

**Reductive Degradation of Chlorinated Organics by
Membrane-Supported Nanoparticles: Synthesis, Characterization
and Modeling Study**

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Introduction

The creation and development of nanosized materials have brought important and promising techniques into the field of catalysis, optical, electronic, magnetic and biological devices [1-3]. Recently, many studies have been reported on the reductive degradation of chlorinated organic compounds by Fe⁰ based bimetallic nanoparticles (Fe/Ni, Fe/Pd). In our previous study [4-5], we described reductive dechlorination of trichloroethylene (TCE) and polychlorinated biphenyl (PCB) using Fe/Pd nanoparticles in polyacrylic acid (PAA)/polyvinylidene fluoride (PVDF) membranes. The PAA (MW 50,000) containing metal salt was added on the PVDF porous support by a dip coating method. The metal nanoparticles were then formed by post reduction with sodium borohydride (NaBH₄).

In this study, we took a different approach based on the combination of ion exchange and reduction to prepare metal nanoparticles in membranes. PVDF microfiltration (MF) membrane provides an ideal support for functionalization due to the open structure, large porosity, and chemical resistance. In addition to the new synthesis process, membrane and nanoparticles characterization is fully examined using various electron microscopy techniques. High resolution X-ray energy dispersive spectroscopy (EDS) mapping performed in scanning transmission electron microscopy (STEM) was employed to reveal the elemental distribution at nano scale.

Our objective is to synthesize nanostructured Fe/Pd bimetallic particles inside PAA functionalized PVDF membranes for reductive dechlorination of toxic organics. The studies included: the role of PAA/PVDF membrane in the metal cations binding through the COO⁻ sites and reduction to form nanoparticles; PCBs dechlorination using convective flow under applied pressure; understand and quantify hydrodechlorination mechanism; the role of second dopant metal palladium; and the role of water, particle size (nano size versus bulk size) and temperature effect in the catalytic reactivity.

Experimental Section

Chemicals

Acrylic acid (AA), benzoyl peroxide, 1,1,1-trimethylolpropane triacrylate (TMPTA), toluene anhydrous, ferrous chloride tetrahydrate (FeCl₂•4H₂O), potassium tetrachloropalladate (K₂PdCl₄), sodium borohydride (NaBH₄), ethanol anhydrous and hexane were purchased from Aldrich. Naphthalene-d₈ (5000 mg L⁻¹ in methyl chloride), 2, 2'-dichlorobiphenyl (100 mg L⁻¹ in hexane), 2-chlorobiphenyl (100 mg L⁻¹ in hexane) and biphenyl (100 mg L⁻¹ in hexane) were obtained from Ultra Scientific. Commercial PVDF microfiltration membrane (0.22 mm pore size, 4.7 cm diameter, 125 mm thickness and 75% porosity) chosen as the substrate for the PAA functionalization was obtained from Millipore.

Preparation of Metal Nanoparticles

Synthesis of Crosslinked PAA/PVDF Composite Membrane

The PVDF MF membranes functionalized with PAA were prepared by filling the membrane pores with the acrylic acid monomer solution, followed by in-situ free radical polymerization via thermal treatment. The monomer solution was prepared by mixing the acrylic acid (30 wt %), benzoyl peroxide (0.5 wt %, initiator), TMPTA (1 wt %, cross-linking agent) in toluene. The solutions were purged with ultra high purity nitrogen for 2 hours to remove any dissolved oxygen that can act as an inhibitor. The PVDF membranes were immersed into the monomer solution for 2 min and quickly placed between two Teflon plates that were subsequently clamped together. The membranes immobilized in the two Teflon plates were then placed into the oven at 90 ± 2 °C with nitrogen purge. After 4 hours, the membranes were released from teflon plates and washed in 200 mL ethanol to remove unreacted monomers.

Synthesis of Fe/Pd nanoparticles in PAA/PVDF Membrane domain

Ferrous ions were first loaded into membranes by ion exchange, and Fe nanoparticles were formed followed by reduction of Fe^{2+} with NaBH_4 . Prior to the ion exchange, the PAA/PVDF membrane (4.7 cm in dia) was soaked into 100 mL sodium hydroxide solution (0.1 M) overnight (12~14 h) to convert PAA from hydrogen form ($-\text{COOH}$) to the sodium form ($-\text{COONa}$). The membrane was then shaken in 100 mL deoxygenated solution of ferrous chloride (5.5 mM) at pH 4.8~5 with nitrogen purge for 12 h. During this process, the ferrous ions were bound with PAA in the membrane by ion exchange with Na^+ . The membrane was then washed with deoxygenated deionized water. Subsequent immersion into 200 mL solution of sodium borohydride (0.07 M) yielded Fe nanoparticles embedded in the PAA/PVDF membrane. After rinsing with deoxygenated deionized water and ethanol sequentially, the membrane supported iron nanoparticles were soaked into 50 mL solution (90/10 vol.% ethanol/water) of K_2PdCl_4 (0.12 mM) for 30 min. This resulted in the deposition of Pd on the Fe surface through the following redox reaction [26]:

