

Catalytic hydrodechlorination of 2-chlorophenol using viral-templated palladium nanoparticles

An honors thesis for the department of Chemical and Biological Engineering

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Table of Contents

Abstract:.....	3
Introduction	3
Materials and Methods.....	7
Materials	7
Creation of viral template Pd nanoparticle catalysts.....	8
Preparation of Gold Chips	8
Self-Assembly of TMV1cys scaffolds and metallization	8
Demonstration of catalytic activity for chlorophenol hydrodechlorination.....	8
Reaction Conditions	8
HPLC Analysis	9
Calculation of Percent Removal and Apparent Rate Constants	9
Catalyst Deactivation Study	10
Air Stripping Trials.....	10
Temperature Stability Study	10
Results.....	11
Catalyst Preparation	11
Demonstration of Catalytic Activity.....	12
Percent Removal and Reaction Rate Analysis.....	12
Catalyst Deactivation	15
Temperature Stability Study	15
Air Stripping Trials.....	17
Discussion.....	17
Bibliography	19

Abstract:

Chlorinated hydrocarbons are of particular environmental concern due to their toxicity in small quantities and usage in several industrial applications. 2-Chlorophenol is one type of chlorinated hydrocarbon which is used as a pesticide to prevent microbial growth in several industries, including oils, adhesives, textiles, and pharmaceuticals. Current methods of removal either rely on activated charcoal absorption techniques, or use air stripping to force the volatile contaminants into the atmosphere where they are degraded. Both methods are costly and particularly wasteful. Thus, there is an urgent need for robust, inexpensive catalysts for hydrodechlorination reactions which could be used at the industrial scale. Recent investigations have demonstrated the effectiveness of nanoscale palladium at catalyzing the hydrodechlorination of similar contaminants, but cost and stability constraints have prevented their widespread use. This study investigates the catalytic properties of palladium nanoparticles reduced onto genetically modified Tobacco Mosaic Virus nanotemplates. The TMV were self-assembled into high surface area scaffolds on gold chips, and were then coated with palladium using aqueous palladium ions in a reducing sodium hypophosphite solution. The resulting chips were analyzed by atomic force microscopy to determine the surface topology. The chips were placed in a hydrodechlorination reactor with a dilute 2-chlorophenol solution and a constant hydrogen sparge, and the products were analyzed by high performance liquid chromatography (HPLC). The results show that air stripping due to the hydrogen sparge significantly reduces the chlorophenol concentrations in the reactor and inhibits kinetic investigations. Deactivation studies suggest that the catalyst retains its form after reaction, but further analysis is needed.

Introduction

Heterogeneous catalysts have been used extensively in industrial applications to achieve desired products and to minimize the environmental damages caused by potentially dangerous chemicals. Catalyst crackers used in the petroleum industry to maximize yields of short-chain hydrocarbons and catalytic converters used to oxidize carbon monoxide in cars are two examples of such applications. In this study, the use of heterogeneous catalysts as a replacement for absorption techniques traditionally used in the treatment of chlorinated hydrocarbon pollutants is examined. There has been substantial current research on catalyst supports for the treatment of chlorinated hydrocarbon waste. Current pilot-plant ready catalysts are currently using only porous alumina beads coated with thin layers of palladium or other catalytic metals in packed columns (Davie, Cheng, Hopkins, Lebron, & Reinhard, 2008). Although these tests have been successful, they typically use large amount of expensive metals and most likely not economically efficient. Other strategies involve increasing the surface area of the catalyst through the formation and stabilization of nanoparticles, either free in solution or bound to zeolite or porous molecular structures. Because of the hazards of untreated chlorinated hydrocarbons in the environment and the costs currently associated with their treatment, there is a strong driving force for the development of low cost, robust catalysts which can quantitatively reduce the toxicity of chlorinated wastewater pollutants.

Chlorophenol and trichloroethylene are perhaps the two most common forms of chlorinated waste. Trichloroethylene was originally developed as an anesthetic, and thought to be significantly less toxic than chloroform. Although its use and production has been reduced since the development of halothane, derivatives are still used as industrial solvents for everything from greases, solvents, and decontaminants. Chlorinated benzene molecules such as chlorophenol are also typically used as disinfectants and fungicides in the textile industry, as well as for preservatives of organic materials (*Encyclopædia Britannica*, 2009). PCP, or pentachlorophenol, is typically used to preserve wood, leather, or latex products from degradation. Chlorophenol derivatives also enter the groundwater supply readily through use as agricultural insecticides and antimicrobial agents in soaps. Although there have been significant legislation by the EPA and other agencies to reduce the environmental effects of these compounds, they are often considered priority contaminants as effects are frequently seen even at concentrations as low as a few parts per billion (Gomez, Matafonova, Gomez, Batoev, & Christofi, 2009).

There are many well documented health risks associated with contact and ingestion of chlorinated hydrocarbons. Almost all toxic derivatives are hepatotoxic, or cause chemically-driven liver damage. Chlorination typically does not prevent the metabolism of the molecule, which typically leads to the formation of free-radical chlorine molecules. These highly reactive molecules typically form peroxides with polyunsaturated lipid molecules in the cell and lead to free radical chain reactions. Although cells have natural defenses against such unwanted reactions, such as vitamin E and other antioxidants, the hazards from overloading the cell's natural defense system include cell lysis or potentially harmful genetic mutations. TCE is also naturally a central nervous system depressant, and can cause associated short and long term problems in high doses. (Levine & Gresham)

Chlorinated hydrocarbons are particularly potent toxins and disinfectants because they are readily reactive with most other organic compounds. Because chlorine is a poor nucleophile, it easily serves as a leaving group in S_N1 and S_N2 substitution reactions (Solomons & Fryhle). These reactions are often exploited in total organic syntheses, where the first step is often the radical chlorination of small saturated hydrocarbons, followed by the addition of functional groups through substitution and elimination reactions. It is therefore unsurprising that these molecules cause havoc in biological systems, where finely tuned functional group interactions are essential for regulation and metabolism. Despite this reactivity, these harmful chemicals typically persist in ground and wastewater due to the slow rate of biodegradation in oxygen-limited environments (Agency for Toxic Substances and Disease Registry, 2009). However, in the atmosphere chlorophenol is rapidly oxidized and has a half-life of approximately 1 – 2 weeks.

