Real-world diesel vehicle emission factors for China
Highlight articles

203 Mobility of toxic metals in sediments: Assessing methods and controlling factors
Yanbin Li and Yong Cai

206 Genotoxic effects of microcystins mediated by nitric oxide and mitochondria
Qingqing Liu and X. Chris Le

Review articles

61 Remediation effect of compost on soluble mercury transfer in a crop of Phaseolus vulgaris
Nora E. Restrepo-Sánchez, Liliana Acevedo-Betancourth, Beatriz Henao-Murillo and Carlos Peláez-Jaramillo

81 Phosphate removal from domestic wastewater using thermally modified steel slag
Jian Yu, Wenyuan Liang, Li Wang, Feizhen Li, Yuanlong Zou and Haidong Wang

104 New generation Amberlite XAD resin for the removal of metal ions: A review
Akil Ahmad, Jamal Akhter Siddique, Mohammad Asaduddin Laskar, Rajeev Kumar, Siti Hamidah Mohd-Setapar, Asma Khatoon and Rayees Ahmad Shiekh

Regular articles

1 Mobility and sulfidization of heavy metals in sediments of a shallow eutrophic lake, Lake Taihu, China
Shouliang Huo, Jingtian Zhang, Kevin M. Yeager, Beidou Xi, Yanwen Qin, Zhuoshi He and Fengchang Wu

12 Predicting the aquatic risk of realistic pesticide mixtures to species assemblages in Portuguese river basins
Emília Silva, Michiel A. Daam and Maria José Cerejeira

21 Treatment and resource recovery from inorganic fluoride-containing waste produced by the pesticide industry
Yang Li, Hua Zhang, Zhiqi Zhang, Liming Shao and Pinjing He

30 Effects of water regime, crop residues, and application rates on control of Fusarium oxysporum f. sp. cubense
Teng Wen, Xinqi Huang, Jinbo Zhang, Tongbin Zhu, Lei Meng and Zucong Cai

38 Microcystis aeruginosa/Pseudomonas pseudoalcaligenes interaction effects on off-flavors in algae/bacteria co-culture system under different temperatures
Xi Yang, Ping Xie, Yunzhen Yu, Hong Shen, Xuwei Deng, Zhimei Ma, Peili Wang, Min Tao and Yuan Niu

44 Greenhouse gas emission and its potential mitigation process from the waste sector in a large-scale exhibition
Ziyang Lou, Bernd Blitewski, Nanwen Zhu, Xiaoli Chai, Bing Li, Youcai Zhao and Peter Otieno

51 Role of secondary aerosols in haze formation in summer in the Megacity Beijing
Tingting Han, Xingang Liu, Yuanhang Zhang, Yu Qu, Limin Zeng, Min Hu and Tong Zhu

68 Enhanced U(VI) bioreduction by alginate-immobilized uranium-reducing bacteria in the presence of carbon nanotubes and anthraquinone-2,6-disulfonate
Weida Wang, Yali Feng, Xinhua Tang, Haoran Li, Zhuwei Du, Aifei Yi and Xu Zhang

74 NH3-SCR denitrification catalyst performance over vanadium-titanium with the addition of Ce and Sb
Chi Xu, Jian Liu, Zhen Zhao, Fei Yu, Kai Cheng, Yuechang Wei, Aijun Duan and Guiyuan Jiang
CONTENTS

89 Acid-catalyzed heterogeneous reaction of 3-methyl-2-buten-1-ol with hydrogen peroxide
Qifan Liu, Weigang Wang and Maofa Ge

98 IKK inhibition prevents PM$_{2.5}$-exacerbated cardiac injury in mice with type 2 diabetes
Jinzhuo Zhao, Cuiqiu Liu, Yuntao Bai, Tse-yao Wang, Haidong Kan and Qinghua Sun

124 Effects of aeration method and aeration rate on greenhouse gas emissions during composting of pig
feces in pilot scale
Tao Jiang, Guoxue Li, Qiong Tang, Xuguang Ma, Gang Wang and Frank Schuchardt

133 Two-year measurements of surface ozone at Dangxiong, a remote highland site in the Tibetan
Plateau
Weili Lin, Xiaobin Xu, Xiangdong Zheng, Jaxi Dawa, Ciren Baima and Jin Ma

146 Synergistic effects of particulate matter (PM$_{10}$) and SO$_2$ on human non-small cell lung cancer A549
via ROS-mediated NF-$\kappa$B activation
Yang Yun, Rui Gao, Huifeng Yue, Guangke Li, Na Zhu and Nan Sang

154 Adsorption and biodegradation of three selected endocrine disrupting chemicals in river-based
artificial groundwater recharge with reclaimed municipal wastewater
Weifang Ma, Chao Nie, Bin Chen, Xiang Cheng, Xiaoxiu Lun and Fangang Zeng

164 Co-adsorption of gaseous benzene, toluene, ethylbenzene, m-xylene (BTEX) and SO$_2$ on recyclable
Fe$_3$O$_4$ nanoparticles at 0-101% relative humidities
Connie Z. Ye and Parisa A. Ariya

175 Weak magnetic field accelerates chromate removal by zero-valent iron
Pian Feng, Xiaohong Guan, Yuankui Sun, Wonyong Choi, Hejie Qin, Jianmin Wang, Junlian Qiao
and Lina Li