Physical Characterization of Metal Particles

Surface of membranes containing metal nanoparticles were observed using the Hitachi S-900 Scanning Electron Microscope (SEM). A Hitachi S-3200 SEM equipped with an energy dispersive spectrometer (EDS) was also used to obtain information regarding the elements present in the nanoparticles. Particle size and distribution were characterized by SEM and transmission electron microscopy (TEM). A specimen-drift-free EDS line profile and EDS mapping system was performed in a scanning transmission electron microscopy (STEM) to determine element composition of particles at nano scale.

Batch Experiments

Batch experiments for dechlorination of 2,2'-Dichlorobiphenyl (DiCB) were conducted in 22 mL serum glass vials. In each batch vial, 16 mg Fe/Pd particles (Pd=2.5 wt %) immobilized on PAA/PVDF (4.7 cm dia) membranes were loaded into the vial containing 15 mg/L TeCB in 20 mL of 50/50 vol.% ethanol/water. The serum glass vials were sealed with Teflon-lined silicon septa and placed on a wrist-action shaker throughout the duration of the experiment. Parallel control experiments with only support membrane (no metal particles) were also performed.

Method of Analysis

DiCB was analyzed by gas chromatography (Varian-3800) equipped with an ion-trap mass spectrometry (Saturn-2200). External standards of DiCB, chlorobiphenyl (CB), and biphenyl in hexane obtained from Ultra Scientific were used to prepare calibration curves. The calibration curves were linear over the concentration range of 0.5~20 mg/L for all three PCB congeners, and the detection limit was approximately 0.1mg/L.

Results and Discussion

Characterization of Metal Particles

TEM analysis at low magnification was performed to verify the nanoparticle formation and distribution inside PAA/PVDF membranes. As shown in the Figure 1a, Fe/Pd nanoparticles in spherical shape were homogeneously dispersed in the PAA phase over the membrane cross-section. While the regions containing no nanoparticles

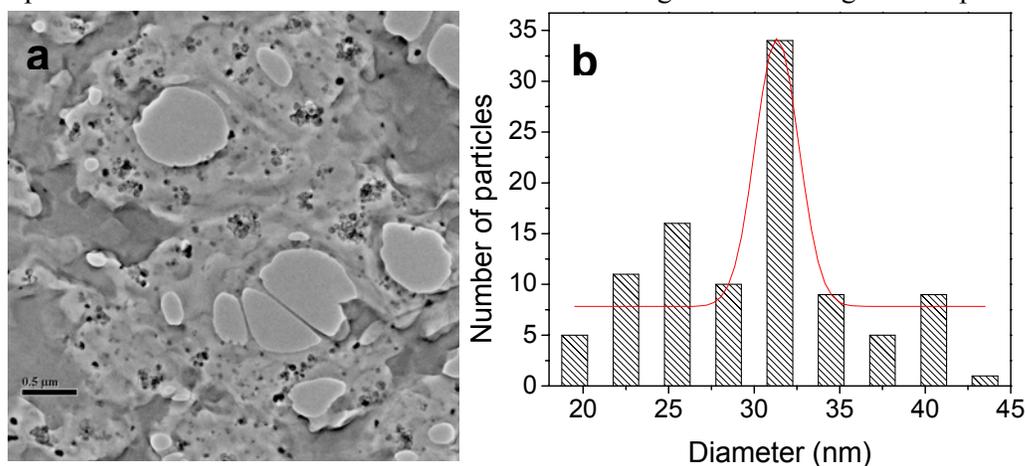


Figure 8. (a): TEM image of PAA/PVDF membrane cross-section containing Fe/Pd nanoparticles; (b): Histogram from the left TEM image of 100 Fe/Pd nanoparticles.

believed to be the PVDF substrate phase. A statistical analysis of the image yielded an average particle size of 30 nm in diameter, with the size distribution standard deviation of 5.7 nm. Based on the mean diameter of 30 nm, the external surface area for nanoparticles was calculated to be $\sim 25 \text{ m}^2 \text{ g}^{-1}$. The EDS analysis was also conducted during the TEM observation using a 2-nm electron beam spot to determine the elements present in the nanoparticles. The composition of nanoparticles identified in the TEM image was also quantified by EDS. The Pd content was found to be 1.9 wt%, which is consistent with the previous ICP analysis results. Boron as a light element at low content was not detected by EDS due to the low energy sensitivity. The mapping images clearly demonstrate that bimetallic Fe/Pd nanoparticles having a Fe-rich core and a Pd-rich shell. This is as expected because the Pd was reduced by Fe and deposited on the Fe surface.

