Nanoparticles Embedded Membrane Reactor for the Reductive Degradation of Chlorinated Organics: TCE and PCB Studies.

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Abstract

The use of chitosan as the polymeric material for the synthesis of novel membrane reactor with bimetallic nanoparticles (Ni/Fe, Pd/Fe) is described. The objective of this study is to test the feasibility of the Ni/Fe and Pd/Fe nanoparticles embedded in the chitosan as the mixed matrix membrane reactor in the degradation of chlorinated organics such as trichloroethylene and polychlorinated biphenyl (PCB). The membrane is characterized by conventional methods such as XRD, TGA, and FTIR. Formation of nanosized particles is confirmed by SEM and X-ray energy dispersive analyses. Nanoparticles distribution is found to be uniform on the surface as well as in the porous membrane matrix. HRTEM micrograph showed that the nanoparticles detected by SEM are actually nanoclusters consist of 3 nm to 5 nm particles. Preliminary kinetic studies of chlorinated organics showed that complete degradation is achieved at room temperature using mg quantity of the embedded bimetallic Ni/Fe and Pd/Fe nanoparticles in the chitosan membranes. The catalytic effect of the second dopant metal in the mixed matrix membrane reactor is shown by the significant enhancement in the reaction rate as well as the end products formation of the bimetallic Ni/Fe as compared to Fe nanoparticles. In addition, the leaching of metals is found to be negligible at the end of the degradation reaction. This is due to the chelating effect of the amine as well as the hydroxyl functional groups that exist in the chitosan backbones. Our research showed that the use of mixed matrix membrane consists of nanostructured metals (Ni/Fe, Pd/Fe) is expected to have significant positive impact on pollution remediation through compact and flexible dechlorination technology development with high reaction rates at room temperature, and significant reduction of metals usage as well as improved recovery of precious metals.

Introduction

The unique chemical and physical properties of nanosized metal as compared to their bulk particles have enhanced the use of nanoparticles for optical, magnetic, electronic and catalytic purposes. Polymeric materials have been used in numerous occasions in the preparation of nano-scaled particles due to the presence of specific functional groups on the backbone of the polymer chain. These groups are often ionic in nature or have lone-pair electrons that can served as a chelating agent as well as imposing stabilizing effect on the synthesized nanoparticles.

The use of organic polymers to prepare membranes with embedded nanoparticles possessing catalytic properties is receiving considerable attention. This include the cellulose acetate[1], poly(amide imide)[2], and poly(dimethylsiloxane)[3] with embedded nano catalysts for catalytic dechlorination and hydrogenation processes. Chitosan, poly(β-[1-4]-2-amino-2-deoxy-D-glucopyranose), a biodegradable, non-toxic polysaccharide with hydroxyl and amine functional groups that can be used chelating/ion exchange agent for metal ions has attracted interests in the synthesis of nanoparticles. Literature data have shown that silver and other precious metals such as gold, palladium, and platinum have been successfully coated and stabilized by polymeric chitosan forming nanosized particles[4-6]. These kind of chitosan-supported materials have shown to be active catalytically in numerous studies. Most of these catalytic systems were in the form of beads or flakes supported on silica or zeolites. Yet very few studies were reported on the

use of chitosan in the form membranes with active nanocatalysts embedded in the polymer matrix for catalytic heterogeneous reactions.

In view of the film-forming properties of chitosan and its unique chelating characteristic, studies were conducted to explore the feasible use of chitosan as the polymeric precursor to prepare membrane with embedded nanocatalysts. The main objective of this work is to use the bimetallic Ni/Fe and Pd/Fe nanocatalysts in the chitosan membrane (Ni/Fe-Chitosan, Pd/Fe-Chitosan) for the degradation study of hazardous chlorinated compounds: trichloroethylene (TCE) and polychlorinated biphenyls (PCE). The first part of the study involved the synthesis of chitosan-embedded bimetallic nanocatalysts membrane using the chemical reduction technique by sodium borohydride. The synthesized membrane is then characterized by conventional methods such as electron microscopy (SEM and TEM), X-ray diffraction spectroscopy (XRD), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FT-IR). This is followed by the catalytic degradation study of TCE and PCB using the mixed matrix membrane reactor conducted in the batch and convective flow experiment, respectively.