184 Trace metal concentrations in hairs of three bat species from an urbanized area in Germany
Lucie Flache, Sezin Czarnecki, Rolf-Alexander Düring, Uwe Kierdorf and Jorge A. Encarnação

194 Preparation and characterization of Pd/Fe bimetallic nanoparticles immobilized on Al$_2$O$_3$/PVDF
membrane: Parameter optimization and dechlorination of dichloroacetic acid
Lijuan Zhang, Zhaohong Meng and Shuying Zang

209 Development of database of real-world diesel vehicle emission factors for China
Xianbao Shen, Zhiliang Yao, Qiang Zhang, David Vance Wagner, Hong Huo, Yingzhi Zhang, Bo Zheng
and Kebin He

221 Anoxic degradation of nitrogenous heterocyclic compounds by activated sludge and their active sites
Peng Xu, Hongjun Han, Haifeng Zhuang, Baolin Hou, Shengyong Jia, Dexin Wang, Kun Li and
Qian Zhao

226 Adsorption of three pharmaceuticals on two magnetic ion-exchange resins
Miao Jiang, Weiben Yang, Ziwei Zhang, Zhen Yang and Yuping Wang

235 Rapid and simple spectrophotometric determination of persulfate in water by microwave assisted
decolorization of Methylene Blue
Lajuan Zhao, Shiying Yang, Leilei Wang, Chao Shi, Meiqing Huo and Yan Li

240 Effect of water vapor on NH$_3$-NO/NO$_2$ SCR performance of fresh and aged MnO$_x$-NbO$_x$-CeO$_2$
catalysts
Lei Chen, Zhichun Si, Xiaodong Wu, Duan Weng and Zhenwei Wu
Preparation and characterization of Pd/Fe bimetallic nanoparticles immobilized on Al$_2$O$_3$/PVDF membrane: Parameter optimization and dechlorination of dichloroacetic acid

Lijuan Zhang, Zhaohong Meng*, Shuying Zang

Key Laboratory of Remote Sensing Monitoring of Geographic Environment, College of Heilongjiang Province, Harbin Normal University, Harbin 150025, China. E-mail: zlj19650205@163.com

ARTICLE INFO

Article history:
Received 27 July 2014
Revised 4 September 2014
Accepted 5 September 2014
Available online 30 March 2015

Keywords:
PVDF membrane
Nano-sized Al$_2$O$_3$ particles
Pd/Fe nanoparticles
Matrix modified
Dichloroacetic acid

ABSTRACT

Using a liquid-solid phase inversion method, a hybrid matrix poly(vinylidene fluoride) (PVDF) membrane was prepared with alumina (Al$_2$O$_3$) nanoparticle addition. Pd/Fe nanoparticles (NPs) were successfully immobilized on the Al$_2$O$_3$/PVDF membrane, which was characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The micrographs showed that the Pd/Fe NPs were dispersed homogeneously. Several important experimental parameters were optimized, including the mechanical properties, contact angle and surface area of Al$_2$O$_3$/PVDF composite membranes with different Al$_2$O$_3$ contents. At the same time, the ferrous ion concentration and the effect of hydrophilization were studied. The results showed that the modified Al$_2$O$_3$/PVDF membrane functioned well as a support. The Al$_2$O$_3$/PVDF membrane with immobilized Pd/Fe NPs exhibited high efficiency in terms of dichloroacetic acid (DCAA) dechlorination. Additionally, a reaction pathway for DCAA dechlorination by Pd/Fe NPs immobilized on the Al$_2$O$_3$/PVDF membrane system was proposed.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Among all organic macromolecular polymer materials, Polyvinylidene difluoride (PVDF) is one of the most valuable materials because of its chemical resistance to acids, alkaline, strong oxidants, and halogens and its thermal stability (Du et al., 2007; Ji et al., 2007; Deshmukh and Li, 1998; Yeow et al., 2005). PVDF has often been used as an ultrafiltration, microfiltration and pervaporation membrane material. Many studies have extensively investigated methods of improving PVDF membrane hydrophilicity and fouling resistance, including surface modification and blending techniques. Surface modification methods include plasma (Kaur et al., 2007; Li et al., 2008), UltraViolet (UV) (Lei et al., 2008; Hua et al., 2008), electron beam surface induced grafting polymerization (Liu et al., 2006, 2007; Zhou et al., 2014), and living surface/controlled radical polymerization (Chen et al., 2006, 2007; Singh et al., 2005; Liu et al., 2006). Blending methods usually involve some amphiphilic copolymers, which require elaborate synthesis through atom transfer radical polymerization (Hester et al., 2002, 2003) or reversible addition-fragmentation chain transfer polymerization (Ying et al., 2004). Besides amphiphilic copolymers, inorganic particles such as TiO$_2$, ZrO$_2$, SiO$_2$, Al$_2$O$_3$, Fe$_3$O$_4$, LiOCl$_4$ and CdS have also been blended in PVDF solutions in fabricating organic-inorganic
hybrid membranes. The presence of finely dispersed inorganic particles in the polymer matrix has proven very useful in the improvement of membrane performance (Wang et al., 2002). Among these inorganic materials, Al₂O₃ particles have received much attention due to their stability, availability, hydrophilicity and suitable mechanical strength. However, most studies of PVDF membrane modification via physical blending with Al₂O₃ have focused on membrane hydrophilicity, permeation flux, morphology, mechanical properties, anti-fouling performance, etc. Few detailed studies have appeared on use of modified Al₂O₃/PVDF membranes as a support in the removal of chlorinated organic contaminants (OCs). Zero-valent iron (ZVI) has been recognized as the most promising and innovative technology for chlorinated organic contaminant dechlorination. But low reactivity and incomplete dechlorination have been the main shortcomings of ZVI. To overcome these shortcomings, researchers have used bimetallic particles, such as Ni/Fe (Meyer and Bhattacharyya, 2007; Wei et al., 2014), Cu/Fe (Fennelly and Roberts, 1998), Pt/Fe (Kim and Carraway, 2000), Ag/Fe (Xu and Zhang, 2000), and Pd/Fe (Xia et al., 2012; Chen et al., 2008), to dechlorinate chlorinated organic contaminants. Furthermore, Ag/Fe (Luo et al., 2011), Ni/Fe (Luo et al., 2012) and Pd/Fe (Huang et al., 2013) were found to enhance the rate of debromination for ZBBPA. In recent years, the use of nanoscale bimetallic particles immobilized on membranes for dechlorination has become a research hot spot, including dechlorination of 2,4-dichlorophenol (2,4-DCP) (Zhao et al., 2014), trichloroacetic acid (TCAA) (Wang et al., 2008), polychlorinated biphenyls (Grittini et al., 1995), chlorophenols (Liu et al., 2001), p-chlorophenol (Su et al., 2011), trichloroethylene (Ma et al., 2012), chlorinated hydrocarbons (Parshetti and Doong, 2012), and 4-chlorophenyl (Wang et al., 2011).