The current study will investigate a new way of creating high surface area catalysts for the hydrodechlorination of 2-chlorophenol using viral templated palladium nanoparticles. In order to discuss the advantages of this technique over other alternatives, current and future methods for 2-chlorophenol removal will be discussed. Most industrial treatment options currently employed to treat chlorophenol and similar hazards do so mostly by removing the more volatile hydrocarbons from the air using air stripping techniques. (Miyake, Sakoda, Yamanashi, Kaneda, & Suzuki, 2003) Often the exhaust gas is released to the atmosphere without further treatment, as the half-life of chlorophenol in air is relatively short. However, the sequestration of chlorophenol can be achieved by using activated carbon filters,

taking advantage of the highly porous nature of the filter to permanently trap unwanted chemicals. However, like all other applications of activated charcoal filters, after the exit concentration of the organic compound of interest passes a certain concentration, the filter must be discarded and replaced. This practice adds a considerable amount of cost and additional waste stream to the remediation process. However, because other treatment options have yet to be adopted by the industry, it is frequently the only option available to companies required to remove chlorinated products from their waste. Conceptually it is a significant energy and resource waste to invest such an effort to treat molecules which are readily broken down in a myriad of possible reactions. Catalysts such as palladium have long been known to effectively catalyze the transformations of chlorinated molecules to much less toxic products, but have yet to be developed into an economically viable treatment solution.

Because most catalytically active metals are very expensive on a gram basis and only effective at high surface areas, extensive research has been made in maximizing the surface area to volume ratio of these metals. In addition to high surface areas, catalysts must be stable, selective, and inexpensive. (Atkins, Overton, Rourke, Weller, & Armstrong) Because of the high surface-area to volume ratio requirement, highly porous solids are often employed. Some traditionally used catalyst supports include γ – alumina and silica gels which are then coated with thin layers of catalyst metals. Although these substances demonstrate a higher surface area to volume ratio than most macroscale structures, it is often possible to obtain better results through the guided deposition of nanoscale metal structures. Zeolites are examples of a more structured approach to displaying catalyst particles. Zeolites are a special form of crystals which form fine structures with large regular channels defined by the structure and interaction of the component ions. Because of their regular pore sizes, zeolites are typically used as molecular sieves, or structures designed to separate molecules based on their size. Because of this functionality, zeolite catalysts typically have excellent selectivity. However, in the wastewater remediation application currently being considered, this functionality is mostly wasted as the catalysts must be able to dechlorinate a range of possible contaminants. It is also possible to use colloidal nanoparticles, which typically have the greatest possible surface area to volume ratio of any catalyst system, and typically demonstrate the best ratio of reaction rate per gram of catalyst. (Nutt, Heck, Alvarez, & Wong, 2006) However, these catalysts frequently encounter problems when used on real wastewater samples, as foreign or unexpected molecules can cause the nanoparticles to precipitate. In addition, development of reactors is difficult as the nanoparticles must be recovered and re-suspended on each end of the process.

An integral part in the development of high surface area catalysts is characterization. A number of techniques exist to determine important information about the physical and chemical properties of a catalyst. Because determining the reaction efficiency for a catalyst is often a time consuming or expensive process, these techniques allow for efficient evaluation and optimization of preparation methods. Catalyst surface area is typically measured using nitrogen adsorption / desorption isotherms. Nitrogen binds to the surface of a metal catalyst through physisorption, and the surface area can be calculated based on an equation developed by Brunauer, Emmett, and Teller, known as the BET equation (Chen, Zhou, Wang, & Zhang, 2009). The equation is an extension of Langmuir theory for unimolecular absorption to multilayer adsorption.

Physical characterization of catalysts can be performed using several microscopy techniques, including atomic force microscopy (AFM), scanning electron microscopy (SEM), and scanning tunneling microscopy (STM). AFM is often the easiest and least invasive technique to perform, as it can be used at ambient conditions without the need to alter or destroy the catalyst. STM is often used when atomic resolution images are required, and can even be used to identify binding patterns of substrates to the surface of the catalyst (Atkins, et al.). However, STM requires smooth catalysts on conductive grids, and therefore cannot be used actual catalyst samples. Chemical properties of the catalysts can be measured using IR spectroscopy to determine acid-base interactions, and x-ray photoelectron spectroscopy (XPS) to determine the surface chemical composition. If the catalyst is a single crystal, traditional diffraction experiments can be used to determine the x, y, and z coordinates of each atom.

In one of the first extended tests of catalytic hydrodechlorination's economic viability and sustainability, a pilot-plant scale reactor filled with palladium-coated alumina packing was installed at the Edwards Air Force Base in Southern California. Wastewater with an average TCE concentration of 1 mg/L was pumped through a 3 m x 16 cm tubular reactor at a rate of 2 gallons per minute. Catalyst deactivation and regeneration was thoroughly studied over a test period of 100 days, and the lifespan of the catalyst packing was predicted to exceed 5 years. Davies et al. calculate the cost associated with such a system to be approximately \$8 (US) per 1000 gallons treated, which is competitive with most other treatment options, although more expensive than air stripping for dilute concentrations of TCE. Because this system uses 2% by weight palladium catalysts, it may be more cost efficient if the techniques used in this study were coupled with newly developed strategies for maximizing the effectiveness of the palladium catalyst.