Experimental Section

Chemicals

High molecular weight chitosan flakes (Mw ≈ 1,000,000 with >75% deacetylation), sulfosuccinic acid (70 wt% in aqueous solution), granular sodium borohydride ($NaBH_4$ = 99.99%), nickel chloride ($NiCl_2.6H_2O$ = 99.99%), palladium (II) acetate ($(CH_3COO)_2Pd$ = 99.98%), silica gel (Davisil® Grade 710, pore size 60 Å, pore volume 0.75 cm^3/g, particle size 4-20 μm), and ethanol (denatured reagent grade) were purchased from Aldrich Chemical Company Inc. Glacial acetic acid (HPLC grade), ferrous chloride ($FeCl_2.4H_2O$ = 102.0), nitric acid (trace metal grade) and deionized ultra-filtered water (DIUF) were from Fischer Scientific. All of the mentioned chemicals and materials were used without further treatment. DIUF were deoxygenated by heating at ~60 ^oC and bubbling with nitrogen gas overnight before used in the study.

Synthesis of Chitosan Membranes

Chitosan-Embedded Nano Fe Membrane with Silica Gel

Chitosan membrane was synthesized by dissolving 1.0 g of chitosan flakes in a 100 ml total volume of 1 vol% acetic acid solution. This is followed by the addition of 1.0 ml of 70 wt% sulfosuccinic acid into the solution. Silica gel was then added slowly into the mixtures and allowed to mix for 30 minutes under intense stirring for homogeneity. 10 ml of 0.18 M Fe^{2+} aqueous solution was added to the chitosan mixture and stirred for 2 hours. Specific amount of the polymer mixture was poured on a petri dish (diameter = 7.5 cm) and allowed to dry overnight in the hood. The dried film was immersed in a 500 ml of 0.4 M $NaBH_4$ solution (pH ≈ 11.0). Intense reaction with bubbling accompanied by the gradual formation of a dark and rigid membrane was observed. Reduction reaction of Fe^{2+} to zero-valent nano Fe and the dissolution of silica gel in alkaline medium continued as the membrane immersed in the BH_4^- solution. This process is repeated twice for a total of 3 hours duration. After the immersion process, the membrane was placed in a pressure cell and filled with 50 ml of 0.4 M $NaBH_4$ (50 vol%

in ethanol). The cell is pressurized to 5.8 bar using nitrogen gas. This second step is to ensure the complete reduction of Fe^{2+} in the membrane matrix to zerovalent nano Fe as the BH_4^- convectively passed through the membrane. This process is also repeated twice with a total volume of 100 ml of 0.4 M $NaBH_4$. Ethanol was convectively passed through the membrane for washing at the end.

Chitosan-Embedded Nano Ni/Fe and Pd/Fe Membrane with Silica Gel

The doping of chitosan-embedded nano Fe membrane with Ni was conducted using 60 ml of 0.50 x 10^{-3} M Ni^{2+} in ethanol solution (Ni^{2+} from stock of 12000 mg/L aqueous solution prepared from $NiCl_2.6H_2O$). The Ni^{2+} was allowed to convectively pass through the membrane in the cell under pressurized condition (5.8 bar). After the doping process, 100 ml of 0.2 M $NaBH_4$ solution (50 vol% ethanol) was added into the cell and convectively passed through the membrane at 5.8 bar. The chitosan-embedded nano Ni/Fe mixed matrix membrane was washed with copious amount of ethanol in the cell followed by rinsing with deoxygenated water. Post coating of the chitosan-embedded nano Fe with palladium was similar as described above. In brief, the membrane in the pressure cell was filled with 6ml of 0.05 x 10^{-3} M Pd^{2+} (550 mg/L Pd^{2+} from palladium (II) acetate) in acetone. The cell was pressurized and post coating of nano Fe with Pd was achieved as the Pd^{2+} convectively passed thorough the membrane. The chitosan-embedded nano Pd/Fe membrane was thoroughly washed with ethanol in the cell. This was followed by rinsing with deoxygenated water.

Methods of Analysis

TCE Analysis

For ethane analysis, head space volume of 0.4 ml was drawn from the reaction vial and injected manually into the sampling port of a cryogenic-capable HP 5890 Series II gas chromatography (column = Supelco–1.4 μm SPB-624) equipped with a Series 6150 mass spectrometer (Hewlett-Packard). Quantitative ethane analysis was conducted by correlation using a five-point calibration curve (correlation coefficient, R^2 = 0.986) constructed by standards obtained from Supelco. For liquid phase analysis, sample volume of 0.4 ml was taken directly from the reaction vial and diluted with 40 ml of DIUF water in another 42-ml serum-seal glass vial. An analytical purge-and-trap instrument (OI, model 4560) interfaced with the Hewlett-Packard 5890 Series II gas chromatography machine was used for the TCE analysis. An internal standard of methylene chloride (0.1 mg/L) was mixed with the diluted liquid sample during the purging stage of the purge-and-trap analysis.