In this study, matrix-modified PVDF membranes have been prepared with different Al₂O₃ content (0%, 1%, 2%, 3%, 4%), which are designated as Al₂O₃/PVDF composite membranes, and the optimum weight ratio of Al₂O₃ micro-particles in the membrane-forming materials was studied. This research aimed to prepare Al₂O₃/PVDF composite membranes as the support to immobilize nanoscale Pd/Fe bimetallic particles to enhance chloroacetic acid dechlorination efficiency through improving the membrane performance. SEM and TEM were used to study the morphology of the Al₂O₃/PVDF membrane and Pd/Fe bimetallic nanoparticles immobilized on the membrane. The Fe loading on the Al₂O₃/PVDF membranes prepared with different crosslinking solutions was investigated. In our research team, the dechlorination of Monochloroacetic acid (MCAA) (Meng et al., 2011), and TCAA (Wang et al., 2008) was previously reported. In order to complete the series of studies on chloroacetic acids (MCAA, Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA)) and contrast the differences in dechlorination, we selected DCAA as the target chemical for dechlorination in the current study. Furthermore, a reaction pathway for DCAA dechlorination by Pd/Fe NPs on Al₂O₃/PVDF membranes was proposed.

### 1. Experimental section

#### 1.1. Materials and chemical reagents

PVDF (FR904) (MW: 600,000) was obtained from Shanghai 3F New Materials Co., Ltd., China. Dimethylacetamide (DMAC, >99%, reagent) was obtained from Ourchem (Sinopharm Chemical Reagent Co., Ltd.). Alumina particles with nanosizes of 10–30 nm were obtained from MaiKaiLun Science and Technology Co., Ltd., China. Sodium hexametaphosphate, polyvinylpyrrolidone (PVP), and a mixture of distilled water and ethanol were used as the non-solvents for the polymer precipitation. Polyacrylic acid (PAA, MW 50,000), acetic acid (analytical reagent), sulfuric acid (analytical reagent), ethylene glycol (EG), ferrous sulfate heptahydrate (FeSO₄·7H₂O), ethanol (analytical reagent), and potassium borohydride (KB₇H₄, 99%) were obtained from Tianjin Chemical Reagents Plant, China. Palladium acetate ([Pd(C₂H₅O₂)₂]₂, 47.4 wt.% Pd) was from Aldrich. DCAA was from Ourchem (Sinopharm chemical Reagent Co., Ltd.). Deionized water was used for the preparation of reagent solutions.

#### 1.2. Membrane preparation

**1.2.1. Preparation of Al₂O₃-modified PVDF membrane**

The Al₂O₃/PVDF membranes were prepared by a phase-inversion method. PVDF was dissolved into DMAC solvent at room temperature, and then nanoscale Al₂O₃ particles used as hydrophilic inorganic matter and sodium hexametaphosphate used as dispersant and PVP used as pore-former were added into the solution at the same time. In order to obtain an optimal dispersion of the particles in the polymer solution, constant stirring for at least 24 hr was necessary. The casting polymer solutions were kept in a dark place for 36 hr to remove air bubbles. An appropriate amount of the casting polymer solution was dispersed uniformly on a glass plate at 25°C and 60% humidity, and exposed in air for 30 sec. Then, it was immersed immediately into a bath which consists of distilled water and ethanol. The procedure of membrane preparation is demonstrated in Scheme 1. It should be mentioned that the weight percentage of Al₂O₃ particles in Al₂O₃/PVDF membranes was varied from 0%–4%. They were labeled as PVDF-0, PVDF-1, PVDF-2, PVDF-3, and PVDF-4, respectively. Modified Al₂O₃/PVDF membranes (60 nm-pore size, 2 cm-side, 200 μm-thickness) were washed with distilled water and also conserved in ethanol till they were used as support.

