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Aqueous – Phase Synthesis of PAA in PVDF Membrane Pores for Nanoparticle Synthesis and Dichlorobiphenyl Degradation

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Abstract

This paper deals with bimetallic (Fe/Pd) nanoparticle synthesis inside the membrane pores and application for catalytic dechlorination of toxic organic compounds from aqueous streams. Membranes have been used as platforms for nanoparticle synthesis in order to reduce the agglomeration, encountered in solution phase synthesis which leads to a dramatic loss of reactivity. The membrane support, polyvinylidene fluoride (PVDF) was modified by in situ polymerization of acrylic acid in aqueous phase. Subsequent steps included ion exchange with Fe²⁺, reduction to Fe⁰ with sodium borohydride and Pd deposition. Various techniques, such as STEM, EDX, FTIR and permeability measurements, were used for membrane characterization and showed that bimetallic (Fe/Pd) nanoparticles with an average size of 20-30 nm have been incorporated inside of the PAA-coated membrane pores. The Fe/Pd-modified membranes showed a high reactivity toward a model compound, 2, 2'-dichlorobiphenyl and a strong dependence of degradation on Pd (hydrogenation catalyst) content. The use of convective flow substantially reduces the degradation time: 43% conversion of dichlorobiphenyl to biphenyl can be achieved in less than 40 s residence time. Another important aspect is the ability to regenerate and reuse the Fe/Pd bimetallic systems by washing with a solution of sodium borohydride, because the iron becomes inactivated (corroded) as the dechlorination reaction proceeds.

Keywords

Fe/Pd bimetallic nanoparticles; catalysis; Dechlorination; PCB; Microfiltration Membrane

1. Introduction

Traditionally, membranes are used for separations based on size exclusion, solution diffusion or Donnan exclusion [1]. However, membrane modification with novel, advanced functional groups [2] or layer-by-layer deposition of polyelectrolytes and the growth of polymer brushes [3] can extend their area of application toward advanced separations, development of biomaterials or catalysis. In the field of catalysis in particular, there is a growing interest in detoxification of organic chlorinated compounds from aqueous streams. Chlorinated organic

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compounds constitute a large group of pollutants of international concern due to their high toxicity, persistence and various sources of distribution in the environment.

In recent years, zero-valent nanoscale metal (especially iron) particles have attracted a growing attention in groundwater remediation of chlorinated solvents [4,5]. However, iron nanoparticles tend to agglomerate in water rapidly to form micron size or larger aggregates, thus losing their reactivity. Various techniques have been employed to control the particle size, by using additives [6,7] controlled seed mediated synthesis [8,9] or coating with a protective layer [10]. For a more rapid and complete dechlorination, a second element is often added, resulting in creation of bimetallic nanoparticles. In these systems, the first metal (most commonly Fe, but also Mg, Sn, etc) is an electron donor to degrade the organic compound and the second metal (usually a more noble metal such as Pd or Ni) promotes the reactivity through hydrogenation, acting as a catalyst. Several bimetallic systems that are used for dechlorination of toxic chlorinated organic compounds, have been reported in the literature: Fe/Ni [11,12], Ni(B)/Fe(B) [13], Fe/Pd [14-19], Mg/Pd [20-22], Sn/Pd [23].

In order to minimize the particle agglomeration and loss, another approach is to synthesize supported nanoparticles on activated carbon [24,25], resins [23] or membranes, as substrates. Among these, membranes have a distinct advantage because of ease of functionalization and the ability to be operated under convective flow conditions (filtration), thus eliminating the mass transfer issues often encountered in diffusive (batch) mode operation. Membranes have received a special attention (including our research group) and have been successfully employed as platforms for nanoparticle synthesis. Membrane's open structure and high internal surface area ensure a high nanoparticle loading and easy active site accessibility. The most common membrane materials used for this purpose are: cellulose acetate [11,26], hydrophilized polysulfone [27], polyacrylic acid – modified polyether sulfone [28,29] and polyvinylidene fluoride [30-32]: these membranes have proven to be very efficient for the degradation of the organic chlorinated compounds from water.