PCBs Analysis

A Varian CP-3800 gas chromatography (column = Varian EZ-Guard capillary column CP-9012) coupled with Varian Saturn-2200 GC/MS was used to measure the concentration of PCB and its degradation products of 2-chlorobiphenyl and biphenyl. For each of the samples collected at different transmembrane pressures and time intervals, 2 ml were added into an 8 ml vial containing 2 ml of hexane for extraction. The vials were clamped to a shaker for 2 hours of extraction process. At the end of the extraction, 1 ml aliquot from the hexane phase was transferred to a 1.5 ml GC autosampler vial. This is followed by the addition of 10 μl of naphthalene d-8 (5000 mg/L in methyl chloride from

Ultra Scientific) as internal standard for the GC-MS analysis. At the end of the degradation study, the used membrane was removed from the convective cell and placed into a 20 ml vial with 10 ml of hexane for membrane phase extraction. The same extraction and sampling procedures described previously was conducted for the membrane's GC-MS analysis. The concentration of PCB, 2-chlorobiphenyl, and biphenyl were correlated using a calibration curve ranged from 0.5 mg/L to 20 mg/L constructed from external standards obtained from Ultra Scientific.

Characterization

ThermoNicolet Nexus 4700 spectrometer was used for FT-IR analysis to detect the presence of functional groups in the membranes. Thin films XRD analysis for all chitosan membranes were characterized using a Siemen diffractometer interfaced with DACO – Kristalloflex using Cu $K_{\alpha 1}$ (λ = 0.1541 nm) as radiation source generated at 40 kV and 30 mA. The membranes thermal properties were evaluated using Perkin-Elmer Thermogravimetric Analyzer (TGA-7**)** interfaced with Pyris Thermal Analysis software Version 7. The total metal loading of Fe and Ni in the membrane was analyzed using Varian Fast Sequential AA Spectrometer (SpectraAA 220/FS) interfaced with SpectraAA V-3.0. The Pd content in the membrane was determined using Varian Vista-Pro Simultaneous ICP-OES machine. High resolution SEM and SEM-EDS analyses were performed by Hitachi S-900 operated at 3 kV and Hitachi S-3200 at 20 kV, respectively. SEM-EDS elemental analysis was conducted using a Noran Voyager EDS detector coupled with Noran Voyager Easy Spectra V-4.2.2 for qualitative and quantitative analyses. A JEOL 2010F FasTEM field emission electron microscopy equipped with EDS detector operated at electron voltage of 200 kV was used to carry out the HRTEM-EDS analysis.

Results and Discussions

Characterization of Chitosan Membranes

FTIR analysis that shows the functional groups in the chitosan membrane with the nano catalysts agrees with the reported results in the literature[7]. XRD analysis showed that the chitosan-embedded nano catalysts membrane has more amorphous hydrated phase than the anhydrous crystalline region than the initial raw materials. The loss of crystalline structure together with the formation of amorphous phase is expected. This is due to the reprecipitation and restructuring of the chitosan after the dissolution in acidic medium as reported in the literature[7]. TGA analysis showed that the thermal property of the chitosan-embedded nanoparticles membrane is slightly better than the raw chitosan membrane. This can be explained by the alteration in the membrane structure with the presence of the nanoparticles. The SEM-EDS analysis showed that the nanoparticles was 30 nm to 70 nm in diameter and homogeneously distributed in the membrane. This is consistent with nanoparticles synthesized by the solution method. It is assumed that the presence of membrane may prevent the aggregation and agglomeration of the nanoparticles during the reduction process.

Batch Degradation Study of TCE

The results of the batch degradation experiments by Ni/Fe-Chi in Figure 1 show the simultaneous conversion of TCE to ethane as the main product. This is consistent with the results obtained in the reported literature using colloidal and membrane-embedded bimetallic Ni/Fe nanoparticles[1, 8-10]. This shows that the bimetallic nano Ni/Fe in the chitosan membrane is catalytically active in the remediation of hazardous TCE. In order to verify that the decrease of TCE concentration in the aqueous phase GC-MS analysis is actually due to the degradation reaction by the embedded nano Ni/Fe and not caused by the sorption of TCE in the chitosan membrane, control experiments using chitosan membrane without the Ni/Fe nanoparticles were conducted. The control study showed that the TCE balance obtained was approximately 96.00 % relative to the initial TCE concentration. Based on the results obtained in the control study, the sorption of TCE in the membrane and the loss due to the volatility of TCE is neglected in the kinetic analysis. Quantitative analysis of the gas phase (Fig.1) shows that the TCE degradation results primarily in ethane formation. The mass balance based on C_2 for ethane analysis is 90.0 ± 2.5 % relative to the initial value of GC-MS analysis.