Chen et al. investigated the catalytic effect of zeolite supported nickel catalysts on the dechlorination of chlorobenzene. Using silica-based hexagonal molecular sieves (HMS), the authors studied the effects of two different methods of incorporating nickel into the mesoporous structures. One method used an impregnation approach where HMS structures were prepared and subsequently coated with nickel, in an approximation of the typical approach used in the development of coated metal structures as seen in the previously described paper. In a second approach, dubbed as direct synthesis, nickel was incorporated into the silica solution before forming the HMS. Because in the former approach (denoted im-4.1% Ni/HMS in figure 2) large nickel particles can clog the pores and reduce catalytic effectiveness, conversions were much lower for the samples produced using the impregnation method. However, the overall conversion for all samples was relatively low.

Hara et al. studied the use of palladium nanoparticles supported by γ -Fe₂O₃ and hydroxyapatite nanocrystallites for the dechlorination of chlorobenzene. The magnetic nanocrystallites are used as catalysts by stirring the particles in the chlorobenzene solution, followed by removal using an external magnetic field. Conversions of over 99% from chlorobenzene to benzene were noticed, and the catalysts could be re-used up to three times without substantial loss in activity. Although their study demonstrates high conversions and re-usability, the design of a steady-state treatment reactor which couples the extraction and regeneration of nanocrystal catalysts would likely be more complicated than a simple plug flow packed-bed column reactor.

Gomez et al. looked at a different approach to the catalytic decomposition of chlorophenol by using photodegradation and biological decomposition. The study used UV light at a wavelength of 222 nm and soybean peroxidase enzyme immobilized on porous glass. The UV excilamp used was able to completely degrade high concentrations of chlorophenol in 5 to 90 minutes, while the enzyme soybean peroxidase was able to remove up to 80% of the initial chlorophenol. The ultimate goal of the research is to combine the use of UV photodegradation with biological treatment, with the former breaking the waste chemicals into less toxic by-products for subsequent biodegradation. This research presents a potentially interesting alternative to traditional transition metal catalyzed hydrodechlorination. Although the costs of treatment in this way would likely be high, it offers the advantage of complete decomposition of the waste molecules.

Although environmental regulations and discontinuation has significantly decreased the impact of several harmful pollutants, in many cases further remediation is necessary. Because traditionally employed techniques are energy and resource intensive, greener alternatives are proving to be both economically and environmentally favorable. The studies described above are examples of developing technologies which should prove to change not only the way chlorinated hydrocarbons are treated, but perhaps increase the efficiencies of most transition metal catalyst applications. The current study investigates the use of genetically modified tobacco mosaic viruses as templates for the deposition of nanoscale palladium particles. The TMV mutants (TMV1cys) were modified to display a cysteine residue on the outside of each coat protein providing evenly spaced sulfhydryl groups as nucleation sites for nanoparticle growth. These biological templates provide an inexpensive and facile method of forming high surface area scaffolds with controlled metallization for catalytic applications.

Specially, the study examined the dechlorination of dilute levels of 2-chlorophenol. Catalyst chips were prepared with TMV1cys and metallized with palladium. Gold chips without TMV, gold chips metallized without TMV, and chips containing TMV scaffolds without palladium metallization were used as controls. Surface topology was determined using atomic force microscopy. The chips were placed in a stirred flask for three hours with 200 ppm chlorophenol and constant hydrogen sparge, and the results were analyzed using high pressure liquid chromatography. The results showed that the contribution by air stripping from the hydrogen sparge outweighed the catalytic activity of the chips, and made calculations difficult. Surface analysis after reaction revealed little change in surface structure with TMV-Pd chips, suggesting retention of catalytic activity. The results will be useful in designing future studies to better understand the reaction kinetics involved with dechlorination reaction.

Materials and Methods

Materials

TMV1cys was grown in the lab by inoculating tobacco plants with genetically modified TMV1cys obtained from Dr. James Culver at the University of Maryland. Gold chips (1000 Å Gold on silicon) were purchased from Platypus Technologies, Madison, WI. All solvents, including acetone, isopropanol, methanol, HPLC grade water, and acetonitrile were purchased from Fisher Scientific, Fair Lawn, NJ. Powdered 99.998% Sodium tetrachloro-palladate(II) was purchased from Aldrich, St. Louis, MO.



Figure 2: Hydrodechlorination reactor. The two needles in each flask are to allow for hydrogen flow in and out of the flask (green and yellow, respectively).

HPLC Analysis

Samples were analyzed by HPLC using a C18 column and a mobile phase of 70% water, 30% acetonitrile (1 mL/min). UV detection was carried out at 275 nm, and spectrums were integrated to find peak area. Standard solutions of 2-chlorophenol and phenol were prepared, with concentrations ranging from 300 ppm to 25 ppm (2-chlorophenol) and 200 ppm to 10 ppm (phenol).

