# Role of membrane pore polymerization conditions for pH responsive behavior, catalytic metal nanoparticle synthesis, and PCB degradation

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## ARTICLE INFO

## ABSTRACT

This article describes the effects of changing monomer and cross-linker concentrations on the mass gain, water permeability, Pd-Fe nanoparticle (NP) loading, and the rate of degradation of 3,3',4,4',5-pentachlorobiphenyl (PCB 126) of pore functionalized polyvinylidene fluoride (PVDF) membranes. In this study, monomer (acrylic acid (AA)) and cross-linker (N, N′- methylene-bis (acrylamide)) concentrations were varied from 10 to 20 wt% of polymer solution and 0.5–2 mol% of monomer concentration, respectively. Results showed that responsive behavior of membrane could be tuned in terms of water permeability over a range of 270–1 $L\,m^{-2}\,h^{-1}\,bar^{-1}$, which is a function of water pH. The NP size on the membrane surface was found in the range of 16–23 nm. With increasing cross-linker density the percentage of smaller NPs (< 10 nm) increases due to smaller mesh size formation during in-situ polymerization of membrane. NP loading was found to vary from 0.21 to 0.94 mg per $cm^2$ of membrane area depending on the variation of available carboxyl groups in membrane pore domain. The NPs functionalized membranes were then tested for use as a platform for the degradation of PCB 126. The observed batch reaction rate ($K_{obs}$) for PCB 126 degradation for per mg of catalyst loading was found 0.08–0.1 $h^{-1}$. Degradation study in convective flow mode shows 98.6% PCB 126 is degraded at a residence time of 46.2 s. The corresponding surface area normalized reaction rate ($K_{sa}$) is found about two times higher than $K_{sa}$ of batch degradation; suggesting elimination of the effect of diffusion resistance for degradation of PCB 126 in convective flow mode operation. These Pd-Fe-PAA-PVDF membranes and nanoparticles are characterized by TGA, contact angle measurement, surface zeta potential, XRD, SEM, XPS, FIB, TEM and other techniques reveal the details about the membrane surface, pores and nanoparticles size, shape and size-distribution. Statistical analysis based on experimental results allows us to depict responsive behavior of functionalized membrane. In our best knowledge this paper first time reports detail study on responsive behavior of pore functionalized membrane in terms of permeability, NPs size, metal loading and its effect on PCB 126 degradation in a quantified approach.

## 1. Introduction

To address the global challenge of water contamination, membrane-based separation methods are being increasingly studied for potential applications for water purification [1,2]. Current advancements in developing functionalized membranes with porous support and different functional polymers, opens-up the possibility to fine-tune the pore structure, permeability (A) and selectivity of the membranes [3–5]. In particular, cross-linked hydrophilic polymers are being studied in different functionalization processes, especially in the preparation of

responsive membranes [6,7]. As diverse membrane separation processes typically require different pH environments, the demand for functionalized pH responsive membranes has increased [8]. Using pH responsive polymers, such as polyacrylic acid (PAA), poly (methylacrylic acid), poly (vinylpyridine) etc., along with a suitable cross-linker, make it possible to functionalize pH responsive membranes [8,9]. Further, incorporation of catalytic nanoparticles (NPs) across the pores of the modified surface of the membrane provides an effective platform for in situ surface reactions in different pH environments [10,11].

Chlorinated organic compounds (COCs) are a serious concern as environmental pollutants due to their high toxicity, chemical stability and presence in soils, sediments as well as in different water sources [11–13]. Nano scale zero valent iron (nZVI) and iron based bimetallic NPs have been intensively studied for the degradation of COCs into less toxic or nontoxic products [14–21]. The addition of a second metal such as Pt, Pd, Au, Ag, Ni, Cu, Zn with Fe will enhance the catalytic activity for dichlorination [22–24]. Among these metals, Pd is well known and the most studied catalyst for hydro-dechlorination of COCs due to its noble nature [25,26]. When bimetallic Pd-Fe is used in COCs degradation in water, Fe acts as an electron source and Pd as a catalyst. Once, hydrogen is produced from nZVI due to its corrosion in water, it is activated by Pd to form highly reactive hydrogen radicals. These hydrogen radicals then serve as effective electron donors for dechlorination of COCs, whether Pd is coated on nZVI or is present as separate NPs [27]. Incorporation of these reactive NPs in membrane results as a suitable platform for water remediation and antifouling application. Different methods for in situ preparation of nanoparticle-based membrane systems for water remediation are well documented in literature [20]. In our previous studies, we reported the synthesis of Fe, Pd-Fe, Ni-Fe, and iron oxide immobilized in polyvinylidene fluoride/ poly (acrylic acid) (PVDF-PAA) membranes for use in the degradation of COCs [28–32]. These functionalized membranes have been used as porous supporting materials to control NPs aggregation, to capture dissolved metal ions, and to perform batch and convective flow degradation studies of COCs through the associate membrane pores. During functionalization, monomer (M) and cross-linker (X) concentrations play a significant role in the functionalization of the membrane pore matrix. They also have influences on NPs loading [7,33,34]. However, the impact of monomer and cross-linker concentrations has not been addressed in previous works.

The main purpose of this study is to investigate the effects of M and X concentrations on the performance of pore functionalized pH responsive membranes for water-based dechlorinations applications, using 3,3',4,4',5-pentachlorobiphenyl (PCB 126) as a model compound. The specific objectives of this work are: i) to functionalize PVDF membranes using different combinations in concentrations of PAA as a monomer, M (wt%), and (N, N′- methylenebis (acrylamide)) (MBA) as a cross-linker, X (mol%), ii) to study the variation of responsive behavior of PAA-PVDF membrane and understand its effects on mass gain, water permeability, Pd-Fe NPs size and metal loading, iii) to depict the details of Pd-Fe-PAA-PVDF membranes and nanoparticles by TGA, contact angle measurement, surface zeta potential, XRD, SEM, XPS, FIB, TEM and other characterization techniques and finally, iv) to investigate the reaction kinetics of Pd-Fe NPs through the reduction of PCB 126. Details of specific objectives are portrayed in Scheme 1.