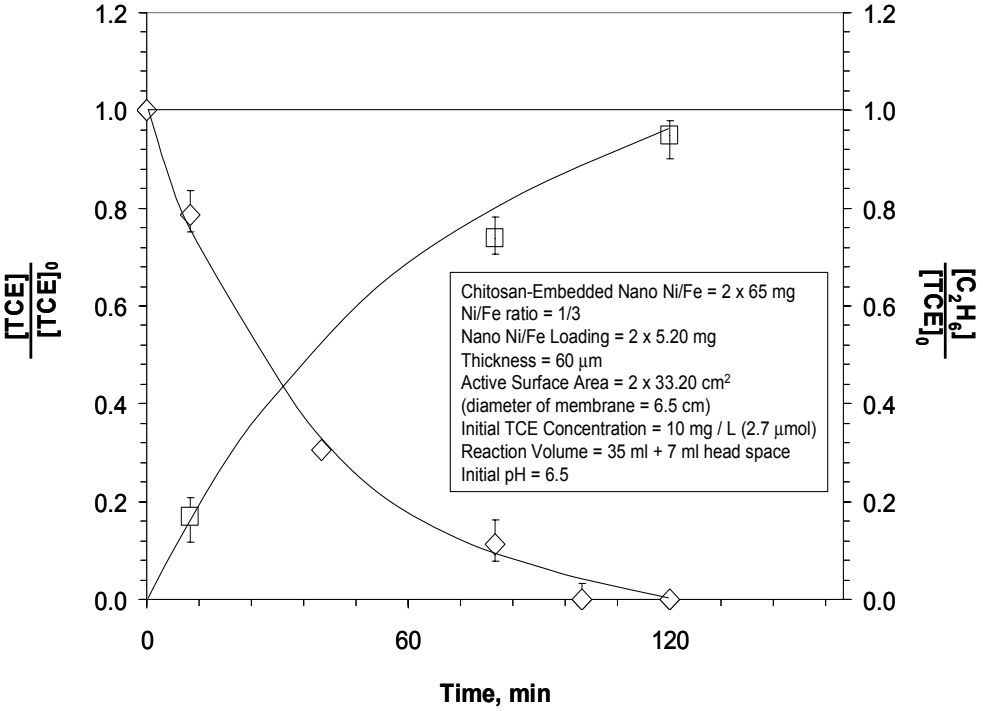

Figure 1. Batch TCE Degradation Study by Chitosan-Embedded Nano Ni/Fe Mixed Matrix Membrane

PCB Degradation under Pressure Induced Membrane Operation

Control study with no Pd/Fe was conducted and the results showed that PCB sorption in the chitosan was approximately 20% (≈ 2 mg/L) of the initial concentration. It is observed that the conversion of PCB to biphenyl increased with the reciprocal of the volumetric flux. As expected, lower volumetric flux (higher $1/J_w$) corresponds to longer residence time of PCB in the membrane phase containing the bimetallic nano Pd/Fe. This

will increase the contact time of the targeted PCB with the catalytically active Pd/Fe and subsequently lead to higher PCB conversion to biphenyl. Up to 80% conversion of PCB to biphenyl was achieved. The conversion of PCB to biphenyl by Pd/Fe was hypothesized to be the hydrodechlorination mechanism where Fe primarily acts as the electron donor to generate the hydrogen needed for the degradation reaction. The hydrogen generated in the iron corrosion process is adsorbed by the Pd and transformed into active hydride in the Pd lattice. The strong reducing agent of active hydride is subsequently used to reductive degrade the adsorbed PCB to biphenyl on the bimetallic Pd/Fe surface.

Conclusions

Nanoparticles of Ni/Fe and Pd/Fe were successfully embedded in the chitosan membrane with exceptional reactive properties. The bimetallic nanoclusters consist of 3 nm to 5 nm particles were found to be homogeneously distributed in the membrane. Rapid TCE degradation rate with the formation of ethane as the main product in the batch experiment study was observed using the chitosan-embedded Ni/Fe nanoparticles. PCB degradation with 80% conversion to biphenyl at low volumetric flux values. This study shows the potential use of chitosan-embedded nanosized metals as novel mixed matrix membranes to achieve environmentally important dechlorination reactions with minimal materials loss by the recapturing/chelating ability of the membrane.

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