**1.2.2. Preparation of crosslinked PAA on Al₂O₃/PVDF membrane**

The modified Al₂O₃/PVDF membrane was dipped into the aqueous coating solution composed of PAA solution, EG and FeSO₄·7H₂O. The molar ratios of PAA, EG, and ferrous ion were 1:2:0.5. It was then immersed into 0.5 mol KBH₄ solution for 15 min, and then washed with ethanol. Zero-valent iron NPs immobilized on the Al₂O₃/PVDF membrane were formed in accordance with Eq. (1):

$$\text{Fe}^{2+} + 2\text{BH}^- + 6\text{H}_2\text{O} \rightarrow \text{FeO} + 2\text{B(OH)}_2 + 7\text{H}_2.$$

**1.2.3. Preparation of Pd/Fe NPs immobilized on Al₂O₃/PVDF membrane**

The crosslinked Al₂O₃/PVDF membrane containing ferrous ion was dipped into 0.5 mol KB₇H₄ solution for 15 min, and then washed with ethanol. Zero-valent iron NPs immobilized on the Al₂O₃/PVDF membrane were formed in accordance with Eq. (1):
The Al₂O₃/PVDF membrane containing iron NPs was soaked in 50 mL palladium acetate dissolved in ethanol for 15 min. Pd/Fe NPs immobilized on Al₂O₃/PVDF membranes were prepared by deposition of Pd on the Fe nanoparticle surface in accordance with Eq. (2):

\[
Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+}.
\]

To determine the loss of Pd, a seven-cycle dechlorination reaction experiment was carried out in a 13 mL vial containing 5 mg/L DCAA solution and the same Pd loading of Pd/Fe nanoparticles. The immobilized Pd/Fe nanoparticles were repeatedly used for DCAA dechlorination. Pd/Fe nanoparticles immobilized on modified Al₂O₃/PVDF membranes were characterized by SEM and EDS after 3, 6, 9, 12, 15, 18 and 21 hr of dechlorination. The EDS elemental analysis showed that the Pd loading of freshly prepared Pd/Fe nanoparticles was 0.511% and decreased to 0.508% after seven cycles of dechlorination reaction, which showed that the loss of Pd can be ignored.

The Al₂O₃/PVDF membrane with immobilized Pd/Fe NPs was rinsed with ethanol three times and stored in absolute ethanol for further study of DCAA dechlorination. The flowchart of Pd/Fe NP immobilization on Al₂O₃/PVDF membranes is shown in Scheme 3.

1.2.4. PVDF membrane hydrophilization

PVDF membrane was dipped in deionized water for 72 hr. Then the PVDF membrane was immersed in 5% dilute sulphuric acid and 1% glutaraldehyde solution. Membrane that had been pretreated was put in hydrophilic solution in a constant 50°C aqueous bath for 25 min. The hydrophilic solution was a proportionally mixed solution composed of 2% (W/V) PVA solution, 5% (W/V) glutaraldehyde solution, 40% (W/V) PEG, dilute sulphuric acid, acetic acid, and methanol. The hydrophilized PVDF membrane was dried at 50°C in a drying oven for 45 min and then was immersed in distilled water for 24 h. So, PVDF membrane had been prepared a hydrophilic layer.

1.3. Batch experiments of DCAA dechlorination

The DCAA dechlorination reaction was conducted in 13 mL glass vials. One piece of Al₂O₃/PVDF membrane with immobilized Pd/Fe NPs (each membrane was 4 cm² and embedded with
2.04 mg of Pd/Fe NPs was loaded into each reaction vial. For all experiments, 5 mg/L DCAA solution was added into each vial until no headspace was left. Each vial was sealed with a Teflon-lined rubber septum instantly, and then placed on a rotary shaker at a speed of 170 rpm. At each specific sampling time, 5 mL of aqueous sample was withdrawn from the vial with a gas-tight syringe and diluted with deionized water to 25 mL. The DCAA in each sample was methyl-esterified before being analyzed.

1.4. Analytical methods

The quantity of DCAA was analyzed by using a HP 6890 GC (Agilent Company, Palo Alto, Santa Clara USA) with electron capture detection (ECD) and a HP-5 column (30 m × 0.53 μm × 1.0 μm). Nitrogen was used as carrier gas with a flow rate of 60 mL/min. The samples were injected with a volume of 1.0 μL using an automatic sample injector. The oven temperature program was 5 min at 40°C, 20°C/min to 140°C, 10°C/min to 160°C, 25°C/min to 240°C, and 3 min at 240°C. The injector and detector temperatures were 220°C and 300°C, respectively.