Batch Reaction of DiCB with Fe/Pd

Figure 2a shows the concentration profiles for the batch reaction of DiCB with Fe/Pd (Pd = 2.3 wt%) nanoparticles in PAA/PVDF membranes at 25 °C. The

membrane supported Fe/Pd nanoparticles exhibit extremely fast DiCB degradation rate. More than 90% dechlorination of DiCB only with 0.8 g L^{-1} metal loading was achieved within 2 hours. Biphenyl was formed as the dominating product. 2-chlorobiphenyl (CB) as the chlorinated intermediate was only identified in the trace level. This indicates a direct reductive pathway due to the higher degradation rate for the chlorinated intermediate. The carbon mass balance based on the sum of DiCB, CB and biphenyl was about 91%~95% of the initial amount of DiCB. The 5%~ 9% mass losses is due to the extraction equilibrium.

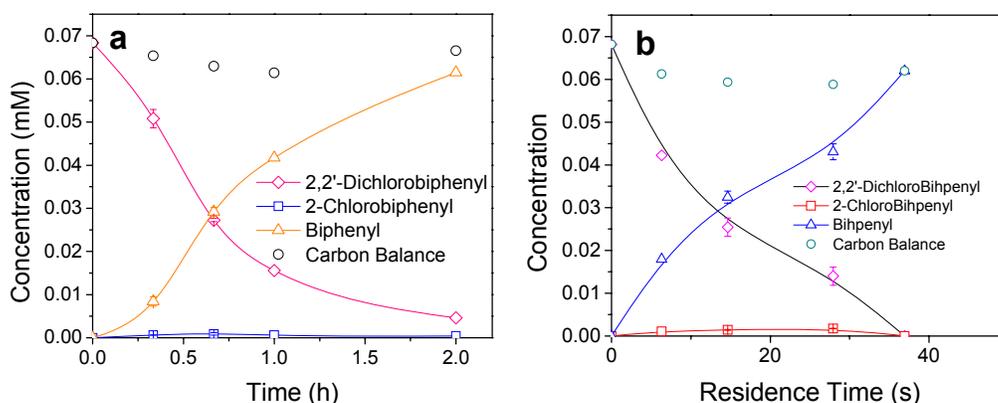


Figure 2. (a) Batch reaction of 2, 2'-chlorobiphenyl with Fe/Pd (Pd = 2.3 wt%) in PAA/PVDF membrane at room temperature; (b) Reaction of 2, 2'-chlorobiphenyl with Fe/Pd (Pd = 2.3 wt %) in PAA/PVDF membrane under convective flow.

Dechlorination of DiCB by Fe/Pd nanoparticles immobilized PAA/PVDF membrane under convective flow was investigated using a dead-end filtration module supplied by Osmonics. This apparatus has a membrane area of 8 cm^2 and contains a stirring device placed in close contact to the feed solution-membrane interface to minimize the effects of concentration polarization. The dechlorination experiments were carried out at four different constant permeation rates of $2.0 \times 10^{-4} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$, $2.6 \times 10^{-4} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$, $5.0 \times 10^{-4} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$ and $11.5 \times 10^{-4} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$ at steady state with the initial DiCB concentration of 15.2 mg L^{-1} . The membrane area is 8 cm^2 which contains 7.4 mg Fe/Pd nanoparticles. Figure 2b shows the PCBs concentration profile at different residence time. The resident time is calculated by: residence time = (membrane pore volume) / (permeation rate), and the membrane pore volume is determined from the water uptake. As expected, the conversion of DiCB increased with the increase of residence time. The reaction needs about 40s residence time for complete dechlorination of DiCB.

Conclusions

Fe/Pd nanoparticles were successfully incorporated in PAA/PVDF membranes by ion exchange and subsequent reduction process. High resolution STEM-EDS mapping analysis was also used to investigate the binding interaction between metal cations and carboxylic acid groups which plays an important role in determining the nanoparticle size and distribution. Fe/Pd nanoparticle size, structure and distribution were analyzed by TEM, HRTEM, STEM-EDS mapping. The membrane supported nanoparticles exhibit high reactivity in terms of dechlorination of chlorinated organics. Biphenyl was

formed as the main dechlorination product. All the intermediates are only found in the low concentration in the first one hour.

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