

Characteristics and Preparation of PVDF Catalytic Membrane Modified by Nano-TiO₂/Fe³⁺

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Abstract: The polyvinylidene fluoride (PVDF)/Fe³⁺-TiO₂ 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/Fe³⁺-TiO₂ catalytic membrane was evaluated by the degradation of refractory dye Orange IV in the presence of H₂O₂. The results show that the addition of appropriate nano-sized TiO₂ 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 Fe³⁺ ion in the preparation of PVDF membrane has greatly improved its catalytic activity to decompose H₂O₂. The catalytic activity of PVDF/Fe³⁺-TiO₂ is increased with the increase of the content of Fe³⁺ ion. When the content of Fe³⁺-TiO₂ sol is 21%, the content of Fe³⁺ 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/Fe³⁺-TiO₂ is not changed with the increase of the content of nano-sized TiO₂. This kind of PVDF/Fe³⁺-TiO₂ catalytic membrane has not only good filtration efficiency but also good catalytic activity to effectively decompose H₂O₂.

Keywords: Modified PVDF membrane, catalytic oxidation, Fenton-like, TiO₂, 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 H₂O₂ 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 ZrO₂, Al₂O₃ and TiO₂ nanoparticles [7-10]. Nano-sized TiO₂ can effectively improve surface polarity of PVDF membrane [11]. Madaeni and Ghaemi [12] have reported that the RO membranes coated with TiO₂ particles have the self-cleaning property under UV irradiation. The photo-catalytic properties of TiO₂/PVDF membrane could be improved through the doping of Fe³⁺ ion, which introduced defects grid position or changed the crystalline structure in nanometer TiO₂, and thereby reduced the recombination of electron and optical cavities [13-16]. The modified PVDF membrane by the addition of Fe³⁺-TiO₂ as Fenton agent has not been reported

till now. The main objective of present study is to investigate the preparation and characterization of PVDF/Fe³⁺-TiO₂ catalytic membrane and investigated its catalytic activity to decompose H₂O₂.

2. EXPERIMENT

2.1. Materials and Reagents

PVDF powder (Chenguang Chemical Engineering Institute), butyl titanate, DMAc, EtOH, glacial acetic acid, Fe(NO₃)₃·9H₂O, 30% H₂O₂, 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 HNO₃.

2.2. Preparation of PVDF/Fe³⁺-TiO₂ 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(NO₃)₃ solution and 10.0mL Ethanol. The pH of solution A and B is 3.0 adjusted by HNO₃. The TiO₂ sol doped with Fe³⁺ is prepared by adding the solution B into solution A at the speed of 1 drop/s in stir.

The casting membrane solution is composed of PVDF, DMAc and a definite mass of TiO₂ sol with mass ratio of PVDF: DMAc=14: 84. It was stirred for a period of time, and then deaerated to film.

2.3. Membrane Testing and Characterization

The catalytic activity of PVDF/Fe³⁺-TiO₂ membrane to catalyze H₂O₂ was evaluated by the degradation of Orange

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IV and the decomposition of H_2O_2 . The concentration of Orange IV was analyzed with Unico Double Beam UV-4802 UV/Vis spectrophotometer at 440 nm. Hydrogen peroxide (H_2O_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 $\text{Fe}^{3+}/\text{TiO}_2$ on the Catalytic Activity of Membrane

When the mass concentration of $\text{Fe}^{3+}\text{-TiO}_2$ sol in the casting solution is 21%, the effect of mass ratio of $\text{Fe}^{3+}/\text{TiO}_2$ on the decomposition of H_2O_2 was investigated, the results are shown in Fig. (1). The effect of mass ratio of $\text{Fe}^{3+}/\text{TiO}_2$ on the discolorization of Orange IV is shown in Fig. (2). It can be seen that the decomposition rate of H_2O_2 increased with the increase of mass ratio of $\text{Fe}^{3+}/\text{TiO}_2$ from 1:65 to 1:9 in $\text{Fe}^{3+}\text{-TiO}_2$ sol, but the decomposition rate of H_2O_2 decreased with the increase of mass ratio of $\text{Fe}^{3+}/\text{TiO}_2$ from 1:9 to 1:6, indicating that the optimum mass ratio of $\text{Fe}^{3+}/\text{TiO}_2$ is 1:9 in $\text{Fe}^{3+}\text{-TiO}_2$ sol.

