_2$. This kind of PVDF/Fe$^{3+}$-TiO$_2$ catalytic membrane has not only good filtration efficiency but also good catalytic activity to effectively decompose H$_2$O$_2$.

**Keywords:** Modified PVDF membrane, catalytic oxidation, Fenton-like, TiO$_2$, hydroxyl radical.

1. INTRODUCTION

The polyvinylidene fluoride (PVDF) membrane for its non-toxic, chemical stability, has been widely used in the field of water separation processes as ultra filtration membrane [1]. Some studies of PVDF ultra filtration membrane are mainly focused on improving its hydrophilic properties [2-4], anti-pollution [5] and magnetic properties [6], but the modified PVDF membrane to catalyze H$_2$O$_2$ as Fenton agent has not been reported till now.

The modified PVDF membrane prepared by sol-gel method is a kind of organic-inorganic hybrid membrane. There have been some literatures to report the modified PVDF membrane prepared by the addition of ZrO$_2$, A1$_2$O$_3$ and TiO$_2$ nanoparticles [7-10]. Nano-sized TiO$_2$ can effectively improve surface polarity of PVDF membrane [11]. Madaeni and Ghaemi [12] have reported that the RO membranes coated with TiO$_2$ particles have the self-cleaning property under UV irradiation. The photo-catalytic properties of TiO$_2$/PVDF membrane could be improved through the doping of Fe$^{3+}$ ion, which introduced defects grid position or changed the crystalline structure in nanometer TiO$_2$, and thereby reduced the recombination of electron and optical cavities [13-16]. The modified PVDF membrane by the addition of Fe$^{3+}$-TiO$_2$ as Fenton agent has not been reported till now. The main objective of present study is to investigate the preparation and characterization of PVDF/Fe$^{3+}$-TiO$_2$ catalytic membrane and investigated its catalytic activity to decompose H$_2$O$_2$.

2. EXPERIMENT

2.1. Materials and Reagents

PVDF powder (Chenguang Chemical Engineering Institute), butyl titanate, DMAc, EtOH, glacial acetic acid, Fe(NO$_3$)$_3$·9H$_2$O, 30% H$_2$O$_2$, Orange IV, pepsin and other chemicals were of analytical grade and used without further purification. The pH of the solution was adjusted by a diluted aqueous solution of NaOH or HNO$_3$.

2.2. Preparation of PVDF/Fe$^{3+}$-TiO$_2$ Catalytic Membrane

First, it is to mix 22.0 mL of tetrabutyl titanate, 22.0 mL of anhydrous ethanol and 12.0 mL of glacial acetic acid to get the solution A. The solution B is to mix 10 mL of a definite concentration Fe(NO$_3$)$_3$ solution and 10.0 mL EtOH. The pH of solution A and B is 3.0 adjusted by HNO$_3$. Then, the TiO$_2$ sol doped with Fe$^{3+}$ ion in the preparation of PVDF membrane was greatly improved its catalytic activity to decompose H$_2$O$_2$. The catalytic activity of PVDF/Fe$^{3+}$-TiO$_2$ is increased with the increase of the content of Fe$^{3+}$ ion. When the content of Fe$^{3+}$-TiO$_2$ sol is 21%, the content of Fe$^{3+}$ ion is from 0.02% to 0.12%, the discolorization rate of Orange IV in this Fenton-like oxidation is from 61.2% to 90.5%. The catalytic activity of PVDF/Fe$^{3+}$-TiO$_2$ is not changed with the increase of the content of nano-sized TiO$_2$. This kind of PVDF/Fe$^{3+}$-TiO$_2$ catalytic membrane has not only good filtration efficiency but also good catalytic activity to effectively decompose H$_2$O$_2$.

