Robust nanocatalyst membranes for degradation of atrazine in water

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ABSTRACT

Solid membranes for degradation of emerging contaminants such as atrazine is of significant interest for water engineering applications. In this study, nanocatalyst particles have been anchored on vertically-aligned carpet-like arrays of carbon nanotubes (CNT) grown on porous carbon foams. This hierarchical architecture combines the advantages of highly surface-active nanoparticles with the robust and reusable structural advantage of porous solid membranes suitable for water treatment devices. Three types of palladium-based nano-catalytic surfaces have been investigated: metallic palladium (Pd), Pd nanoparticle with a layer of oxide (PdO-coated Pd), and Pd nanoparticle coated with thin film of silver (Ag-Pd). Their catalytic activities have been compared by analysing the degradation rate of atrazine in water. It is noted that all three catalysts show high levels of atrazine degradation, with the PdO-coated nanoparticles showing the highest kinetics. These results demonstrate that hierarchical hybrid architectures can provide compact and powerful surface-active materials such as adsorbents and catalytic degradation devices in future water treatment applications.

1. Introduction

A wide variety of pollutants have been identified by the United States Environmental Protection Agency (USEPA) as contaminants of emerging concern (CECs) in water, which pose potential threat to environment and public health [1–5]. These come from common industrial products such as detergents, pharmaceuticals, antimicrobial agents, plasticizers, fertilizers, herbicides, and pesticides. Specific compounds include atrazine, bisphenol-A, triclosan, triclocarban, perfluorooctanoic acid, octylphenol, nonylphenol, carbamazepine, and progestron, which can be present in ground water as well as in treated wastewater effluents released into waterways. There is significant need for sustainable and viable approaches of removing, preferable degrading, these contaminants. Potential techniques investigated include adsorption, ozonation, bio-reduction, photo-degradation, electro-catalytic and catalytic methods [6–15].

For any reaction involving heterogeneous catalysts, the available surface area for active catalytic sites and their structural/chemical/electronic states are important variables to consider. It is well-recognized that nanoscale catalysts can provide significant improvements over conventional solids due to their high surface/volume ratios and high chemical activities. However, the widespread use of nanomaterials is limited in real-life applications because of challenges related to their environmental proliferation, reusability, recovery and safety. These issues can be addressed by anchoring catalytic nanoparticles on larger solids, in which case the available surface area of nanocatalyst may be significantly constrained by the morphology of the underlying solid. Our research group has extensively investigated how these limitations can be overcome by durable attachment of functional nanoparticles on bio-mimetic hierarchical membranes that can pack exceptionally high density of surface active nano-catalytic particles into compact space, which can be safely deployed in flowing water [16–22]. A very effective architecture for aqueous environments is a high porosity foam made of inert carbon, which is enriched with strongly anchored carpets of carbon nanotubes that are, in turn, activated with selected catalytic nanoparticles.

In this study, we have used this architecture to build three types of palladium-based nano-catalysts. These have been used to degrade a model emerging contaminant, atrazine. Atrazine, chemically known as 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine or 2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, has a chemical formula of $C_8H_{14}ClN_5$ and a molecular weight of 215.1. Its solubility in water at 20 °C is 30 mg/L. It is a triazine herbicide that inhibits photosynthetic electron transport and is commonly used for controlling the growth of weed on various crops such as wheat, sugarcane, guava, corn, sorghum and a wide range of grasses. It is widely used in the United States, maybe about 64–75 million pounds per year [23,24]. As an herbicide, atrazine is directly applied to the soil during the pre-planting process and, due to its solubility in water, it can easily migrate into the ground and surface waters. Moreover, it has very low natural biodegradability, and persists in the environment once introduced. Due to its potential ecological and health effects, the USEPA has recommended

that the maximum contamination level of atrazine in drinking water should not exceed 3 µg/L or ppb [24,25].

The adsorption of atrazine on adsorbents is not very effective due to its low adsorption ability. It is therefore of interest to treat it using biological, oxidative/reductive, or catalytic techniques, as reported by earlier investigators [10–15]. Reducing agents reported include photocatlytic oxides, zerovalent iron (ZVI), and palladium [10,11,13]. There have been an earlier report [10] of Pd catalyst on polypyrrole-coated cellulose fibers tested on various contaminants in aerobic conditions. It was shown that while some of the other contaminants could be degraded, atrazine was extremely persistent in aerobic conditions. Investigations on electro-catalytic hydrogen-dehalogenation of atrazine using Pd-containing bimetallic catalysts [14] indicate need for certain threshold currents.

In this paper, we have investigated the possibility of using Pd-based nanocatalysts in robust reusable structures to degrade atrazine without any electric field or light activation. Three Nanoparticles tested are: pure metallic palladium (Pd-NPs), palladium oxide coated Pd (PdO-NPs), and silver-coated palladium (Ag/Pd-NPs), each supported on hierarchical carbon supports in the presence of hydrogen (anaerobic conditions). Structural and chemical properties of the hierarchical solid material were investigated using Field Emission Scanning Electron Microscopy (FE-SEM) and X-ray Photoelectron Spectroscopy (XPS) respectively. Liquid chromatography – Mass Spectroscopy (LC–MS) techniques were used to analyse the degradation kinetic rates and intermediate products formed during degradation.