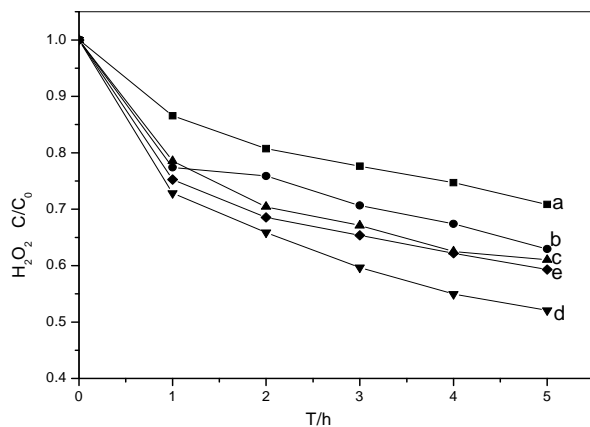


Fig. (1). Effect of different $\text{Fe}^{3+}/\text{TiO}_2$ ratio on the decomposition of H_2O_2 . Operational initial conditions: [Orange IV]=0.4 mM 50 mL; [H_2O_2]=15 mM; pH=4.5; Temperature= 20°C. (a) $\text{Fe}^{3+}:\text{TiO}_2=1:65$; (b) $\text{Fe}^{3+}:\text{TiO}_2=1:22$; (c) $\text{Fe}^{3+}:\text{TiO}_2=1:13$; (d) $\text{Fe}^{3+}:\text{TiO}_2=1:9$; (e) $\text{Fe}^{3+}:\text{TiO}_2=1:6$.

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 $\text{Fe}^{3+}/\text{TiO}_2$ from 1:65 to 1:9 in $\text{Fe}^{3+}\text{-TiO}_2$ sol, which is corresponding to the Fig. (1). The discolorization rate of Orange IV changed a little for the cases of mass ratio of $\text{Fe}^{3+}/\text{TiO}_2$ from 1:9 to 1:6. This suggested that the catalytic activity of PVDF/ $\text{Fe}^{3+}\text{-TiO}_2$ 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 PVDF/ $\text{Fe}^{3+}\text{-TiO}_2$ is under a definite concentration range of Fe^{3+} .

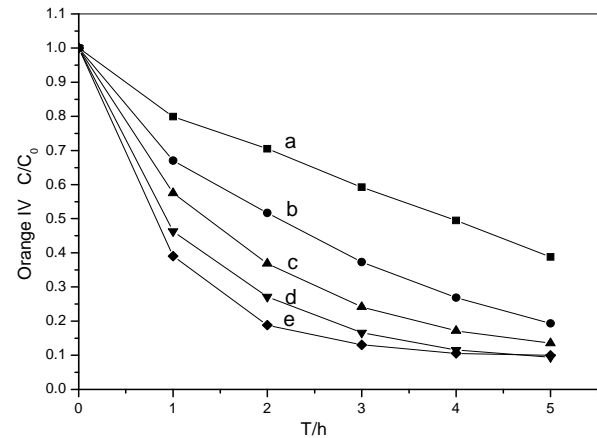


Fig. (2). Effect of different $\text{Fe}^{3+}/\text{TiO}_2$ ratio on the removal of Orange IV. Operational initial conditions: [Orange IV]=0.4 mM 50 mL; [H_2O_2]=15 mM; pH=4.5; Temperature= 20°C. (a) $\text{Fe}^{3+}:\text{TiO}_2=1:65$; (b) $\text{Fe}^{3+}:\text{TiO}_2=1:22$; (c) $\text{Fe}^{3+}:\text{TiO}_2=1:13$; (d) $\text{Fe}^{3+}:\text{TiO}_2=1:9$; (e) $\text{Fe}^{3+}:\text{TiO}_2=1:6$.