Calculation of Percent Removal and Apparent Rate Constants

2-Chlorophenol removal was calculated by using a standard curve to determine concentrations, followed by using equation 2 to calculate the time dependent percent removal of 2-chlorophenol.

$$\%Removal(t) = \frac{(2Cp(0) - 2Cp(t))}{2Cp(0)} \times 100\%(2)$$

Time dependent concentrations of phenol production were calculated from a phenol standard curve. First-order air stripping kinetics were determined for all three controls and the TMV-Pd catalysts. For samples without phenol production, equation 3 describes the rate of removal of 2-chlorophenol.

$$-\frac{dC_{cp}}{dt} = k_{air}C_{cp}(t)(3)$$

This differential equation was solved and linearized to develop an equation for the air stripping rate constant, k_{air} , shown in equation 4.

$$\ln\left(\frac{C_{cp}(t)}{C_{cp}(0)}\right) = k_{air}t(4)$$

The k_{air} constant was determined from the slope of the line of experimental data. For samples which produced chlorophenol, it was not possible to use the same approach, since chlorophenol was depleted both by air stripping and by reaction with the catalyst. Equation 5 describes the rate of removal of chlorophenol in these systems.

$$-\frac{dC_{cp}}{dt} = k_{air}C_{cp}(t) + k_{rxn}C_{cp}(t)(5)$$

Where k_{air} is the first order rate constant for the air stripping component and k_{rxn} is the first order rate for the catalytic reaction. Solving this differential equation yields equation 6, the time-dependent concentration profile of 2-chlorophenol.

$$C_{cp}(t) = C_{cp}(0) e^{-(k_{air}+k_{rxn})t}(6)$$

However, because it is impossible to separate the rate of air stripping from the rate of reaction from the 2-chlorophenol data alone, k_{rxn} must be determined from the phenol concentration data. From equation 1, the rate of production of phenol is equal to the rate of reaction of 2-chlorophenol, expressed in equation 7.

$$\frac{dC_{ph}}{dt} = k_{rxn}C_{cp}(t)(7)$$

Substituting equation 6 into equation 7 and solving yields equation 8, the time dependent concentration profile of phenol.

$$C_{ph}(t) = \frac{C_{cp}(0)k_{rxn}}{k_{air} + k_{rxn}} - \frac{C_{cp}(0)k_{rxn}e^{-(k_{air}+k_{rxn})t}}{k_{air} + k_{rxn}}(8)$$

Using MATLAB, it was possible to fit parameters for k_{air} and k_{rxn} to the experimental data to find appropriate values for each rate constant.

Catalyst Deactivation Study

Catalysts were studied for possible deactivation by analysis with atomic force microscopy (AFM) to determine surface topology. Scans were performed at 3 μ m and 1 μ m square sizes.

Air Stripping Trials

Reaction conditions were mimicked without the presence of a catalyst chip for solutions of 2-chlorophenol and phenol. Concentrations were measured every hour using an HPLC.

Temperature Stability Study

The TMV1cys chips, both metallized and non-metallized, were subjected to temperatures of 80°C, 110°C, and 140°C for 1 hour. AFM scans were performed before and after to determine if high temperatures disfigured the catalysts.

Results

Catalyst Preparation

Catalysts were prepared by self-assembling TMV1cys on cleaning gold chips, followed by subsequent metallization with palladium. AFM images show the changes in surface topology in each step, shown in figure 3. In the first image, only a smooth gold surface is seen, with slight indentations occurring on the surface. In figure 2, TMVs are scattered on top of the gold, binding to the gold surface and to each other through sulfhydryl bonds. In the third image, the catalyst is complete, with palladium nanoparticles covering the surface of the chip. Of particular note is how the metal particles bind preferentially to the TMVs in the rightmost picture, showing the affinity of the palladium nanoparticles to nucleate on the cysteine residues. Figure 4 shows a three dimensional plot of the TMV1cys-Pd catalyst, showing the roughness of the surface. This roughness is an important benefit, as it greatly increases the available surface area of the chip.

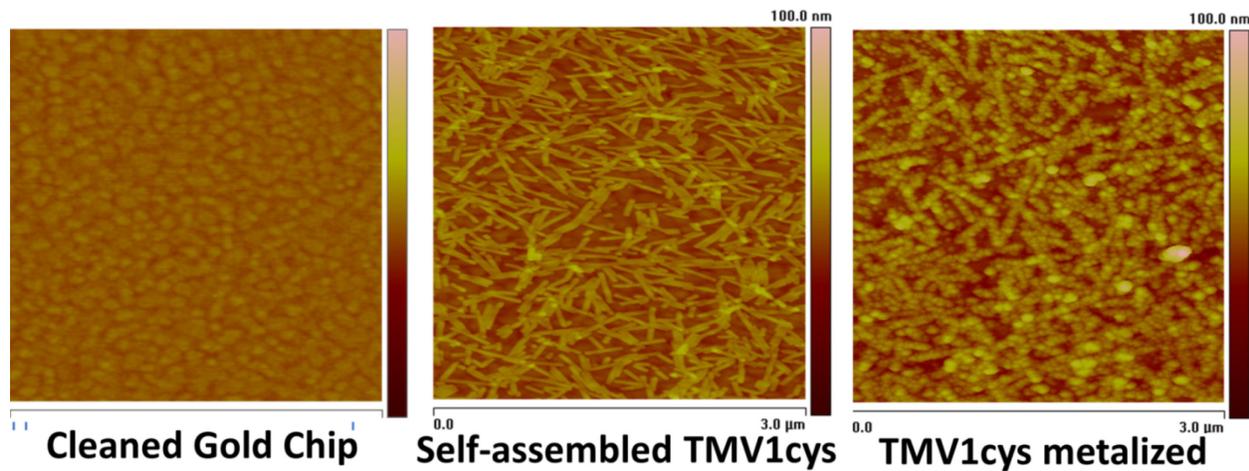


Figure 3: Changes in surface topology in catalyst preparation

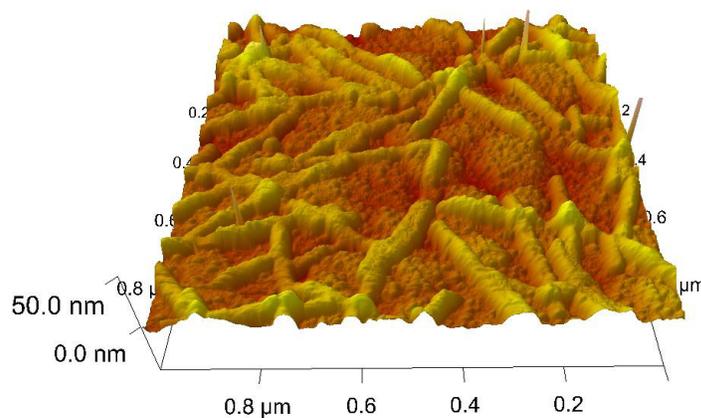


Figure 4: AFM 3d surface map of the TMV1cys catalyst chip.