2.3. Membrane Testing and Characterization

The catalytic activity of PVDF/Fe$^{3+}$-TiO$_2$ membrane to catalyze H$_2$O$_2$ was evaluated by the degradation of Orange...
IV and the decomposition of H$_2$O$_2$. The concentration of Orange IV was analyzed with Unico Double Beam UV-4802 UV/Vis spectrophotometer at 440 nm. Hydrogen peroxide (H$_2$O$_2$) was analyzed by titanium oxalate spectrophotometry [17]. The static experiments were conducted in a thermostated shaker at 25 °C. Each experiment was repeated for two times and an average value was calculated. The pH value was monitored by a pHs-3C pH meter.

The water flux was measured on Shanghai Mosu ultra filtration cup system. The contact angle measurement was measured on SL 2008 apparatus. The membrane morphology was measured on HITACHI S-520 scanning electron microscope (SEM). The composition of catalytic membrane was measured on Rigaku X-ray diffraction.

3. RESULTS AND DISCUSSION

3.1 Membrane Catalytic Activity

3.1.1. Effect of Mass Ratio of Fe$^{3+}$/TiO$_2$ on the Catalytic Activity of Membrane

When the mass concentration of Fe$^{3+}$-TiO$_2$ sol in the casting solution is 21%, the effect of mass ratio of Fe$^{3+}$/TiO$_2$ on the decomposition of H$_2$O$_2$ was investigated, the results are shown in Fig. (1). The effect of mass ratio of Fe$^{3+}$/TiO$_2$ on the discolorization of Orange IV is shown in Fig. (2). It can be seen that the decomposition rate of H$_2$O$_2$ increased with the increase of mass ratio of Fe$^{3+}$/TiO$_2$ from 1:65 to 1:9 in Fe$^{3+}$-TiO$_2$ sol, but the decomposition rate of H$_2$O$_2$ decreased with the increase of mass ratio of Fe$^{3+}$/TiO$_2$ from 1:9 to 1:6, indicating that the optimum mass ratio of Fe$^{3+}$/TiO$_2$ from 1:9 in Fe$^{3+}$-TiO$_2$ sol.

As can be seen from Fig. (2), the discolorization rate of Orange IV increased from 61.2% to 90.5% with the increase of mass ratio of Fe$^{3+}$/TiO$_2$ from 1:65 to 1:9 in Fe$^{3+}$-TiO$_2$ sol, which is corresponding to the Fig. (1). The discolorization rate of Orange IV changed a little for the cases of mass ratio of Fe$^{3+}$/TiO$_2$ from 1:9 to 1:6. This suggested that the catalytic activity of PVDVF/Fe$^{3+}$-TiO$_2$ membrane is mainly depended on the Fe$^{3+}$ content in the casting solution. The more concentration of Fe$^{3+}$ content, the more catalytic activity of PVDVF/Fe$^{3+}$-TiO$_2$ is under a definite concentration range of Fe$^{3+}$.

3.1.2. Effect of Concentration of Fe$^{3+}$-TiO$_2$ Sol on the Catalytic Activity of Membrane

When the mass ratio of Fe$^{3+}$/TiO$_2$ is 1:9 in Fe$^{3+}$-TiO$_2$ sol, the effect of concentration of Fe$^{3+}$-TiO$_2$ sol in casting solution on the decomposition of H$_2$O$_2$ was investigated, the results are shown in Fig. (3). The effect of concentration of Fe$^{3+}$-TiO$_2$ in casting solution on the discolorization of Orange IV is shown in Fig. (4). It can be seen that the decomposition rate of H$_2$O$_2$ increased with the increase of concentration of Fe$^{3+}$-TiO$_2$ from 4% to 27% in casting solution, but the decomposition rate of H$_2$O$_2$ changed a little with the increase of concentration of Fe$^{3+}$-TiO$_2$ from 21% to 27%, indicating that the optimum concentration of Fe$^{3+}$-TiO$_2$ sol in casting solution is 21% in casting solution.
Fig. (4). Effect of different concentration sol on the degradation of Orange IV. Operational initial conditions: [Orange IV]=0.4 mM 50 mL; [H₂O₂]=15 mM; pH=4.3; Temperature= 20 °C. (a) 4%; (b) 12%; (c) 19%; (d) 21%;(e) 27%.