In recent years there has been a great interest in our laboratory in PVDF membrane modification with PAA by dip coating or solvent phase in situ polymerization of acrylic acid, with subsequent Fe/Pd nanoparticle incorporation [30,31,33]. Dechlorination studies using a variety of toxic chlorinated organic compounds were performed and a mathematical model was developed. Currently we investigate a method of PAA modification of PVDF membranes using aqueous phase polymerization (no organic solvent use) and study the nanoparticle longevity and stabilization by protecting the Fe/Pd nanoparticle surface.

The main goals of present study are: i) synthesize bimetallic Fe/Pd nanoparticles within the pores of a functionalized membrane (polyacrylic acid-coated polyvinylidene fluoride) using green chemistry, ii) characterize the membrane and nanoparticles characterization, iii) study the reactivity toward a target toxic organic compound, 2,2'-dichlorobiphenyl, iv) evaluate nanoparticle stability during operation (dechlorination) and regeneration, and v) demonstrate operation under convective flow conditions.

2. Materials and Methods

2.1 Materials

All chemicals used were of reagent grade. Ferrous chloride, deionized ultrafiltered (DIUF) water were purchased from Fisher Scientific. Potassium persulfate was purchased from EM Science and ethylene glycol (EG) from Mallinckrodt. Acrylic acid and potassium tetrachloropalladate (II) were purchased from Sigma-Aldrich. Naphthalene-d8 and 2, 2'-dichlorobiphenyl (DiCB) were purchased from Ultra Scientific. Hydrophilic polyvinylidene

fluoride (PVDF) microfiltration membranes (DVPP) with a thickness of 125 μm and nominal pore size of 650 nm were obtained from Millipore Corporation.

2.2. Methods

2.2.1. Membrane Functionalization—The pores of PVDF membranes were functionalized with polyacrylic acid (PAA) by in situ polymerization of acrylic acid. Although various membrane materials can be used for this application, PVDF was chosen for its high chemical and thermal stabilities. The polymerization reaction was carried out in aqueous phase (green chemistry) and the procedure was adapted from literature [34-36]. The polymerization solution contained 30 wt% acrylic acid (monomer), ethylene glycol (cross-linker, added in a 1:6.5 molar ratio of EG to acrylic acid), and 1 wt% potassium persulfate (initiator). In order to ensure the proper wetting, hydrophilized PVDF membranes were used for the aqueous phase polymerization. The PVDF membrane was dipped in the polymerization solution for 2 min, sandwiched between two teflon plates and placed in an oven at 90 $^{\circ}\text{C}$ for 4 hours. Raising the temperature is necessary for the formation of ester bonds between the ethylene glycol crosslinker and carboxylates on the formed polyacrylate. Nitrogen gas was continuously supplied to remove oxygen, which acts as an inhibitor for the polymerization reaction.

2.2.2 Bimetallic Fe/Pd Nanoparticle Synthesis—The flowchart for membrane functionalization and nanoparticle synthesis is shown in Figure 2. Prior to Fe^{2+} ion exchange, PAA-coated PVDF membranes were immersed in NaCl (5 to 10 % wt) solution at pH 10 for 10 h to convert the $-\text{COOH}$ to COONa form. The purpose was to minimize the pH effects on ion exchange equilibrium, thus enhancing the ion exchange capacity. In the next step, the membrane was washed with DIUF until the pH of the washing solution became neutral. Then, the membrane was immersed in FeCl_2 solution at a pH of 5.5 for 4 h. The feed solution volume and concentration varied from 50 to 200 mL and 100 to 180 mg/L Fe^{2+} , respectively, depending on the desired amount of ion exchange required on the membrane. Nitrogen gas was bubbled to minimize Fe^{2+} oxidation. The reduction with NaBH_4 ensured Fe nanoparticle formation and the membranes were stored in ethanol to prevent oxidation. The secondary metal, Pd, was deposited on the Fe nanoparticles by immersing the membrane (typically for 2 h) in a K_2PdCl_4 solution (in closed vials, vigorous shaking) of ethanol/water (90:10 vol% mixture), preventing the oxidation of the highly reactive Fe nanoparticles. The concentration of the K_2PdCl_4 solution varied between 8 and 25 mg/L Pd, depending on the amount of Pd desired to be deposited on the Fe-modified membrane. This created core-shell nanoparticles. The deposition occurred via the well known redox reaction:

The amount of Pd deposited on the Fe nanoparticles was expressed in wt% with respect to the amount of Fe. The Fe/Pd – modified membranes were stored in ethanol until the use for dechlorination experiments. Batch and convective mode experiments were performed, using DiCB as a model compound, in order to determine the reactivity of the immobilized Fe/Pd nanoparticles.