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

When the mass ratio of $\text{Fe}^{3+}/\text{TiO}_2$ is 1:9 in $\text{Fe}^{3+}\text{-TiO}_2$ sol, the effect of concentration of $\text{Fe}^{3+}\text{-TiO}_2$ sol in casting solution on the decomposition of H_2O_2 was investigated, the results are shown in Fig. (3). The effect of concentration of $\text{Fe}^{3+}\text{-TiO}_2$ in casting solution on the discolorization of Orange IV is shown in Fig. (4). It can be seen that the decomposition rate of H_2O_2 increased with the increase of concentration of $\text{Fe}^{3+}\text{-TiO}_2$ sol from 4% to 27% in casting solution, but the decomposition rate of H_2O_2 changed a little with the increase of concentration of $\text{Fe}^{3+}\text{-TiO}_2$ sol from 21% to 27%, indicating that the optimum concentration of $\text{Fe}^{3+}\text{-TiO}_2$ sol in casting solution is 21% in casting solution.

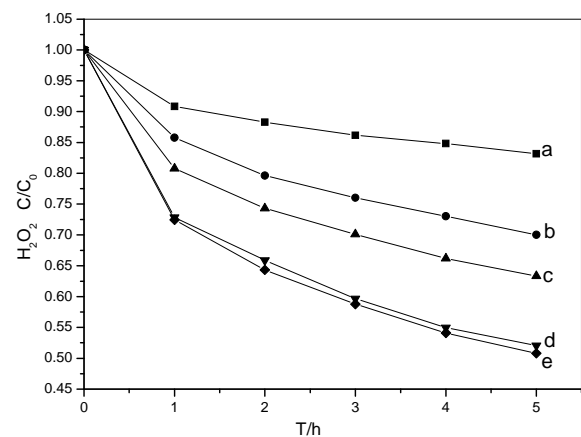


Fig. (3). Effect of different concentration sol on the decomposition of H_2O_2 . Operational initial conditions: [Orange IV]=0.4 mM 50 mL; [H_2O_2]=15 mM; pH=4.3; Temperature= 20°C. (a) 4%; (b) 12%; (c) 19%; (d) 21%; (e) 27%.

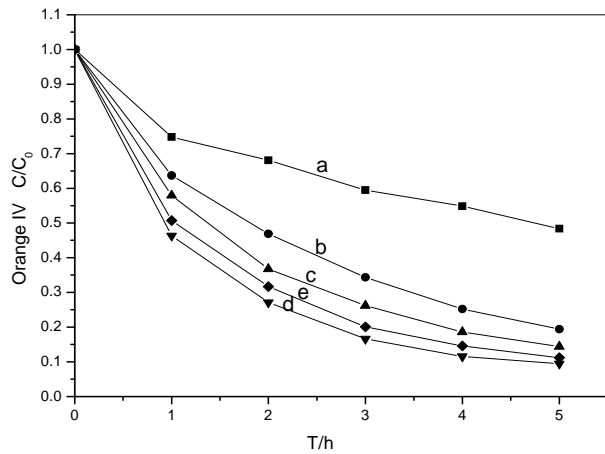


Fig. (4). Effect of different concentration sol on the degradation of Orange IV. Operational initial conditions: [Orange IV]=0.4 mM 50 mL; [H₂O₂]=15 mM; pH=4.3; Temperature= 20°C. (a) 4%; (b) 12%; (c) 19%; (d) 21%;(e) 27%.

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.