Demonstration of Catalytic Activity

Catalysts were added to flasks containing 200ppm 2-chlorophenol and a constant hydrogen sparge to determine their effectiveness. Samples taken every hour were analyzed using HPLC, with optical detection at 275 nm. An example chromatogram for the TMV1cys-Pd chip is shown in figure 5. The results show the peaks at each time point. The initial peak is an injection disturbance, and is constant across all samples. The next peak is phenol, and increases with time. The last (rightmost) peak is 2-chlorophenol, and diminishes with time. These results establish qualitatively the effectiveness of the TMV1cys-Pd catalyst.

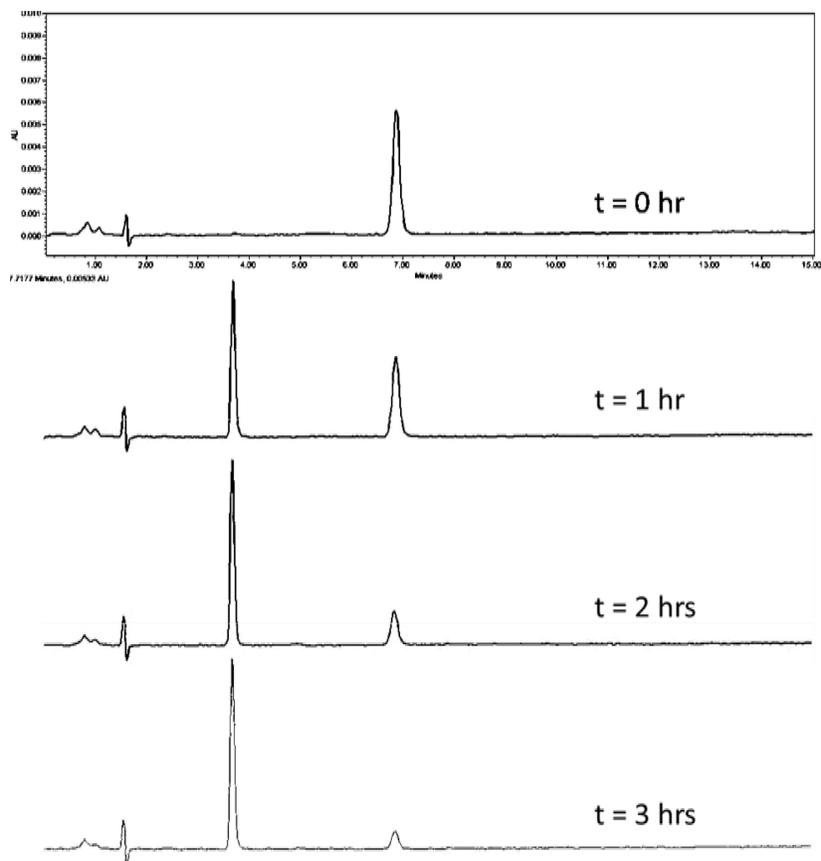
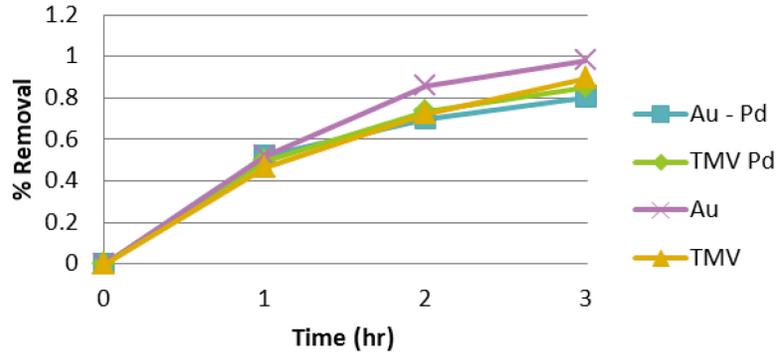


Figure 5: Chromatograms for TMV1cys-Pd sample. Peaks (from left to right): injection, phenol, 2-chlorophenol.

Percent Removal and Reaction Rate Analysis

Standard curves for 2-chlorophenol and phenol stock solutions were prepared by integrating the peak area for known concentrations. Comparison of peak integrations for other samples to these values allowed for quantitative analysis on the reaction kinetics. The results for 2-chlorophenol removal (calculated using equation 2) are shown in figure 6, along with the phenol concentrations at each time point. The chips studied are Au (plain gold chip), TMV (TMV1cys on gold chip, no palladium), Au – Pd (palladium deposited on gold chip, no TMV), and TMV Pd (TMV1cys with palladium nanoparticles).