2.2.3. Membrane and Nanoparticle Characterization

STEM-EDS: PAA-coated and nanoparticle-modified membrane samples were prepared by sectioning with a diamond knife (slices of about 50 nm thickness). Nanoparticle-modified membrane morphology and nanostructure were examined by a transmission electron microscope (JEOL JEM-2010F), equipped with a scanning (STEM) unit. This instrument was also coupled with an Oxford EDS detector, used for membrane elemental analysis. High

resolution EDS mapping was employed to obtain the composition and distribution of elements (Fe/Pd) in the membrane.

FTIR: The Fourier Transform Infrared spectra of the bare and PAA-coated PVDF membranes were recorded on a Varian 7000e FTIR with attenuated total reflectance (ATR). Membranes were dried at 90 °C for four hours before testing. Data were collected using 128 scans at a resolution of 4 cm⁻¹.

2.2.4. Metal Analysis—The amount of Fe or Ca captured during ion exchange and Pd deposited on the Fe-modified membrane was determined from material balance. The concentrations for Fe, Ca and Pd in the feed and permeate solutions were quantified using a Varian SpectrAA 220 Fast Sequential atomic absorption spectrometer equipped with a Fisher Scientific hollow cathode lamp. For Fe, the lamp was operated at a wavelength of 386.0 nm. The calibration plot was created using 4 different concentrations of Fe ranging from 25 to 200 mg/L with $R^2 = 0.9993$ and average analytical error of 2%. In the case of Pd, the lamp was operated at a wavelength of 246.6 nm and the linear calibration range is between 0.2 and 28 mg/L Pd. The error of analysis was <2%. Lastly, in the case of Ca the lamp was operated at a wavelength of 239.9 nm with the linear calibration range between 10 and 200 mg/L Ca, and the error of analysis was <2.5%.

2.2.5 Dechlorination reactions and DiCB analysis by GC-MS—Dechlorination reactions were carried out at room temperature in diffusive (batch) and pressure-driven convective modes. For batch mode operation, the dechlorination of DiCB (typically 40 mL of 5 mg/L feed concentration of DiCB in 50:50% ethanol:water mixture) was conducted in 40 mL closed vials and sample probes were collected at different times. For the convective mode experiments, the membrane (external area of 13.2 cm²) was mounted in a filtration cell, Sepa ST from GE Osmonics, and the feed solution, containing DiCB (same concentration as in the batch mode) solution was permeated through the membrane and permeate probes were collected. In order to change the permeate flow rate (also the residence time) through the membrane, the pressure was varied from 0.8 to 4 bar during dechlorination experiments.

In both cases, the samples were extracted in hexane (1:1 volume ratio), with the addition of internal standard, naphthalene-d8, and analyzed with a Varian CP-3800 GC coupled with a Varian Saturn 2200 MS. The average analytical error in the analysis of the starting compound - DiCB, intermediate - chlorobiphenyl, and final product - biphenyl, was less than 2%.

3. Results and Discussion

3.1 Functionalized Membrane Characterization

The functionalization of the PVDF membranes with PAA was characterized by FTIR – ATR spectroscopy and stimulus-responsive water flux to pH. The organic functionalities for the hydrophilized PVDF and PAA-coated PVDF membranes were studied by FTIR-ATR spectroscopy. The PAA-coated PVDF membrane shows a peak at 1710 cm⁻¹, which is not present in the spectrum for the blank PVDF membrane. This peak is due to the presence of C=O bond stretching in carboxylic acid groups, indicating successful PAA immobilization within the functionalized membrane. The strong absorption band at 1140-1280 cm⁻¹ is characteristic of CF₂ found in PVDF.