Acetic acid was analyzed using an HP 6890 GC equipped with an Inwax capillary column (30 m, 1.53 mm, 1.0 μm) and an FID. The samples were injected with a volume of 1.0 μL. The temperatures of injector and detector were fixed at 220°C. The oven temperature condition was programmed as follows: initial oven temperature of 90°C with a hold time for 2 min, ramped at a rate of 35°C/min to 170°C with a hold time of 25 min, and increased at a rate of 65°C/min to the final temperature of 230°C. DCAA dechlorination efficiency \( F \) is calculated according to Eq. (3):

\[
F = \left(1 - \frac{C}{C_0}\right) \times 100\% 
\]

(3)

where, \( C \) and \( C_0 \) are the concentrations of DCAA at time \( t \) and initial concentration.

For the analysis of palladium, the concentrations of palladium ion from the \textit{aqua regia} extract of Pd/Fe NPs immobilized on the \( \text{Al}_2\text{O}_3 \)/PVDF membrane were determined using an Optima 5300D inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin-Elmer Instrument Co. Ltd., Norwalk, Conn. USA).

For the analysis of iron, the \( \text{Al}_2\text{O}_3 \)/PVDF membranes with immobilized Pd/Fe NPs were dipped in 50 mL of 0.5 mol/L \( \text{H}_2\text{SO}_4 \) for 1 hr, then the \( \text{H}_2\text{SO}_4 \) solution was diluted by deionized water. The concentration of iron was quantified using a 752 UV-Vis Spectrophotometer at 510 nm.

The surface and cross-sectional morphologies of \( \text{Al}_2\text{O}_3 \)/PVDF membranes and \( \text{Al}_2\text{O}_3 \)/PVDF membranes with immobilized Pd/Fe NPs were examined by a MX2600FE SEM (Camscan Ltd., Electron Optics, Waterbeach, Cambridge U.K.) and a JEOL JEM 200CX transmission electron microscope (TEM) at 100 kV for morphological measurement. The samples were coated with a thin layer of gold before being scanned.

2. Results and discussion

2.1. Influence of \( \text{Al}_2\text{O}_3 \) content on PVDF properties

To determine the influence of \( \text{Al}_2\text{O}_3 \) content on PVDF mechanical properties, \( \text{Al}_2\text{O}_3 \)/PVDF membranes with varying \( \text{Al}_2\text{O}_3 \) content (0%, 1%, 2%, 3%, 4%) were prepared and the mechanical properties were measured. Table 1 shows that the maximum stress, tensile strength and rupture elongation were enhanced with increasing \( \text{Al}_2\text{O}_3 \) addition, but the mechanical properties declined with the increasing \( \text{Al}_2\text{O}_3 \) content when the \( \text{Al}_2\text{O}_3 \) concentration exceeded 2%. The decline in PVDF mechanical properties with increasing \( \text{Al}_2\text{O}_3 \) addition was in accord with previous studies that found increased nanoparticle content would lead to contact between particles in the composite. The current research indicated that \( \text{Al}_2\text{O}_3 \) content of 2% led to the optimum mechanical properties.

2.2. Effect of different \( \text{Al}_2\text{O}_3 \) content on membrane contact angle

The contact angle reflected the membrane surface hydrophilicity. The greater the contact angle, the smaller the PVDF membrane surface hydrophobicity, and a smaller contact angle indicated increased surface hydrophilicity.
Contact angle is related to the material properties, surface morphology, roughness and porosity, and all of these factors are related to how easily Pd/Fe nanoparticles can be immobilized on modified PVDF membrane. The contact angle declined gradually with increasing Al2O3 content (0% (58.4°), 1% (50.6°), 2% (39.5°), 3% (37.8°), 4% (37.1°)), which showed that Al2O3 addition can increase PVDF hydrophilicity. Comparing the results and considering the cost, the optimal Al2O3 content was 2%.

### 2.3. Impact of different Al2O3 content on membrane surface area

In order to have more space to immobilize more Pd/Fe nanoparticles on the Al2O3-modified PVDF membranes, the impact of different Al2O3 content on membrane surface area was measured. The greater the membrane surface area, the greater the membrane surface space and internal space would be, which would provide more space on which to immobilize Pd/Fe nanoparticles. Fig. 1 indicates that the PVDF membrane surface area was maximized when Al2O3 content was 2%, which is optimum Al2O3 content. In the casting solution, as Al2O3 content gradually increased, there was an accumulation of Al2O3 nanoparticles in the membrane surface and interior space, which blocked the tiny pores on the surface of the modified membrane, thus resulting in a decline of surface area.

### 2.4. Optimization of ferrous ion concentration

Table 2 shows that Fe loading (mg/cm²) was augmented with increasing FeSO4·7H2O, but Fe loading barely increased when FeSO4·7H2O exceeded 2.9 wt.%. This showed that the quantity of Fe loading had reached the maximum of about 0.51 mg/cm² on the Al2O3/PVDF membrane. Taking into account the experimental results and economic cost, 2.9 wt.% FeSO4·7H2O, 0.73 wt.% EG and 3.0 wt.% PAA were chosen as the optimal coating solution in subsequent experiments.

### 2.5. Effect of hydrophilization on Al2O3/PVDF composite membrane

The hydrophilization study not only showed matrix-modified PVDF membrane as the support had excellent performance but also verified that the hydrophobic PVDF membrane can been changed into a hydrophilic membrane by adding Al2O3 into the polymer.