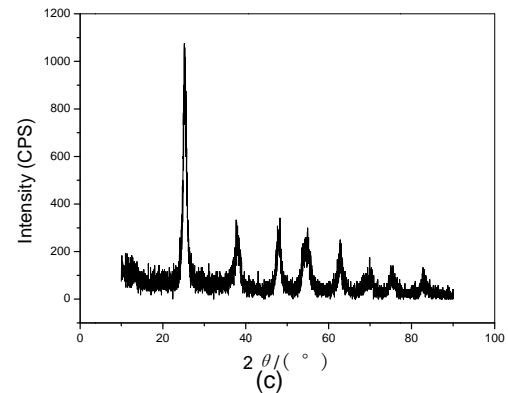
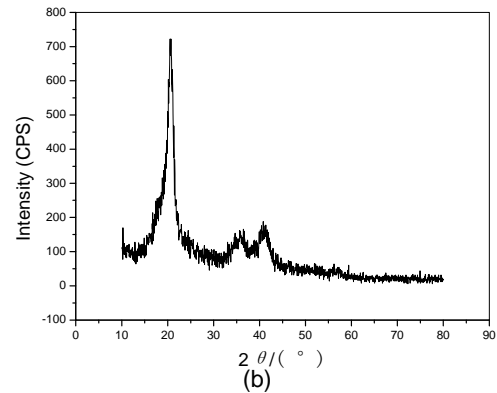
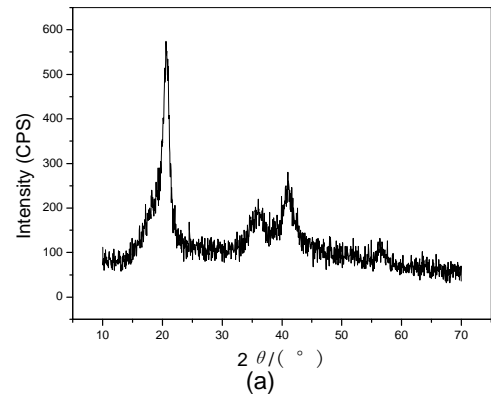


Fig. (5). XRD spectrum of PVDF/Fe³⁺-TiO₂ catalytic membrane, pure PVDF membrane and TiO₂ doped Fe³⁺. (a) Fe³⁺/TiO₂; (b) PVDF/Fe³⁺-TiO₂ catalytic membrane; (c) pure PVDF membrane.

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.