As mentioned earlier, the polymerization reaction was carried out in the presence of a cross-linker, ethylene glycol. This is a bidentate molecule which can react with two –COOH groups at 90° C cross-linking the PAA chains, thus preventing their leaching from the membrane [32]. Because ethylene glycol binds to carboxyl groups from PAA, the amount of cross-linking agent has to be kept low in order to maintain free –COOH groups for ion exchange. The effect

of cross linker on exchange capacity was tested for three membranes, in which the amount of ethylene glycol was 6.5, 20 and 40 mol % with respect to acrylic acid. Ion-exchange capacity was confirmed by Ca^{2+} pick up on the three membranes. The following assumptions were made: each ethylene glycol molecule reacts with 2 $-\text{COOH}$ groups and 1 mol Ca^{2+} is bound to 2 mol carboxyl, based on ion-exchange principles. The amount of Ca^{2+} picked up varied from 0.014 to 0.008 mmol/cm² membrane area for the lowest and highest degree of cross linker, respectively. Figure 3 shows a normalized plot (compared to the Ca^{2+} at lowest degree of cross linking): it can be observed that at a low degree of cross-linking (up to 20 %), there is an agreement between the experimental data and theoretical prediction based on the assumptions presented above. However at higher degree of cross linking, the experimental Ca^{2+} pick up is significantly higher. It might be possible that due to scarcity of adjacent COOH groups (being used up by random cross linking), some of the Ca^{2+} ions are loosely bound to just one carboxyl ($\text{COO}-\text{Ca}^+$), the electroneutrality being restored by other anion species present in solution. Under our experimental conditions of 6.5 mole % ethylene glycol to acrylic acid molar ratio and using the assumptions mentioned above, it was estimated that about 87% of the $-\text{COOH}$ groups are free, and thus available for ion exchange.

With PAA present within the membrane pores, as indicated by FTIR, one would expect to see a stimulus-responsive water flux to pH. The effect of varying pH on water flux through the PAA/PVDF functionalized membrane is shown in Figure 4. It can be observed that as the pH of the feed solution is increased, the permeability (the slope) decreases. This is in agreement with the findings reported previously [34], where similar tests were conducted on PVDF membrane pores filled with PAA. Since the pK_a of acrylic acid is approximately 4.25, the PAA network will maintain a relatively neutral charge at a low pH, leaving it in a compacted state. As the pH is increased, more $-\text{COOH}$ groups will become ionized, resulting in an elongation of the PAA network due to charge repulsion. While in the elongated state, the permeate flux is lower than in the compacted state. The linear relationship between the pure water flux (J_v) and applied pressure (ΔP) shows that the pore functionalized PAA assembly is stable.

Membrane permeability at neutral pH decreases after each functionalization step, as it is shown in Table 1 for two membranes. The permeability variation for bare and PAA-coated membranes (Na^+ form) is less than 10%. The addition of Fe^{2+} causes a decrease in permeability, Fe^{2+} can act as a cross linker reducing the spacing between PAA chains. The flux is lower for the case where higher amount of Fe^{2+} was ion exchanged on the membrane, as expected. After the reduction with NaBH_4 and formation of zero valent Fe nanoparticles, the permeability is dramatically reduced; as the membrane pore void fraction is decreasing, the resistance to water permeation is increased. It can be also observed that the decrease in permeability (by a factor of 2.3) is approximately proportional to the increase in the metal loading (reduction of the void fraction in the membrane) which is a factor of 2.9. Permeability measurements can be used to estimate the equivalent pore diameter, d_c , applying Hagen – Poiseuille's law of capillary flow:

$$d_c = 2 \left(\frac{8 J_v \mu L}{\pi N \Delta P} \right)^{\frac{1}{3}} \quad (1)$$

where N , ΔP , μ and L represent the number of pores, transmembrane pressure, liquid viscosity, and membrane thickness, respectively. The equivalent diameter of the pores was calculated on the basis of permeability changes for the bare and functionalized membrane. Assuming no change in membrane thickness and no pores are completely blocked following functionalization,

$$J_v/J_{v0} = (d_p/d_{p0})^4 \quad (2)$$

where J_{v0} and d_{p0} are the pure water flux and the equivalent diameter for the bare membrane, respectively, and J_v and d_p are the pure water flux and the estimated equivalent diameter for the functionalized membrane after each step. Thus, assuming a cylindrical pore and uniform gel distribution throughout the membrane pores, based on permeability measurement for bare and PAA-functionalized membrane, d_p can be obtained from equation 2. Then, it can be estimated that 65 % of the pore volume is not covered by polymeric chains.