## 2. Materials and methods

### 2.1. Materials

All chemicals used during the laboratory-scale membrane functionalization and the other studies were reagent grade and used without further purification. Acrylic acid (AA, 98%), N, N′-methylenebis (acrylamide) (MBA, 99%) and sodium borohydride (98%) were received from ACROS ORGANICS. Potassium persulfate (KPS, > 99%) was procured from EM SCIENCE. Potassium tetrachloropalladate(II) (99%) was purchased from STREM Chemicals. Naphthalene_$d_8$ (99 atom% D) was purchased from Sigma-Aldrich. Sodium hydroxide (0.1 N), sulfuric acid (0.5 M), hydrochloric acid (0.1 N), hexanes (> 99%) and ferrous chloride tetrahydrate (> 99%) were obtained from Fisher Scientific. 3,3',4,4',5-pentachlorobiphenyl (PCB 126) (> 97%, neat) and biphenyl (> 97%, neat) along with their analytical solution (100 ppm in hexane) were acquired from Ultra Scientific. Ethyl alcohol and methanol were bought from EMD Millipore Corporation. Sodium chloride (99%) was purchased from Alfa Aesar. Full scale PVDF microfiltration membranes

(PV700, pore diameter of 250–400 nm, thickness around 172 ± 5 μm and porosity around 38–46%) were obtained from Nanostone Water, Inc.

### 2.2. Functionalization of PVDF membranes

Lab scale PVDF membranes were functionalized via an in-situ polymerization method, as reported before [31,35]. Before functionalization, membranes were soaked in methanol for 5–10 min to remove dirt, clean the pores and increase the hydrophilicity of the surface [36]. After that a mixture of monomer solution (pH = 5.5–5.6) of AA (10–20 wt% aqueous solution) with MBA as the cross-linker (0.5–2.0 mol% of AA), and KPS as an initiator (1.0 mol% of AA) was passed through the membrane under vacuum (0.14–0.16 bar vacuum) [37]. The solution was passed 3–4 times through the top surface of the membrane and once through the back of the membrane to confirm a homogenous polymerization across the pores. The membranes were then baked at 70–75 °C for 1–1.5 h under $N_2$ atmosphere or vacuum. This allows functionalization of the membrane via a thermal initialized polymerization of AA inside the PVDF membrane pores. After that, functionalized membranes were washed thoroughly with deionized ultrafiltered (DIUF) water to eliminate any unreacted constituents and then dried for 30 min at around 50–55 °C. Finally, the membranes were weighed to confirm polymerization through mass gain. In Fig. 1 a step by step process of the functionalization of the PVDF membrane, the Pd-Fe NP loading, and the degradation of PCB 126 solution using a Pd-Fe-PAA-PVDF membrane is depicted.

In order to study the effects of M and X concentrations, six different batches of functionalized membranes were prepared. M concentration was varied from 10 to 20 wt% of solution, and X concentration was varied from 0.5 to 2 mol% of monomer concentration. In our previous studies we have taken monomer concentration to vary from 10 to 20 wt % with 1 mol% of cross-linker concentration [31,38–40]. However, in those studies we have not addressed the effect that M and X have on mass gain, permeability (A), metal loading, NP size and degradation of COCs (in this case, PCB 126) besides membrane characterizations. In this study, we have extended the variation of cross-linker concentration in the range of 0.5–2 mol% of monomer concentration. For all the prepared batches of membrane, the initiator (KPS), concentration was kept constant to 1 mol% of M concentration in polymer solution. In Table 1 the matrix of chemicals used for preparing different batches of pore functionalized membranes to evaluate the effect of monomer and cross-linker concentration variation is shown.

### 2.3. Nanoparticle immobilization in functionalized membranes

In-situ immobilization of Fe and Pd NPs in the functionalized membrane pores was achieved by first doing ion exchange followed by reduction of Fe and subsequent Pd coating as reported in previous works [38,40]. For cation exchange, PVDF-PAA membranes were soaked in NaCl (~ 68 mM) solution (pH ≥ 10). The ionized carboxyl groups chelated with $Na^+$ while releasing $H^+$ to cause a decrease in the pH of the solution. Therefore, to maintain the pH, NaOH was added in intervals. After 12–14 h, (solution pH > 8), the membranes were then washed with deoxygenated water to remove any excess NaCl/NaOH from the pores. For a second ion exchange, the membrane was put into a dead-end filtration cell. Then, 200 mL of $FeCl_2$ solution (~ 3.57 mM, pH = 5.0–5.5) was passed through under $N_2$ pressure (2–3 bar). This convective mode operation allows all $Na^+$ ions to be replaced by $Fe^{2+}$, thereby forming iron-carboxylate conjugates both in the surface and inside the pores. In the reduction step, $Fe^{2+}$ was immediately reduced to zerovalent iron NPs by passing 300 mL of $NaBH_4$ solution (~ 26 mM) under $N_2$ pressure (3–5 bar) through the membrane. Finally, the immobilization of Pd NPs on Fe surface was achieved by passing 200 mL (ethanol:water = 9:1 v/v) of $K_2PdCl_4$ solution (~ 153 μM, Pd as 1 wt% of Fe) through the Fe-PAA-PVDF membrane under $N_2$ pressure