



# Preparation and characterization of Pd/Fe bimetallic nanoparticles immobilized in PVDF·Al<sub>2</sub>O<sub>3</sub> membrane for dechlorination of monochloroacetic acid

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## ABSTRACT

An innovative matrix composed of a poly(vinylidene fluoride) (PVDF) membrane modified by adding alumina (Al<sub>2</sub>O<sub>3</sub>) nanoparticles was prepared. Pd/Fe nanoparticles (NPs) were successfully immobilized in the PVDF·Al<sub>2</sub>O<sub>3</sub> membrane, which was initially crosslinked by polyacrylic acid (PAA). The PVDF·Al<sub>2</sub>O<sub>3</sub> membrane and the Pd/Fe NPs immobilized in PVDF·Al<sub>2</sub>O<sub>3</sub> were characterized by scanning electronic microscope (SEM), energy dispersive spectrometry (EDS) and Fourier transform infrared spectroscopy (FT-IR). Studies showed that the amount of Fe immobilized in the PVDF·Al<sub>2</sub>O<sub>3</sub> membrane was four times more than the amount in a traditional PVDF membrane carrier of the same surface size. Pd/Fe NPs immobilized in PVDF·Al<sub>2</sub>O<sub>3</sub> exhibited high efficiency and stability in terms of dechlorination of monochloroacetic acid (MCAA). The effects of several important experimental parameters, including the added Al<sub>2</sub>O<sub>3</sub> amount in PVDF, ferrous concentration in crosslinking solution and Pd content in Pd/Fe NPs were investigated. The reasons behind the improved properties of the PVDF·Al<sub>2</sub>O<sub>3</sub> membrane were discussed.

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## 1. Introduction

Because Gillham and O'Hannesin [1] proposed that zero-valent Fe (ZVI) could be used for in situ remediation of groundwater in 1994, researchers have conducted a large number of studies on dechlorination of chlorinated organic contaminants (COCs) with zero-valent Fe. Now, ZVI is recognized as the most promising and innovative technology for dechlorination of COCs. However, ZVI does present some shortcomings, namely, low reactivity and incomplete dechlorination. To overcome these shortcomings, researchers have used bimetallic particles such as Ni/Fe [2,3], Cu/Fe [4], Pt/Fe [5,6], Ag/Fe [7], and Pd/Fe [8] to dechlorinate COCs, and nano-scale Pd/Fe bimetallic particles have successfully dechlorinated chlorinated methanes and chlorinated ethenes [9,10]. In Pd/Fe bimetallic particles, ZVI as a strong and cheapest reductant, metal Pd not only serves as catalyst absorbing H<sub>2</sub> generated from the iron corrosion but also decomposing H<sub>2</sub> into atomic H\*, a highly activated intermediate hydrogen radical. Although bimetal particles are easily dispersed in water, they tend to aggregate, possibly resulting in decreased dechlorination efficiency without surface protection (immobilized bimetal particles on solid supports). Additionally, recycling the dispersed bimetal particles from

water is extremely difficult. To solve these problems, researchers have immobilized bimetal particles on solid supports such as active carbon, metal oxide, zeolite, and bauxite [11–13]. In recent years, the use of membrane-immobilized nanoscale bimetallic particles for dechlorination of organic compounds has become a research hot topic. Nanoscale bimetallic particles immobilized on a membrane were used for dechlorination of 2,4-dichlorophenol (2,4-DCP) [14], trichloroethylene [3], trichloroacetic acid [15], chlorophenols [16], polychlorinated biphenyls [17,18], and p-dichlorobenzene [19] and reductive transformation of halogenated organic compounds [20].