Another way to estimate the fraction of the pore volume occupied by gel is based on the weight gain of the PAA-functionalized in comparison to the bare membrane. The amount of PAA present in the membrane pores under our experimental conditions was estimated to be 6.3 mmol PAA / g dry membrane (7.4 mmol / cm³ membrane pore volume), which corresponds to a weight gain of about 51%. Knowing the mass of PAA immobilized on the membrane and using the density, the volume of PAA can be computed. The total pore volume for the bare membrane can be estimated using the membrane thickness, porosity, and external surface area. Based on the ratio of the two volumes (for the PAA and the pores of the bare membrane), the PAA gel occupies approximately 51% of the membrane pore volume, 49% being void. It can be observed that the estimation of the pore fraction covered by gel through two different methods is relatively close, within 25%. The importance of the pore fraction not covered by PAA will be discussed in the convective mode dechlorination section.

Fe/Pd bimetallic nanoparticles were synthesized within the membrane nanodomain, as described in Section 2.2.2. STEM imaging was used to examine the surface morphology of the nanoparticle-modified PVDF membranes (Figure 5). The Fe nanoparticles have an average size between 20 and 30 nm. The Pd coating reaction formed particles on the Fe surface that had an average size of approximately 3 nm (bright spots in the STEM image). The EDS spectrum and mapping shows the elemental composition and distribution of species (Figure 6).

Based on the mass of metal loaded on the membrane and assuming an average particle size of 30 nm for each nanoparticle it is possible to determine the metal fraction in the mixed matrix membranes. For metal loadings between 3.7 and 30.3 mg, the metal content was estimated to be in the range from 0.8 to 6.6 % vol and 2 to 17 % wt, as compared to the final mixed matrix membrane. This also corresponds to a metal content in the range from 1.6 to 13 % vol and 6 to 49 % wt, as compared to the PAA gel only.

3.2 Catalytic dechlorination

3.2.1 Batch mode dechlorination studies—As mentioned earlier, Fe/Pd-modified membranes were tested for dechlorination of DiCB as a target toxic organic compound. The dechlorination results performed with different membranes and metal (Fe/Pd) loadings are shown in Figure 7. It can be observed that for the same amount of Fe⁰ (17 mg) the conversion to biphenyl produced at 1 h of the reaction time, increases linearly with the amount of Pd in the bimetallic particles.

In a Fe/Pd bimetallic system, the role of Fe (reactant) in zero-valent form is to generate hydrogen (near neutral pH operation) via a corrosion reaction. Pd acts as a hydrogenation catalyst and thus can be considered as providing the active sites in the bimetallic system. The Pd surface coverage (assuming uniform deposition of Pd on the Fe-modified membrane) on bimetallic particles can be estimated on a basis of 30 nm particle size and a Pd cross-sectional area of 0.0787 nm² [37]. For the three membranes used in these experiments, Pd coverage was

estimated to be in the range between 0.6 and 0.7 monolayers. Since Pd coverage is less than 1 monolayer for all membranes, all Pd atoms are considered active sites, thus linear dependence on Pd loading. The following reaction model can be used to quantify the reactivity of different metal systems:

$$dC/dt = k_{\text{obs}} C = k_{\text{SA}} a_s \rho_m C \quad (3)$$

For each membrane, a pseudo-first order rate law (from a $\ln(C/C_0)$ vs time plot (data not shown here) was observed and, k_{obs} , the observed pseudo-first order constant was determined. The surface-area-normalized rate constant, k_{SA} ($\text{L}/\text{m}^2\text{h}$), can be calculated from these k_{obs} values using Equation 3 where C_0 is the initial concentration of the DiCB, C is the concentration of DiCB at time t (h), a_s is the specific surface area of the nanoparticles (m^2/g), and ρ_m is nanoparticle loading (g/L). Assuming discrete spherical particles with a diameter of 30 nm, as observed from STEM imaging, a_s was calculated to be $25 \text{ m}^2/\text{g}$. The nanoparticle loading was determined by dividing the amount of metal loaded on the membrane by the volume of the DiCB containing solution (0.04 L). Based on these assumptions, the k_{SA} value for each membrane was determined to be 0.027 (30.3 mg Fe, 3.6 wt% Pd), 0.020 (17 mg Fe, 3.6 wt% Pd) and 0.011 $\text{L}/\text{m}^2\text{h}$ (17 mg Fe, 1.9 wt% Pd), respectively.

At constant Fe loading, the reaction rate and thus conversion increases with increasing wt% of Pd, as long as all Pd atoms are active sites (less than 1 monolayer coverage); this was also reported previously [30]. For the case when the amounts of both metal loadings are varied but the ratio of Fe:Pd is kept constant, one might expect an increase in conversion with increasing metal loading (and thus higher surface area). This is the case (Figure 7), the membrane with higher loading of Fe^0 (30.3 mg corresponding to 0.75 g/L vs 17 mg or 0.43 g/L) shows higher conversion. As mentioned before, the conversion increases with wt% Pd deposited on the membrane; this also suggests that at constant Fe:Pd ratio, the actual amount of Pd plays an important role in dechlorination. It is interesting to observe that the conversion to biphenyl for a metal loading of 0.75 g/L is close (within 25%) to the one previously reported by us [30], under similar conditions (0.8 g/L metal loading). For that case, the matrix for Fe/Pd nanoparticle formation was prepared using a different methodology, solvent-based acrylic acid polymerization.

3.2.2 Nanoparticle stability and regeneration—Nanoparticle longevity is an important issue, and it was studied previously in solution phase [15] and also with nanoparticles supported on different membrane systems, for dechlorination of a variety of toxic chlorinated organics such as trichloroethylene [28] and trichloroacetic acid [32]. During the dechlorination reaction, there are two main factors that affect the reactivity of Fe/Pd bimetallic nanoparticle systems: iron oxidation and Pd deactivation due to the coverage of the oxide/hydroxide layers. Changes in the reaction media (pH, formation of iron oxide and hydroxide, etc) are less pronounced in terms of catalyst activity in short term experiments (2-3 h). In order to study the stability of the bimetallic nanoparticle system over time, dechlorination studies (9 h cycles) were carried out while deliberately lowering the amount of metal loaded on the membranes (7.8 mg Fe and 0.6% wt Pd) to reduce the reaction rate.

It is known that iron nanoparticles can be protected from corrosion by passivation or coating [10]. In order to study the effect of oxygen and reaction media on nanoparticle stability, two identical membranes were used in long term dechlorination studies. One membrane contained Fe/Pd nanoparticles only while the other was additionally treated with a Fe^{2+} solution so that Fe^{2+} can be incorporated in the membrane by ion exchange. It should be noted that during the preparation of the nanoparticle-loaded membrane Fe^{2+} is first immobilized on $-\text{COO}^-$ from PAA by ion exchange and is reduced (with NaBH_4) to Fe^0 . To maintain electroneutrality,

Na^+ becomes the counter ion on the carboxyl groups and this can be replaced by Fe^{2+} if the PVDF-PAA-Fe/Pd is immersed in FeCl_2 aqueous solution. During this process deoxygenated water was used to prevent nanoparticle oxidation and the pH was maintained between 5.3–5.5, as carboxyl groups must be ionized during ion-exchange. It was shown previously [33] that $\text{Na}^+:\text{Fe}^{2+}$ exchange occurs in a molar ratio of 2:1, as expected from ion exchange principles. The purpose of exchanging Na^+ with Fe^{2+} in the PVDF-PAA-Fe/Pd membrane is to having Fe^{2+} act as an oxygen scavenger, thus reducing the formation of iron oxide and hydroxide layers. The latter may deposit on the particles, reducing the catalytic activity.