Investigation of how hydrophilization impacted the modified Al2O3/PVDF composite membrane (0%, 1%, 2%, 3%, 4%) was composed of hydrophilization and control treatments, in order to determine whether there was

---

**Table 1 – Effect of Al2O3 adding on PVDF mechanical properties.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum stress (MPa)</th>
<th>Tensile strength (N)</th>
<th>Rupture elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-0</td>
<td>0.5793</td>
<td>13.3231</td>
<td>4.83</td>
</tr>
<tr>
<td>PVDF-1</td>
<td>0.7034</td>
<td>17.9869</td>
<td>5.72</td>
</tr>
<tr>
<td>PVDF-2</td>
<td>0.9538</td>
<td>19.3518</td>
<td>7.38</td>
</tr>
<tr>
<td>PVDF-3</td>
<td>0.8957</td>
<td>18.3651</td>
<td>6.94</td>
</tr>
<tr>
<td>PVDF-4</td>
<td>0.8420</td>
<td>18.3518</td>
<td>6.91</td>
</tr>
</tbody>
</table>

PVDF-0, 1, 2, 3, 4 present Al2O3 content of 0%, 1%, 2%, 3%, and 4% in PVDF.

---

**Table 2 – Fe loading by different FeSO4·7H2O amount of coating solution with molar ratios of carboxyl of PAA, EG, and ferrous was 4:1:1.**

<table>
<thead>
<tr>
<th>Crosslinking solution</th>
<th>FeSO4·7H2O (wt.%</th>
<th>EG (wt.%</th>
<th>PAA (wt.%</th>
<th>Fe loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>0.15</td>
<td>0.62</td>
<td>0.080</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>0.30</td>
<td>1.24</td>
<td>0.180</td>
</tr>
<tr>
<td>3</td>
<td>1.8</td>
<td>0.45</td>
<td>1.86</td>
<td>0.210</td>
</tr>
<tr>
<td>4</td>
<td>2.4</td>
<td>0.60</td>
<td>2.48</td>
<td>0.290</td>
</tr>
<tr>
<td>5</td>
<td>2.7</td>
<td>0.68</td>
<td>2.79</td>
<td>0.390</td>
</tr>
<tr>
<td>6</td>
<td>2.8</td>
<td>0.70</td>
<td>2.90</td>
<td>0.481</td>
</tr>
<tr>
<td>7</td>
<td>2.9</td>
<td>0.73</td>
<td>3.00</td>
<td>0.51</td>
</tr>
<tr>
<td>8</td>
<td>3.0</td>
<td>0.75</td>
<td>3.10</td>
<td>0.512</td>
</tr>
<tr>
<td>9</td>
<td>3.3</td>
<td>0.83</td>
<td>3.41</td>
<td>0.515</td>
</tr>
<tr>
<td>10</td>
<td>3.6</td>
<td>0.90</td>
<td>3.72</td>
<td>0.512</td>
</tr>
</tbody>
</table>

PAA: polyacrylic acid; EG: ethylene glycol.

---

![Fig. 1 – BET of different Al2O3 addition.](image1.png)

![Fig. 2 – Fe loading on the Al2O3/PVDF with hydrophilization and unhydrophilization.](image2.png)
a need to carry out additional hydrophilization treatment in subsequent research. The quantity of Fe loaded on the modified Al$_2$O$_3$/PVDF membrane with hydrophilization and control treatments was researched. Fig. 2 indicates that the quantity of Fe loaded on unhydrophilized membranes was more than that on hydrophilized matrix-modified Al$_2$O$_3$/PVDF membranes with varying Al$_2$O$_3$ contents (0%, 1%, 2%, 3%, 4%), which would be due to the enhancement of the hydrophilicity of the PVDF membrane by the matrix modification method. Thus Fe nanoparticles became more easily immobilized on the Al$_2$O$_3$/PVDF membrane. The DCAA dechlorination by Pd/Fe immobilized on the modified Al$_2$O$_3$/PVDF membrane with hydrophilization and control treatments was investigated. Fig. 3 shows that DCAA dechlorination efficiency by Pd/Fe immobilized on the modified Al$_2$O$_3$/PVDF membranes without hydrophilization exceeded that for the Pd/Fe immobilized on hydrophilized Al$_2$O$_3$/PVDF membranes. This study further proved that the matrix modification method was feasible and had better effect than hydrophilization treatment.

2.6. Characterization of Pd/Fe NPs immobilized on the Al$_2$O$_3$/PVDF membrane

The SEM images of Al$_2$O$_3$/PVDF membrane are shown in Fig. 4 and the TEM images in Fig. 5. Fig. 4a shows the Pd/Fe NPs immobilized on the surface of the Al$_2$O$_3$/PVDF membrane; the Pd/Fe NPs appeared to be spherical and smooth, with size was about 50–100 nm. In addition, it can be seen that the surface of the matrix was completely covered by compactly arranged Pd/Fe NPs and that the Pd/Fe NPs were dispersed homogeneously. The cross-sectional morphology of the Pd/Fe NPs immobilized in the Al$_2$O$_3$/PVDF membrane (Fig. 4b) showed that the Pd/Fe NPs can be immobilized in the cross-section. This was because the modified Al$_2$O$_3$/PVDF membrane had a porous microstructure, which provided more space to immobilize Pd/Fe NPs.