Among all of the organic macromolecule polymer materials, PVDF has been shown to be an excellent membrane material. It is well-documented [21–25] that PVDF exhibits excellent chemical resistance and thermal stability and is often used as an ultrafiltration, microfiltration and pervaporation membrane material. Much of the PVDF used in previous studies is merchandise material. However, the main shortcoming of using this kind of membrane to immobilize bimetal particles is that the PVDF membrane is hydrophobic. Previous studies have shown that the hydrophilicity of PVDF is a very important factor in the immobilization of metallic particles, and thus, technical modifications of the PVDF membrane are needed to immobilize bimetal particles. It has been reported that ZrO<sub>2</sub> [24], LiClO<sub>4</sub> [25], Al<sub>2</sub>O<sub>3</sub> [22,26], silica [27], TiO<sub>2</sub> [28,29], Fe<sub>3</sub>O<sub>4</sub> [30], or polymeric nanoparticles [31] can be added to polymer membranes to modify the membrane hydrophilicity, per-

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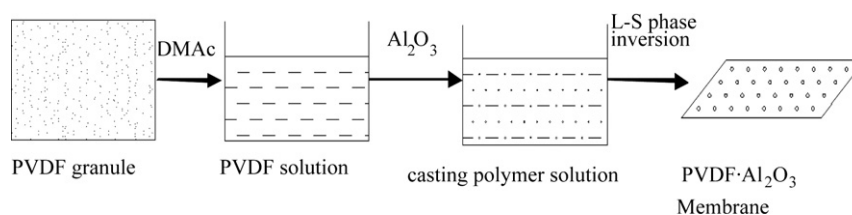


Fig. 1. The membrane preparation procedure.

meation flux, morphology, mechanical properties, and anti-fouling performance.

Nevertheless,  $\text{Al}_2\text{O}_3$ -modified PVDF membranes have not yet been used as matrices for immobilization of Pd/Fe NPs, and there has been no detail research into dechlorination of MCAA using PVDF- $\text{Al}_2\text{O}_3$  membrane-immobilized nanoscale bimetallic particles. In the present work, an innovative and applicable technology has been invented to prepare the PVDF- $\text{Al}_2\text{O}_3$  membrane. The effects of several important experimental parameters, including the amount of added  $\text{Al}_2\text{O}_3$ , the ferrous concentration and the Pd content on dechlorination were sequentially investigated. Scanning electronic microscopy (SEM), energy dispersive spectrometry (EDS) and Fourier transform infrared spectroscopy (FT-IR) were utilized to characterize the properties of the PVDF membrane. Furthermore, the activity and stability of Pd/Fe NPs immobilized in a PVDF- $\text{Al}_2\text{O}_3$  membrane were investigated in terms of the dechlorination of MCAA. Finally, the reasons for the improved properties of the PVDF- $\text{Al}_2\text{O}_3$  membrane were discussed.

## 2. Experimental

### 2.1. Materials and chemical agents

PVDF (FR904) (MW: 600,000) was obtained from Shanghai 3F New Materials Co. Ltd. China. Dimethylacetamide (DMAC, >99%, reagent). Alumina particles 10–30 nm in diameter size were obtained from MaiKaiLun Science and Technology Co. Ltd. China. Hexad-sodium phosphate, polyvinylpyrrolidone (PVP), and a mixture of distilled water and ethanol were used as the non-solvents in the polymer precipitation. Polyacrylic acid (PAA, MW 50,000), acetic acid (analytic reagent), sulfuric acid (analytic reagent), ethylene glycol (EG), ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), ethanol (analytic reagent), and potassium borohydride ( $\text{KBH}_4$ , 99%) were obtained from Tianjin Chemical Reagents Plant, China. Palladium acetate ( $[\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2]_3$ , 47.4 wt.% Pd) was obtained from Aldrich. MCAA was obtained from Ourchem (Sinopharm Chemical Reagent Co., Ltd.). Deionized water was used in the preparation of reagent solutions.