2-Chlorophenol Removal



Phenol Concentration

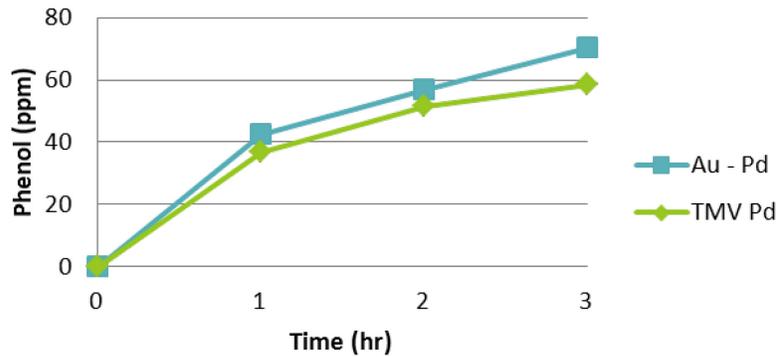


Figure 6: 2-chlorophenol removal and phenol concentration for catalyst and control chips.

The results show that all samples demonstrated a high and similar level of 2-chlorophenol removal. This result is likely due to air stripping of 2-chlorophenol, a volatile compound, by the gaseous hydrogen feed. However, phenol is only seen in chips containing palladium. In addition, the phenol production is slightly higher (although likely within experimental error) in the Au – Pd sample than in TMV Pd. This result indicates there is little advantage in this experiment of the TMV scaffold. However, its beneficial to separate the air stripping kinetics from the reaction taking place, so the controls and catalyst chip can be more accurately compared. To do this, equations 4 and 8 are fit to the experimental data to determine values for k_{air} , the air stripping first order rate constant, and k_{rxn} , the first order reaction rate constant. Plots illustrating the calculation of these rate constants are shown in figure 7 and 8.

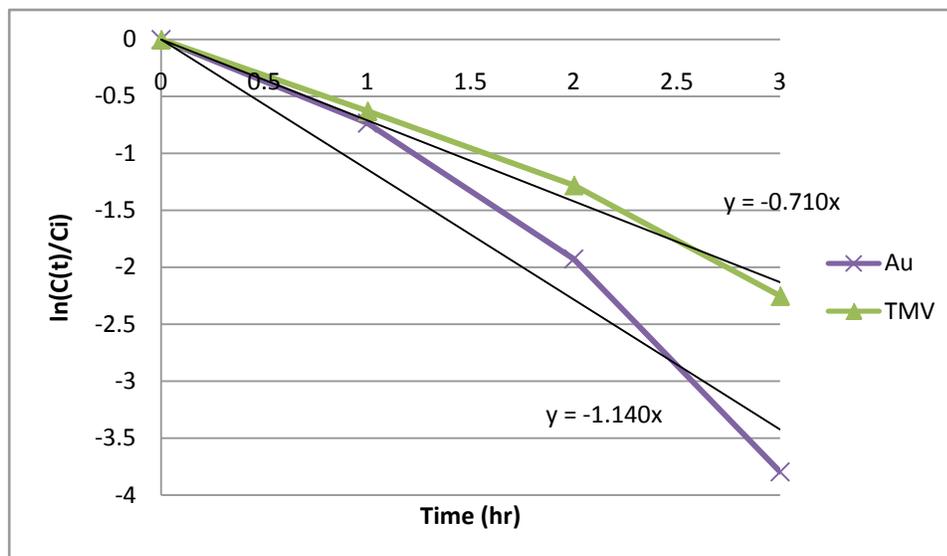


Figure 7: k_{air} calculations for Au and TMV

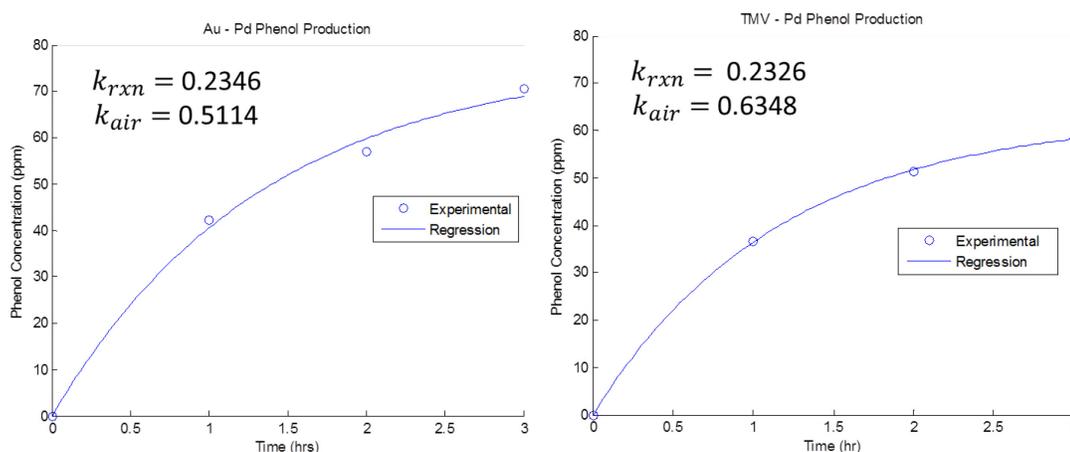


Figure 8(a,b): Left (a) and Right (b), nlinfit for Au – Pd and TMV – Pd (respectively) phenol production to determine k_{rxn} and k_{air} .

Values for k_{air} and k_{rxn} are tabulated in table 1 below. The results show that the k_{rxn} is only present in samples with palladium, showing that palladium is essential to the hydrodechlorination reaction. In addition, the values for k_{air} are smaller for samples with palladium, implying that the presence of palladium inhibits the air-stripping of 2-chlorophenol. This effect is likely caused by surface absorption of the reactants on the palladium nanoparticles. If this is indeed the case, the lower air-stripping coefficient for Au - Pd and Au than equivalent TMV samples may suggest that, after palladium, the 2-chlorophenol binds better to gold than TMV. This is also a reasonable explanation, as although the chemisorption potential of gold is typically fairly low due to its filled 5d orbital, it likely has a higher potential for binding 2-chlorophenol than the proteinaceous TMV capsule. Unfortunately, due to lack of available data, similar air stripping of the phenol was unable to be investigated. This is likely a significant factor and may have altered the calculated constants in table 1.