On the basis of former research (Xu et al., 2005; Xu and Bhattacharyya, 2005), PAA was speculated to be able to infiltrate and fill the pores of the Al$_2$O$_3$/PVDF membrane so that it could favor increased Fe loading. Therefore, according to both surface and cross-sectional morphologies, it can be concluded that the Pd/Fe NPs were immobilized not only on surface pores but also in interior pores of Al$_2$O$_3$/PVDF membranes. Generally speaking, the Al$_2$O$_3$/PVDF membrane prepared in this study is considered to be a good matrix for immobilizing Pd/Fe NPs.

2.7. Reaction pathway of DCAA dechlorination

Fig. 6 shows that 97.71% of DCAA was dechlorinated within the first 90 min. Along with the removal of DCAA, the rapid appearance of acetic acid provided evidence of direct conversion of DCAA to acetic acid. The previous study demonstrated that degradation of TCAA with Fe$^{0}$ was processed via sequential hydrogenolysis (Zhang et al., 2004). The concentration of MCAA was found to increase along with
DCAA dechlorination. This proved that MCAA produced by the dechlorination of DCAA might be dechlorinated to MCAA or to acetic acid directly. The proposed pathway for dechlorination of DCAA by Pd/Fe–Al2O3/PVDF is illustrated in Fig. 6.

Additional support for the reliability of the removal results for DCAA using the Pd/Fe–Al2O3/PVDF membrane system was provided by a control experiment (Fig. 7). Before the dechlorination experiment, methyl tert-butyl ether (MTBE) was used to leach the dichloroacetic acid adsorbed by Pd/Fe bimetallic nanoparticles immobilized on Al2O3/PVDF membrane, and the results showed that almost all the dichloroacetic acid could be leached in 120 min. Adsorption was considered to be negligible. For the case of a Pd/Fe NPs-free membrane, the determined concentration of dichloroacetic acid over the time scale of the dechlorination experiment showed that almost no adsorption took place between the targeted pollutant and the components of the coating.

### 3. Conclusions

The phase-inversion method was utilized for preparation of Al2O3/PVDF membranes. Pd/Fe NPs were successfully immobilized on modified Al2O3/PVDF membranes and used for DCAA dechlorination.

1. When the Al2O3 content was 2%, the prepared Al2O3/PVDF membrane showed the best features in terms of mechanical properties, contact angle and surface area.
2. Results showed that 2.9% FeSO4·7H2O could result in the largest Fe loading per unit area (0.51 mg/cm²). Matrix-modified Al2O3/PVDF composite membranes did not need hydrophilization processing, which showed that the matrix modification was a good method to immobilize Pd/Fe NPs and had high dechlorination efficiency.
3. SEM and TEM showed that Pd/Fe NPs were not only stably immobilized on the surface of Al2O3/PVDF membranes but also immobilized in the cross-section, and that the distribution of Pd/Fe–Al2O3/PVDF was uniform and even.
4. The Pd/Fe–Al2O3/PVDF membrane system showed high reactivity in catalytic dechlorination of DCAA, and nearly complete dechlorination of DCAA was achieved by Pd/Fe NPs immobilized on the Al2O3/PVDF membrane. In the catalytic dechlorination of DCAA by
concentration of DCAA was 5 mg/L, Pd/Fe NP loading was 
Pd/Fe NPs at different reaction time. Conditions: initial 

with zero-valent metals and bimetallic reductants. Environ. 

dechlorination of polychlorinated biphenyls on the surface of 
a Pd/Fe bimetallic system. Environ. Sci. Technol. 29 (11), 
2898–2900.

Hester, J.F., Mayes, A.M., 2002. Design and performance of 
fool-resistant poly(vinylidene fluoride) membranes prepared 
119–135.

Hester, J.F., Banerjee, P., Won, Y.Y., Akthakul, A., Acar, M.H., 
Mayes, A.M., 2002. ATRP of amphiphilic graft copolymers 
based on PVDF and their use as membrane additives. 
Macromolecules 35 (20), 7652–7661.

2008. Anti-fouling ultrafiltration membrane prepared from 
polysulphone-graft-methyl acrylate copolymers by UV-induced 

Huang, Q., Liu, W., Peng, P.A., Huang, W.L., 2013. Reductive 
debromination of tetrabromobisphenol A by Pd/Fe bimetallic 

PVDF membrane via thermally induced phase separation with 
diluent mixture of DBP and DEHP. J. Appl. Polym. Sci. 105 (5), 
1496–1502.

Kaur, S., Ma, Z.W., Gopal, R., Singh, G., Ramakrishna, S., Matsuura, 
T., 2007. Plasma-induced graft copolymerization of 
poly(methacrylic acid) on electrospun poly(vinylidene 
fluoride) nanofiber membrane. Langmuir 23 (26), 13085–13092.


for the surface modification of poly(vinylidene fluoride) 
membrane via surface-initiated atom transfer radical 

characterization of a novel bipolar membrane by 
plasma-induced polymerization. J. Membr. Sci. 318 (1–2), 
429–434.

dechlorination of chlorophenols in water by palladium/iron. 
Water Res. 35 (8), 1887–1890.

grafting of polymer brushes on poly(vinylidene fluoride) films 
by surface-initiated atom transfer radical polymerization. 