As can be seen from Fig. (4), the discolorization rate of Orange IV increased with the increase of concentration of Fe³⁺_TiO₂ sol, which is corresponding to the Fig. (3). However, the discolorization rate of Orange IV decreased with the increase of concentration of Fe³⁺_TiO₂ sol from 21% to 27%, indicating that the optimum concentration of Fe³⁺_TiO₂ sol is 21% in casting solution. Another experiment showed that the catalytic activity of PVDF/Fe³⁺-TiO₂ is not changed with the increase of the content of nano-sized TiO₂. So the catalytic activity of PVDF/Fe³⁺-TiO₂ is mainly depended on the concentration of Fe³⁺ ion rather than the concentration of TiO₂.

3.2. Characteristics of PVDF/Fe³⁺-TiO₂ Membrane

3.2.1. XRD Measurement

The XRD spectrums of PVDF/Fe³⁺-TiO₂ catalytic membrane, pure PVDF membrane and nano-sized TiO₂/Fe³⁺ are shown in Fig. (5). The diffraction peaks in pure PVDF membrane are in 2θ of 20.5°, 36.5° and 40.8°. The diffraction peaks in nano-sized TiO₂/Fe³⁺ are in 2θ of 25.1°, 38.0°, 48.2° and 55.0°. The diffraction peaks in PVDF/Fe³⁺-TiO₂ catalytic membrane are composed of the diffraction peaks of TiO₂/Fe³⁺ and pure PVDF membrane. This showed that there were nano-sized TiO₂ crystals formed in the preparation of PVDF/Fe³⁺-TiO₂ catalytic membrane.

3.2.2. SEM Measurement

The morphology of cross section of PVDF/Fe³⁺-TiO₂ membrane with different concentration of Fe³⁺_TiO₂ sol was measured on the SEM, the results are shown in Fig. (6). It can be seen that the asymmetric property of membrane decreased with the increase of concentration of Fe³⁺_TiO₂ sol in casting solution, the cortical layer of membrane thickened, the finger hole in the membrane decreased, and the mesh hole increased. This showed that the addition of Fe³⁺_TiO₂ sol made the phase inversion speed rate slow to depress the formation of finger hole and to increase the formation of mesh hole in membrane. This will benefit to enhance and improve the service performance of PVDF/Fe³⁺-TiO₂ membrane.

Fig. (5). XRD spectrum of PVDF/Fe³⁺-TiO₂ catalytic membrane, pure PVDF membrane and TiO₂ doped Fe³⁺. (a) Fe³⁺/TiO₂; (b) PVDF/Fe³⁺-TiO₂ catalytic membrane; (c) pure PVDF membrane.

3.2.3. Water Flux, Pepsin Retention and Contact Angle of PVDF/Fe³⁺-TiO₂ Membrane

The water flux, the intercept of pepsin and the contact angle of PVDF/Fe³⁺-TiO₂ catalytic membrane are shown in Tables 1 and 2.
Fig. (6). SEM micrographs of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} membrane with different concentration of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol. (a) 0%; (b) 4%; (c) 21%.

It can be seen that the water flux of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} catalytic membrane increased with the increase of the concentration of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol from 0 to 15% and from 19% to 27%, the maximum water flux is 955.23 L/(m\textsuperscript{2}·h) at the concentration of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol 15%. Losito et al. [18] thought that the Fe\textsuperscript{3+}-TiO\textsubscript{2} sol contained a large number of hydroxyl radicals to improve the surface polarity, thus to increase the water flux of membrane. Kim et al. [19] thought that a definite amount of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol was a kind of heterogeneous deposition agent to transfer the finger hole to the mesh hole, thus to decrease the water flux of membrane.

In addition, the addition of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol made the pepsin retention of the membrane changed. Ren et al. [20] considered that the reunion and disperse of in the membrane formed finger hole and mesh hole respectively, thus to lead to the difference of pepsin retention of the membrane.