Table 1: Tabulation of first order rate constants k_{air} and k_{rxn}

Sample	k_{air}	k_{rxn}
Au	0.7101	0
TMV	1.141	0
Au – Pd	0.5114	0.2346
TMV – Pd	0.6348	0.2326

Catalyst Deactivation

TMV-Pd samples were imaged using AFM before and after reaction to determine the extent of deactivation. The results are shown in figure 9. The results show very little change in the surface topology of the catalysts before and after reaction. These results mean that the activity of the catalysts is hopefully not altered appreciably from only one run, which is essential in industrial applications.

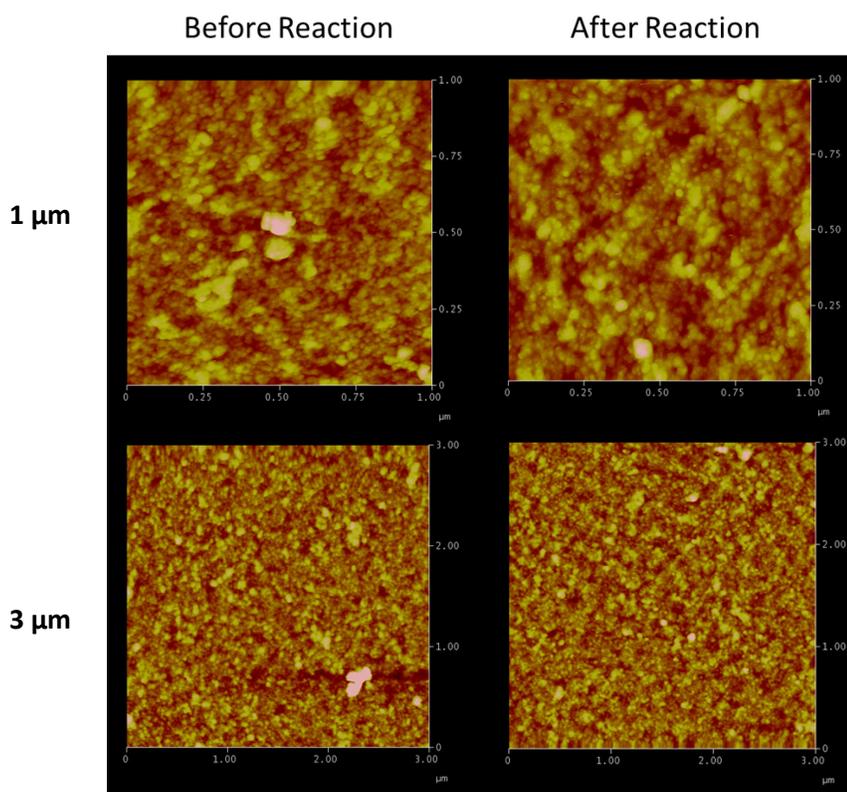


Figure 9: Deactivation of TMV1cys - Pd catalysts

Temperature Stability Study

TMV1cys – Pd and TMV1cys catalyst chips were exposed to 80°C, 110°C, and 140°C temperatures for one hour to determine if high temperatures eliminated catalytic activity. AFM images before and after the temperature study are shown in figure 10. The images show that there is very little difference in surface topology before and after heating, even at temperatures up to 140°C. These results indicate that the catalyst likely retains its catalytic activity, even at high temperatures. This is a good indication for industrial applicability and ability for TMV1cys – Pd to be used for additional reactions which require nanoscale palladium catalysts, even at elevated temperatures.