Liu, F., Zhu, B.K., Xu, Y.Y., 2006b. Improving the hydrophilicity of 
poly(vinylidene fluoride) porous membranes by electron beam 
initiated surface grafting of AA/SSS binary monomers. Appl. 

Liu, F., Zhu, B.K., Xu, Y.Y., 2007. Preparation and characterization of 
poly(vinyl chloride)-graft-acrylic acid membrane by electron beam. 

reduction/subsequent oxidation for treating tetrabromobisphenol 

degradation of tetrabromobisphenol using iron-silver and 
iron-nickel bimetallic nanoparticles with microwave energy. 

Enhanced dechlorination of trichloroethylene using 
electrospun polymer nanofibrous mats immobilized with 
211–212, 349–356.

Fig. 7 – DCAA dechlorination efficiency by freshly prepared 
Pd/Fe NPs at different reaction time. Conditions: initial 
concentration of DCAA was 5 mg/L, Pd/Fe NP loading was 
0.157 g/L, Pd content was 0.511 wt.%, rotary shaker at a 
speed of 170 rpm, 2 cm-side 4 cm² membrane.

Pd/Fe–Al₂O₃/PVDF membranes, the rapid production of 
acetic acid suggested the occurrence of parallel 
pathways besides the stepwise reaction.

Acknowledgments

This work was supported by the Nature Science Foundation of 
Heilongjiang Province (No. B201410), the Postdoctoral 
Foundation Project of Heilongjiang Province (No. LH–Z13128), the 
Science and Technology Research Program of Education 
Bureau of Heilongjiang Province (No. 12531206), the Special 
Scientific Research Projects of Harbin Normal University 
(12XQXG02), the National Nature Science Foundation of 
China (No. 41030743), and the National Nature Science 
Foundation of China (No. 42171217).

References

Chen, Y.W., Sun, W., Deng, Q.L., Chen, L., 2006. Controlled grafting 
from poly(vinylidene fluoride) films by surface-initiated 
reversible addition-fragmentation chain transfer 

microfiltration membranes via reverse atom transfer radical 
polymerization and antifouling properties. Polymer 48 (26), 
7604–7613.

disinfection by-product monochloroacetic acid in drinking water 
by nanoscale palladized iron bimetallic particle. J. Environ. Sci. 
20 (8), 945–951.

in water coagulation bath on morphology of PVDF hollow fibre 

characterization of PVDF hollow fiber membranes by 

with zero-valent metals and bimetallic reductants. Environ. 


Editorial Board of Journal of Environmental Sciences

Editor-in-Chief
X. Chris Le
University of Alberta, Canada

Associate Editors-in-Chief
Jiuhui Qu
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Shu Tao
Peking University, China
Nigel Bell
Imperial College London, UK
Po-Keung Wong
The Chinese University of Hong Kong, Hong Kong, China

Editorial Board

Aquatic environment
Baoyu Gao
Shandong University, China
Maohong Fan
University of Wyoming, USA
Chihpin Huang
National Chiao Tung University
Taiwan, China
Ng Wun Jern
Ng Wun Jern Environment 
& Water Research Institute, Singapore
Clark C. K. Liu
University of Hawaii at Manoa, USA
Hokyong Shon
University of Technology, Sydney, Australia
Zijian Wang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhigu Wang
The Ohio State University, USA
Yuxiang Wang
Queen’s University, Canada
Min Yang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhiwu Wang
University of Science & Technology of China, China

Terrestrial environment
Christopher Anderson
Massey University, New Zealand
Zaocong Cai
Nanjing Normal University, China
Xinbin Feng
Institute of Geochemistry,
Chinese Academy of Sciences, China
Hongqing Hu
Huanzhong Agricultural University, China
Kia-Chek Lam
The Chinese University of Hong Kong
Hong Kong, China
Erwin Klumpp
Research Centre Juelich, Agrosphere Institute
Germany

Environmental toxicology and health
Jingwen Chen
Dalian University of Technology, China
Jianying Hu
Peking University, China
Guibin Jiang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Sijin Liu
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Tsuyoshi Nakanshi
Gifu Pharmaceutical University, Japan
Willie Peijnenburg
University of Leiden, The Netherlands
Bingsheng Zhou
Institute of Hydrobiology,
Chinese Academy of Sciences, China

Environmental catalysis and materials
Hong He
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Junhua Li
Tsinghua University, China

Environmental analysis and method
Zongwei Cai
Shanghai Jiao Tong University, China

Environmental biology
Yong Cai
Florida International University, USA
Henner Holland
RWTH Aachen University, Germany
Jae-Seong Lee
Sungkyunkwan University, South Korea
Christopher Rensing
University of Copenhagen, Denmark
Bojan Sedmak
National Institute of Biology, Slovenia
Lirong Song
Institute of Hydrobiology,
Chinese Academy of Sciences, China
Chunxia Wang
National Natural Science Foundation of China

Municipal solid waste and green chemistry
Puning He
Tongji University, China

Copyright© Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.
Aims and scope

*Journal of Environmental Sciences* is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition
Elsevier is responsible for subscription of the journal. Please subscribe to the journal via http://www.elsevier.com/locate/jes.

For subscription to print edition
China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at http://www.jesc.ac.cn. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@rcees.ac.cn. Instruction to authors is available at http://www.jesc.ac.cn.