The contact angle of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} catalytic membrane decreased with the increase of the concentration of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol in casting membrane solution, which is due to the hydrophilicity of membrane improved by the introduction of a certain amount of hydroxyl radical [21]. But the decrease of contact angle was not significant because of the incomplete crystallization of nano-sized TiO\textsubscript{2}/Fe\textsuperscript{3+} and the existence of various kinds of defects in crystal.

From Table 2, when the mass ratio of Fe\textsuperscript{3+}/TiO\textsubscript{2} is 1:9, the performance of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} catalytic membrane is the best.

4. CONCLUSIONS

A TiO\textsubscript{2} sol doped with Fe\textsuperscript{3+} in the dispersion was prepared by using sol - gel in situ mixing method. The Fe\textsuperscript{3+}-TiO\textsubscript{2} sol was added into the PVDF casting solution with various contents and different Fe\textsuperscript{3+}/TiO\textsubscript{2} proportions. Thus, a series of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} catalytic membrane are obtained by phase inversion technology. There is a notable improvement in the microstructure and the ultra filtration properties of (PVDF)/Fe\textsuperscript{3+}-TiO\textsubscript{2} catalytic membrane compared with the PVDF membrane. The results of XRD and SEM measurements showed that the nano-sized Fe\textsuperscript{3+}/TiO\textsubscript{2} particles in the PVDF membrane would depress the formation of finger holes, and would benefit to form mesh holes to certain extents. Furthermore, the hydrophilicity of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} also has notable improvement. With the increase of Fe\textsuperscript{3+} TiO\textsubscript{2} sol contents and the increase of Fe\textsuperscript{3+} content in the Fe\textsuperscript{3+}-TiO\textsubscript{2} sol, the

<table>
<thead>
<tr>
<th>Mass Ratio of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol</th>
<th>Water Flux (L/m\textsuperscript{2}·h)</th>
<th>Pepsin Retention %</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>207.82</td>
<td>69.65</td>
<td>77.4</td>
</tr>
<tr>
<td>4%</td>
<td>310.77</td>
<td>75.86</td>
<td>75.6</td>
</tr>
<tr>
<td>8%</td>
<td>579.95</td>
<td>77.24</td>
<td>74.8</td>
</tr>
<tr>
<td>15%</td>
<td>955.23</td>
<td>58.62</td>
<td>72.6</td>
</tr>
<tr>
<td>19%</td>
<td>459.41</td>
<td>73.10</td>
<td>70.9</td>
</tr>
<tr>
<td>21%</td>
<td>521.32</td>
<td>82.07</td>
<td>68.5</td>
</tr>
<tr>
<td>27%</td>
<td>853.64</td>
<td>37.93</td>
<td>68.1</td>
</tr>
</tbody>
</table>

Table 1. The Water Flux, Pepsin Retention and Contact Angle of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} Catalytic Membrane of Different Mass Ratio of Fe\textsuperscript{3+}-TiO\textsubscript{2} sol

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water Flux (L/m\textsuperscript{2}·h)</th>
<th>Pepsin Retention %</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure PVDF</td>
<td>207.82</td>
<td>69.65</td>
<td>77.4</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+}:TiO\textsubscript{2}=1:65</td>
<td>151.36</td>
<td>64.83</td>
<td>73.8</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+}:TiO\textsubscript{2}=1:9</td>
<td>521.32</td>
<td>82.07</td>
<td>68.5</td>
</tr>
</tbody>
</table>

Table 2. The Water Flux, Pepsin Retention and Contact Angle of PVDF/Fe\textsuperscript{3+}-TiO\textsubscript{2} Catalytic Membrane of Different Mass Ratio of the Fe\textsuperscript{3+}/TiO\textsubscript{2} in Fe\textsuperscript{3+}-TiO\textsubscript{2} sol
catalytic activity of the membrane increased for the decolorization rate of Orange IV from 51.6% to 90.5%.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

This work is supported by the National Natural Science Foundation of China (No.50978067), the 11th five-year specific events of water (2008ZX07421-002, 2009ZX07424-005, 2009ZX07424-006) and the Science and Technology Development Program of Jilin Province (20116022).

REFERENCES