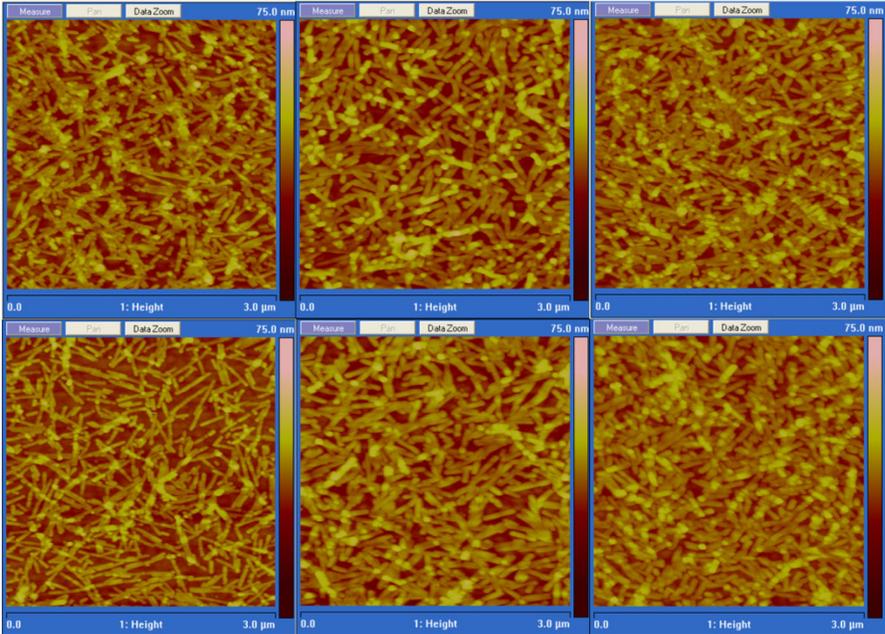
TMV1cys Unmetalized

80°C

110°C

140°C

Before



After

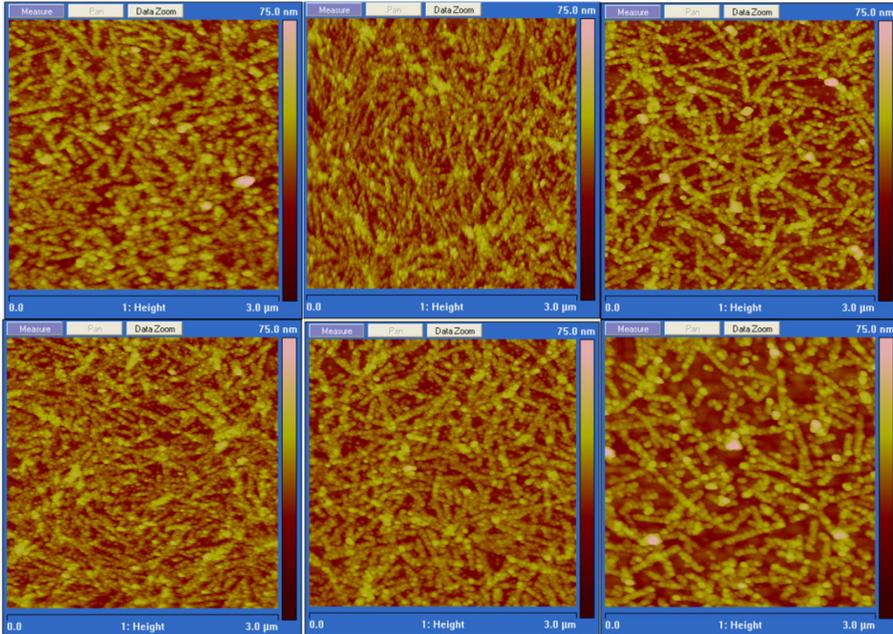
TMV1cys - Pd

80°C

110°C

140°C

Before



After

Figure 10: Temperature Study - TMV1cys and TMV1cys - Pd chips before and after heating at the designated temperature

Air Stripping Trials

Vials were loaded with solutions of chlorophenol and phenol under constant hydrogen sparge to verify if air stripping occurred without the presence of a catalyst chip. Figure 1 shows that over time, the concentrations of 2-chlorophenol decrease significantly, while those of phenol do not. These observations are supported by vapor pressure values of phenol and 2-chlorophenol, found in their respective MSDS's. Phenol which has a vapor pressure of 0.357 mmHg (20°C) is much less volatile than 2-chlorophenol, with a vapor pressure of 2.2 mmHg (20°C). Errors with the HPLC prevented some data points with the phenol sample from yielding results. HPLC results also indicated the presence of trace levels of phenol in the 2-chlorophenol sample, perhaps evidence of hydrodechlorination. These results indicate that 2-chlorophenol is removed from solution more readily than phenol, implying the above rate analysis is justified.

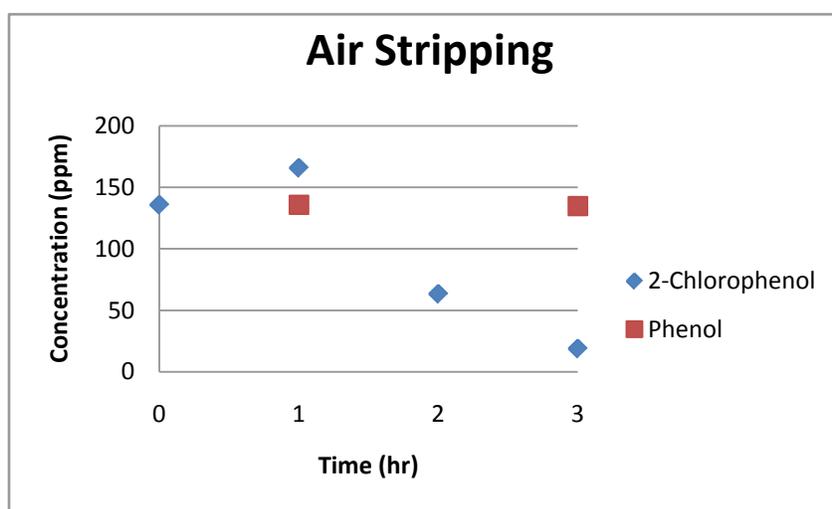


Figure 11: Air Stripping for 2-Chlorophenol and Phenol samples. Time points with significant noise were not displayed.

Discussion

The catalytic activity of the viral template nanoparticles discussed in this study may have a profound impact on the treatment of wastewater contaminated with chlorinated hydrocarbons. Because current methods often use prohibitively expensive levels of palladium, maximizing the activity and stability of the catalyst is essential. The results discussed above constitute a preliminary study of the palladium catalyzed reaction and help point to where further investigation is needed. Primarily, a more fundamental understanding of the rate law associated with the reaction is needed. This could be determined by running additional experiments, such as varying the mixing rate to determine if the reaction is diffusion limited, varying the concentration of 2-chlorophenol and hydrogen to synthesize an appropriate rate law, and varying the reaction temperature to determine the activation energy and pre-exponential constant of the rate constant. In addition, deactivation kinetics must be determined by re-using the same chip multiple times to determine successive reaction rates. In order to more reliably separate the reaction kinetics from air stripping, aqueous hydrogen donors such as sodium formate should be used. This substitution will also allow for a more fine-tuned control of hydrogen concentration during rate studies. Finally, the amount of palladium on the catalyst chip must be reliably determined in

order to compare this method of preparation to the many other alternatives presented in the introduction. TMV1cys – Pd catalysts potentially possess a very high activity per gram of Pd ratio, although further studies are needed to properly understand the reaction kinetics.

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