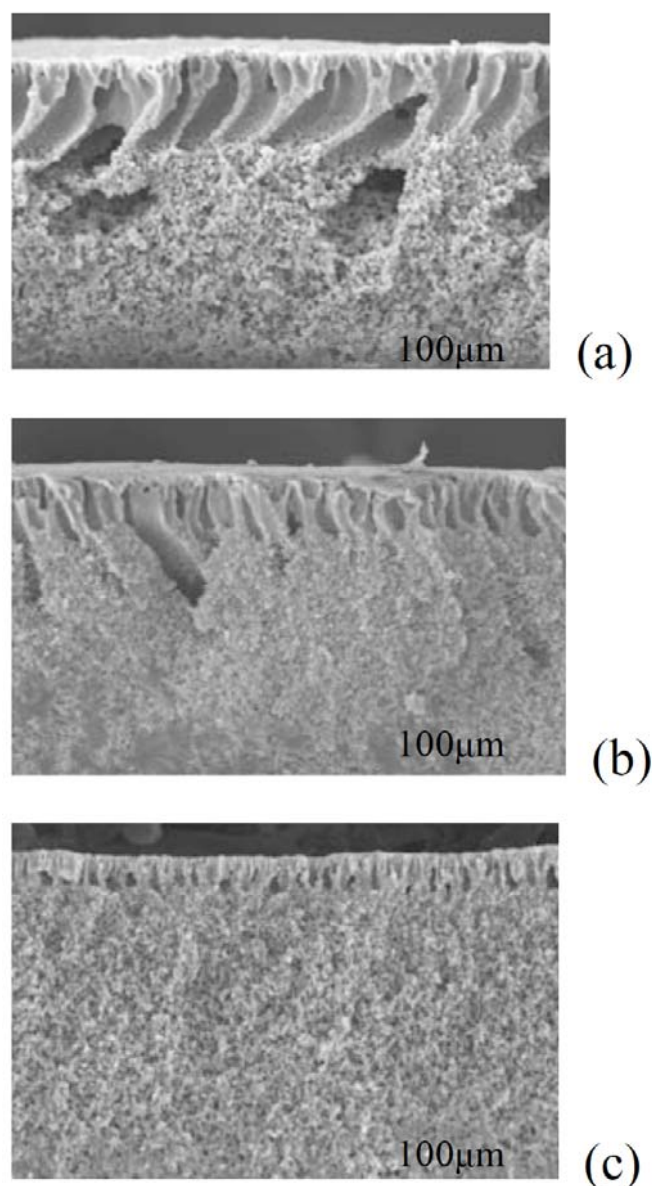


Fig. (6). SEM micrographs of PVDF/Fe³⁺-TiO₂ membrane with different concentration of Fe³⁺-TiO₂ sol. (a) 0%; (b) 4%; (c) 21%.

It can be seen that the water flux of PVDF/Fe³⁺-TiO₂ catalytic membrane increased with the increase of the concentration of Fe³⁺-TiO₂ sol from 0 to 15% and from 19% to 27%, the maximum water flux is 955.23 L/(m²·h) at the concentration of Fe³⁺-TiO₂ sol 15%. Losito *et al.* [18] thought that the Fe³⁺-TiO₂ 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 Fe³⁺-TiO₂ 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 Fe³⁺-TiO₂ 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.

Table 1. The Water Flux, Pepsin Retention and Contact Angle of PVDF/Fe³⁺-TiO₂ Catalytic Membrane of Different Mass Ratio of Fe³⁺-TiO₂ sol

Mass Ratio of Fe ³⁺ -TiO ₂ sol	Water Flux (L·m ⁻² ·h ⁻¹)	Pepsin Retention %	Contact Angle (°)
0%	207.82	69.65	77.4
4%	310.77	75.86	75.6
8%	579.95	77.24	74.8
15%	955.23	58.62	72.6
19%	459.41	73.10	70.9
21%	521.32	82.07	68.5
27%	853.64	37.93	68.1

Table 2. The Water Flux, Pepsin Retention and Contact Angle of PVDF/Fe³⁺-TiO₂ Catalytic Membrane of Different Mass Ratio of the Fe³⁺/TiO₂ in Fe³⁺-TiO₂ sol

Sample	Water Flux (L·m ⁻² ·h ⁻¹)	Pepsin Retention %	Contact Angle (°)
pure PVDF	207.82	69.65	77.4
Fe ³⁺ :TiO ₂ =1:65	151.36	64.83	73.8
Fe ³⁺ :TiO ₂ =1:9	521.32	82.07	68.5

The contact angle of PVDF/Fe³⁺-TiO₂ catalytic membrane decreased with the increase of the concentration of Fe³⁺-TiO₂ 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 TiO₂/Fe³⁺ and the existence of various kinds of defects in crystal.

From Table 2, when the mass ratio of Fe³⁺/TiO₂ is 1:9, the performance of PVDF/Fe³⁺-TiO₂ catalytic membrane is the best.

4. CONCLUSIONS

A TiO₂ sol doped with Fe³⁺ in the dispersion was prepared by using sol - gel in situ mixing method. The Fe³⁺-TiO₂ sol was added into the PVDF casting solution with various contents and different Fe³⁺/TiO₂ proportions. Thus, a series of PVDF/Fe³⁺-TiO₂ catalytic membrane are obtained by phase inversion technology. There is a notable improvement in the microstructure and the ultra filtration properties of (PVDF)/Fe³⁺-TiO₂ catalytic membrane compared with the PVDF membrane. The results of XRD and SEM measurements showed that the nano-sized Fe³⁺/TiO₂ 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/Fe³⁺-TiO₂ also has notable improvement. With the increase of Fe³⁺-TiO₂ sol contents and the increase of Fe³⁺ content in the Fe³⁺-TiO₂ sol, the

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.