2. Experimental

2.1. Materials and chemicals

The chemical reagents used in this study were of analytical grade and consumed without further purification. These include atrazine ($C_8H_{14}ClN_5$, Sigma Aldrich, Fluka Analytical Pesternal® Analytical Standard 45330), d_5-atrazine ($C_8H_9D_5ClN_5$, Sigma Aldrich, Fluka Analytical Pesternal® Analytical Standard) and 2-propanol (99.9%, HPLC Grade, Fisher Scientific). Teflon-lined butyl rubber stoppers (PTFE-lined) of size 20 mm and aluminium crimp were purchased from Wheaton Inc, and PTFE syringe filters (Supelco©) were used. Other materials include de-ionized water (DI water) and laboratory grade gases that include 5% H_2 balance N_2. The atrazine stock solution of 100 µg/mL concentration was prepared by dissolving 5 mg of atrazine in 50 mL methanol.

2.2. Fabrication of substrates and nano-catalysts

The substrates used in this study are carpet-like arrays of vertically aligned carbon nanotubes (CNT) grown on the surfaces of carbon foam (reticulated vitreous carbon or RVC foams provided by Ultramet). CNT arrays are grown using a two-step technique discussed in earlier publications (16–17). The first step involves microwave plasma deposition of silica film on the porous foam surface. This is followed by thermal chemical vapour deposition (CVD) of carbon nanotube arrays using floating catalyst technique.

These CNT-coated foams are used as supports to grow palladium nanoparticles (Pd-NP) using liquid-phase synthetic approach elaborated in earlier papers [18,19]. This technique involves soaking the CNT-coated substrate in tetra-amine palladium solution, and subsequently heat-treating in three stages: (i) Drying at 100 °C, (ii) Calcination at 400 °C in oxygen deficient inert atmosphere (Ar), and (iii) Final reduction and annealing at 450 °C in reducing environment containing hydrogen in Ar as the carrier gas. This produces base metallic Pd, with average particle size of 10–15 nm. The palladium-oxide coated nanoparticles were prepared by thermally oxidizing the Pd-NPs by heating them in ambient environment at 250 °C for 2 h. The Ag-Pd bimetallic nanoparticles were fabricated by taking the base Pd-CNT-Foam
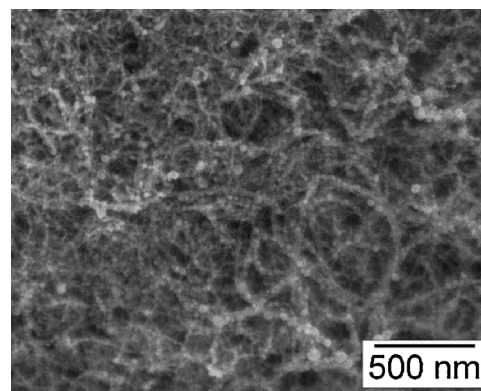

Fig. 1. SEM micrograph of palladium nanoparticles (Pd-NPs) fabricated on CNT-coated RVC foams.

materials and subsequently depositing silver films on them using a liquid phase approach. Deposition of silver was done by infiltrating the CNT-foam supported Pd-NP s with AgNO3 precursor solution and subsequently heating them at 40 °C using dimethyl siloxane (DMS) as reducing agent and sodium citrate as capping agent. More details of the Ag coating process are available in earlier publication [20].

2.3. Batch degradation studies

Catalytic materials compared in this study are (i) RVC foam, (ii) CNT-RVC foam, (iii) Pd-CNT-RVC foam, (iv) PdO-CNT-RVC foam, and (v) Ag-Pd on CNT-RVC foam. They were tested in batch reactors consisting of 160 mL glass serum bottles. The palladium-based catalyst supports (Pd-CNT, PdO-CNT, and Ag-Pd CNT on RVC foams), were rinsed in 2-propanol and water. Subsequently, two samples, each of size Ø 8 mm x 5 mm and total weight ~ 25 mg (total of 50 mg of solid, which contains about 0.15-0.16 mg of Pd) were attached to the inside wall of the serum bottle using double-sided carbon tape. Approximately 80 mL of 5% v/v methanol in Milli-Q water was added to the reactors, maintaining the solution to headspace ratio of 50:50. The pH was monitored using a pH meter every 20 min, and stayed within a slightly acidic range of 6.7-6.9. The reactors were sealed with Teflon-lined butyl rubber stoppers and aluminium crimps and then treated in two ways. In one set of experiments, they were sealed with ambient air. In another set, they were purged with high purity hydrogen-nitrogen mixture (5% H_2 and a balance N_2) for approximately 30 min. Atrazine stock solution was injected into each reactor (initial atrazine conc. = 1 µg mL^{-1} or 4.63 µM; initial atrazine amount = 0.463 µmol in 100 mL) using a gas-tight syringe. The reactors were then placed on an end-over-end rotary shaker at room temperature (60 rpm, 30° inclination). The bottles were placed on the rotator at an inclination such that the solid samples attached on the walls of the reactors remained immersed in liquid-phase at all times during rotation. A blank reactor without any support or catalyst material was also investigated.

Aliquot samples of 2 mL were derived from the bottles using a syringe at specified time intervals (20 min). Samples collected in the syringe at different reaction times were filtered using disposable PTFE syringe filters. Initially, a 1 mL aliquot sample was discarded by running it through the filter in order to saturate the filter and then the remaining liquid sample was collected through the saturated filter in a 2 mL vial for HPLC analysis.

2.3.1. Internal standard – d_5-atrazine

An internal standard was added to the aliquot samples collected in a 2 mL vial for high performance liquid chromatography (HPLC) quantification. In this study, a deuterated atrazine – 'd_5-atrazine' compound was used as an internal standard for atrazine analysis. Stock solution of d_5-atrazine was prepared to obtain the concentration 10 µg/mL in 65%