The effect of Fe^{2+} treatment can be observed in Figures 8 and 9, which depict the ratio of biphenyl formed to DiCB reacted during the dechlorination reaction and amount of DiCB reacted vs time. In both cases, 9 h cycles were used. During four cycles for both Fe^{2+} coated and uncoated membranes, there is a high nanoparticle activity toward biphenyl formation (in the range from 60 to 80% compared to the amount of DiCB reacted, as shown in Figure 9). Biphenyl is the final product of the dechlorination reaction and monochloro biphenyl is the intermediate (by GC-MS), thus the molar ratio DiCB consumed to biphenyl formed is less than 1. However, in terms of DiCB reacted vs time, it can be observed that for the uncoated (no additional Fe^{2+}) membrane, compared to the initial cycle, the amount of DiCB reacted decreased dramatically to 45 and 10% after the 2nd and 3rd cycles, respectively. For the Fe^{2+} coated membrane, the decrease in performance (amount of DiCB reacted) is much lower.

Another important aspect is membrane regeneration. During the dechlorination reaction, some iron may be oxidized forming an oxide layer that could passivate the nanoparticle. In that respect two main routes can be chosen to convert the oxidized metal to zero-valent state: reduction (using a variety of reducing agents, including NaBH_4 , ascorbic acid, etc) or pretreatment with an acidic solution. The latter dissolves the external oxide layer, cleaning the Fe surface and exposing the active sites (Pd). It was previously reported [15] that for Fe/Pd nanoparticles in homogeneous phase (solution), neither the regeneration with NaBH_4 nor acid treatment did give satisfactory results. It was observed that during the corrosion reaction which takes place simultaneously with dechlorination, iron was released in water and as a consequence Pd could be dislodged when the iron base corrodes. In the membrane immobilized Fe/Pd nanoparticles, the Fe^{2+} is not released in solution, but it is recaptured by carboxyl groups on the membrane (Fe^{2+} was not detected in solution using atomic absorption spectroscopy). For our system the reduction of the spent (oxidized) Fe/Pd nanoparticles was easily achieved by treating the membrane with a solution of NaBH_4 either in soaking or convective flow mode.

For the case of the Fe^{2+} immobilized membrane, the nanoparticle reactivity after four cycles (dropped to about 60% of the initial value) is easily restored to about 85% of the initial value, by reacting with NaBH_4 . This is not the case for the membrane that had not been post-treated with Fe^{2+} where more complex regeneration techniques might have to be employed, such as acid treatment (washing the oxide or hydroxide layers deposited on the membrane). Unfortunately during acid treatment not only oxide/hydroxide is dissolved, but also some of the iron is washed away into the solution phase. The loss of metal can significantly reduce the dechlorination performance.

The reactivity in dechlorination studies (up to 3 h) was tested with four different membranes. The rate of dechlorination decreased from 15 to 20% per cycle, but it could be completely restored by washing the membrane with NaBH_4 .

3.2.3 DiCB dechlorination under convective conditions—The dechlorination reaction was also conducted under pressure (between 0.8 and 4 bars) in convective mode, in which the feed solution containing DiCB was permeated through the membrane, and permeate samples were collected at different times. The membrane was dried with nitrogen prior to carrying out

the reaction in order to ensure that no water (which can dilute the permeate in the beginning of the reaction) is present beneath the membrane.

The PAA gel and thus nanoparticles are also immobilized on both the membrane external area and at the pore mouth. This could result in the product formation at the membrane feed side/solution interface. However, due to the fact that the operation occurs under convective flow conditions, we assumed that once the product is formed at this interface, it will be transported through the membrane. That means, the product will not accumulate on the membrane's feed side. Under our operating conditions (flux in the range from 2.4×10^{-4} to 3.9×10^{-4} cm³/cm² s), no product was detectable in the feed solution. The permeate flux is inversely proportional to the residence time. The residence time in the membrane was calculated as $\tau = V/(AJ_v)$, where V is the membrane volume, A is the external area (13.2 cm²), and J_v is the permeated flux. Also, $V = \epsilon AL(1-\phi)$, where ϵ is the porosity (70% on average, from manufacturer's data), L is the membrane thickness (125 μ m) and ϕ is the fraction of the membrane volume, with no immobilized nanoparticles and it was estimated as explained below.