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REFERENCES

- [1] Liu Chun T, Jin Z, Hou HG, *et al.* Research progress in PVDF ultra-filtration membranes prepared by phase inversion method and their modifications. *Chem Adhes* 2009; 36(6): 54-7.
- [2] Miao XY, Li JS, Wang LJ, Sun XY. Review on hydrophilic modification of poly (vinylidene fluoride) membranes. *Mater Rev* 2006; 3: 56-9.
- [3] Li X, Lu XF, Shi LQ, *et al.* Surface hydrophilicity of PVDF ultra filtration membrane by simultaneous γ -ray grafting copolymerization. *J Radiat Res Radiat Proc* 2007;2: 65-9.
- [4] Wei LC, Liu Z, Zhou J. Research progress of hydrophilic modification of poly (vinylidene fluoride) separation membranes. *New Chem Mater* 2008; 10: 7-9.
- [5] Xiao J, Zhao X Y, Tan G Z. Effect of SiO₂ nanoparticles on polyvinylidene fluoride (PVDF) ultrafiltration membrane. *Mater Sci Eng* 2008; 2(1): 5-8.
- [6] Li LL. Study on magnetic PSF/CoFe₂O₄ composite ultra filtration membrane. *Membr Sci Technol* 2008; 28(5): 11-15.
- [7] Bottion A, Capannelli G, Comite A. Preparation a characterization of novel porous PVDF-ZrO₂ composite membranes. *Desalination* 2002; 146: 35-40.
- [8] Yan L, Li Y S, Xiang C B. Effect of nano-sized Al₂O₃ particles addition on PVDF ultra-filtration membranes performance. *J Membr Sci* 2006, 276:162-7.
- [9] Cao XC, Ma J, Shi X, *et al.* Effect of TiO₂ nanoparticle size on the performance of PVDF membrane. *Appl Surf Sci* 2006; 253: 2003-10.
- [10] Zhang JQ, Li Q, Fan LJ. Preparation and photocatalytic properties of Fe₂O₃/TiO₂/montmorillonite photocatalyst. *J Henan Norm Univ (Nat Sci)* 2009; 5: 79-82.
- [11] He H Y. Development of Study on TiO₂ Photocatalyst. *Jiangsu Ceram* 2008;41(1): 20-2.
- [12] Madaeni S S, Ghaemi N. Characterization of self-cleaning RO membranes coated with TiO₂ particles under UV irradiation. *J Membr Sci* 2007; 303: 221-33.
- [13] Wang WW, Zhang ZK. The influence of Fe³⁺ on crystalline phase transition of TiO₂. *J Funct Mater* 2003; 4: 429-30.
- [14] Hou L, Liu K, Gao FM. Synthesis of Fe³⁺-doped TiO₂ by Sol- Gel method and its photocatalytic activities. *Bull Chin Ceram Soc* 2005; 3: 46-9.
- [15] Shu BT, Sun JX, Hu CL, *et al.* Preparation and characterization of Fe³⁺-doped TiO₂ photocatalytic fiber materials. *Acta Phys Chim Sin* 2009; 8: 1561-6.
- [16] Yu HM, Ding XY. Preparation and photocatalytic property of iron-doped TiO₂ nanoparticles. *New Chem Mater* 2008; 1: 67-9.
- [17] Zhang YJ, Ma J. Spectrophotometric determination of hydrogen peroxide in acidic dye system with titanate oxalate. *Ind Water Treat* 2008; 28(11): 72-4.
- [18] Losito I, Amorisco A, Palmisano F. X- ray photoelectron spectroscopy characterization of composite TiO₂- poly(vinylidene fluoride) films synthesised for applications in pesticide photocatalytic degradation. *Appl Surf Sci* 2005, 240: 180-8.
- [19] Kim KM, Park NG, Ryu KS. Characteristics of PVDF-HFP/TiO₂ composite membrane electrolytes prepared by phase inversion and conventional casting methods. *Electrochim Acta* 2006;51: 5636-44.
- [20] Ren P, Zhang H, Zhang GF. Study of the crystalline of the melt-spinning fiber of PVDF. *J Tianjin Inst Text Sci Technol* 2003; 22(4): 8-10.
- [21] Diebold AU. The surface science of titanium dioxide. *Surf Sci Rep* 2003; 48:53-229.

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