### 2.2. Membrane preparation

#### 2.2.1. Preparation of PVDF- $\text{Al}_2\text{O}_3$ membrane

PVDF- $\text{Al}_2\text{O}_3$  membrane was prepared by the phase-inversion method. PVDF (19%, wt.%) dissolved into DMAC solvent at room temperature. Then, nanoscale  $\text{Al}_2\text{O}_3$  particles used as hydrophilic inorganic matter, hexad-sodium phosphate used as a dispersant and PVP used in pore-forming were simultaneously added to the solvent. To obtain optimal dispersion of the particles in the polymer solution, it was necessary to constantly stir for at least 24 h. The casting polymer solution was deposited in a dark place for 36 h to remove air bubbles. An appropriate amount of the casting polymer solution was uniformly dispersed on a glass plate at 25 °C and 60% humidity and exposed to air for 30 s. It was then immediately immersed in a bath consisting of distilled water and ethanol. The membrane preparation procedure was demonstrated in Fig. 1. It

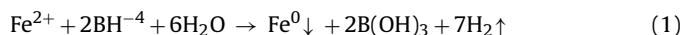
should be mentioned that the weight percentage of the  $\text{Al}_2\text{O}_3$  particles in the PVDF- $\text{Al}_2\text{O}_3$  membrane was varied from 0 to 4%. The various membranes were labeled PVDF-0, PVDF-1, PVDF-2, PVDF-3, and PVDF-4. The quadrate modified PVDF- $\text{Al}_2\text{O}_3$  membrane (60-nm pore size, 20 mm × 20 mm × 0.2 mm) was washed with distilled water and conserved in distilled water until it was crosslinked with PAA.

#### 2.2.2. Preparation of crosslinked PAA/PVDF- $\text{Al}_2\text{O}_3$ membrane

The modified PVDF- $\text{Al}_2\text{O}_3$  membrane was dipped into a coating solution composed of PAA solution, EG and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  for 15 min. The molar ratios of PAA, EG, and ferrous were 4:1:1. Ferrous, the precursor of the iron NPs, was chelated by the PAA and EG, which were used as crosslinking agents. A crosslinked PAA composite PVDF- $\text{Al}_2\text{O}_3$  membrane was produced by thermally treating the carrier in an oven under vacuum at 115 °C for 3 h.

#### 2.2.3. Preparation of Pd/Fe NPs immobilized in PAA/PVDF- $\text{Al}_2\text{O}_3$ membrane

The crosslinked PVDF- $\text{Al}_2\text{O}_3$  membrane containing ferrous was dipped into 0.5 M  $\text{KBH}_4$  solution for 15 min and then washed with ethanol. Zero-valent iron NPs immobilized in the PVDF- $\text{Al}_2\text{O}_3$  membrane were formed in accordance with Eq. (1):



The PVDF- $\text{Al}_2\text{O}_3$  membrane containing iron NPs was soaked in 50 mL palladium acetate, which had been dissolved in ethanol for 15 min. Pd/Fe NPs immobilized in the PVDF- $\text{Al}_2\text{O}_3$  membrane were produced by deposition of Pd on the Fe nanoparticles' surfaces in accordance with Eq. (2):



The Pd/Fe NPs immobilized in PVDF- $\text{Al}_2\text{O}_3$  membrane is shown in Fig. 2. The PVDF- $\text{Al}_2\text{O}_3$  membrane containing Pd/Fe NPs was rinsed with ethanol three times and stored in absolute ethanol for further study involving MCAA dechlorination.

### 2.3. Batch MCAA dechlorination experiments

MCAA dechlorination was conducted in 13 mL glass vials. One piece of PVDF- $\text{Al}_2\text{O}_3$  membrane with immobilized Pd/Fe NPs (each carrier was 20 mm × 20 mm × 0.2 mm and embedded with 2.04 mg of Pd/Fe NPs) was loaded into each reaction vial. In all experiments, each vial was filled with 5 mg/L MCAA solution until no space was left. Each vial was sealed with Teflon-lined rubber septa and placed on a rotary shaker at 170 rpm. At each sampling time, 5 mL of the aqueous sample was withdrawn from the vial with a gas-tight syringe and diluted with deionized water to 25 mL. The MCAA in each sample was methyl esterified before analysis.

### 2.4. Analytical methods

The quantity of MCAA was analyzed with an HP 6890 GC (Agilent Company, USA) with electron capture detection (ECD) and an HP-5 column (30 m × 0.53 μm × 1.0 μm). Nitrogen was used as the

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