The nanoparticles are incorporated within the polymeric gel chains, which extend from the pore wall towards the pore center, and the chains do not cover the entire pore volume. The size of the pore volume (channel) unoccupied by the polymer chains will have a significant effect on the kinetics DiCB molecules can freely pass through the membrane without encountering the active site (Pd). As a consequence, there will be no chemical reaction. The size of the channel (49% or 0.49 from the total pore volume), was estimated from permeability measurements for the bare and functionalized membrane. It should be noted that a better pore coverage can be easily achieved by choosing a membrane with a smaller pore diameter as a platform for nanoparticle immobilization.

Figure 10 shows the dependence between the concentration of the product, biphenyl, in permeate and residence time. As expected, the product concentration in the permeate (and thus the DiCB conversion) is proportional to the residence time, and increases from 14 to 43% as the residence time is varied from 23 to 37 s.

4. Conclusions

In this paper, the synthesis of an effective dechlorination system (using green chemistry) that incorporates Fe/Pd nanoparticles into a PAA-coated PVDF membrane, is presented. High active site (Pd) accessibility and fast dechlorination rates at a relatively low metal loading (about one order of magnitude lower, compared to solution phase), are among the major advantages of this method. The dechlorination rates are highly dependent on Pd content. The immobilization of Fe²⁺ on the Fe/Pd modified membrane can increase the nanoparticle stability, making them more suitable for prolonged applications. The ease of nanoparticle regeneration by washing with NaBH₄ constitutes an additional benefit.

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AA – acrylic acid

EG – ethylene glycol, cross-linking agent

KPS – potassium persulfate, initiator

PAA – polyacrylic acid

PVDF – polyvinylidene fluoride

Figure 1.

Schematic for PAA coating and Fe/Pd nanoparticle synthesis in PVDF membranes (green chemistry, no solvent use)

Figure 2.
FTIR-ATR spectrum for bare and PAA-functionalized PVDF membranes

Figure 3.
Effect of cross linking on availability of COOH groups (normalized with respect to lowest cross linking case)

Figure 4. pH effect on pure water flux for PAA-coated PVDF membrane (13.2 cm^2 external area)

Figure 5.
STEM image A) and EDS mapping B) for Fe/Pd bimetallic nanoparticles

Figure 6.
EDS spectrum for bimetallic Fe/Pd nanoparticles

Figure 7. DiCB conversion to biphenyl, within 1 h reaction time in batch mode (pH 6.3), for different Fe/Pd loadings on PVDF/PAA membranes (13.2 cm² external area)

Figure 8.
Effect of Fe^{2+} immobilization on Fe/Pd – modified membrane (13.2 cm² external area)
dechlorination performance in time

Figure 9.
Effect of Fe^{2+} immobilization on Fe/Pd –the nanoparticle reactivity toward biphenyl formation (pH 6.3)

Figure 10.

The concentration of the product in permeate as a function of residence time for convective mode dechlorination (pH 6.3) of DiCB on Fe/Pd membrane 13.2 cm² external area, 125 μm thickness)

Table 1

Pure water flux permeabilities for different functionalization steps at pH 5.9 (13% PAA cross linking)

Membrane	Water permeability (cm ³ /cm ² s bar) × 10 ⁻⁴	Water permeability (cm ³ /cm ² s bar) × 10 ⁻⁴
PVDF	4824	4824
PVDF – PAA – Na ⁺	589.5	654.3
PVDF – PAA – Fe ²⁺	468.7 [*]	604.2 ^{**}
PVDF – PAA – Fe ⁰	4.3 [*]	9.9 ^{**}

PVDF membrane (650 nm pore size, 125 µm thick and 13.2 cm² external area)

* - 10.8 mg Fe immobilized on the membrane (Final mixed matrix membrane, 9.2 wt% and 1.2 vol% Fe)

** - 3.7 mg Fe immobilized on the membrane (Final mixed matrix membrane, 2.0 wt% and 0.4 vol% Fe)