

**POLYMER NANOCOPMOSITE MEMBRANES WITH HIERARCHICALLY
STRUCTURED CATALYSTS FOR HIGH THROUGHPUT DEHALOGENATION**

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A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Environmental Engineering – Doctor of Philosophy

2016

ABSTRACT

POLYMER NANOCOMPOSITE MEMBRANES WITH HIERARCHICALLY STRUCTURED CATALYSTS FOR HIGH THROUGHPUT DEHALOGENATION

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Halogenated organics are categorized as primary pollutants by the Environmental Protection Agency. Trichloroethylene (TCE), which had broad industrial use in the past, shows persistence in the environment because of its chemical stability. The large scale use and poor control of TCE resulted in its prolonged release into the environment before the carcinogenic risk associated with TCE was fully understood. TCE pollution stemmed from industrial effluents and improper disposal of solvent waste. Membrane reactors are promising technology for treating TCE polluted groundwater because of the high throughput, relatively low cost of membrane fabrication and facile retrofitting of existing membrane based water treatment facilities with catalytic membrane reactors. Compared to catalytic fluidized or fixed bed reactors, catalytic membrane reactors feature minimal diffusional limitation. Additionally, embedding catalyst within the membrane avoids the need for catalyst recovery and can prevent aggregation of catalytic nanoparticles. In this work, Pd/xGnP, Pd-Au/xGnP, and commercial Pd/Al₂O₃ nanoparticles were employed in batch and flow-through membrane reactors to catalyze the dehalogenation of TCE in the presence of dissolved H₂. Bimetallic Pd-Au/xGnP catalysts were shown to be more active than monometallic Pd/xGnP or commercial Pd/Al₂O₃ catalysts. In addition to synthesizing nanocomposite membranes for high-throughput TCE dehalogenation, the membrane based dehalogenation process was

designed to minimize the detrimental impact of common catalyst poisons (S^{2-} , HS^- , and H_2S) by concurrent oxidation of sulfide species to gypsum in the presence of Ca^{2+} and removal of gypsum through membrane filtration. The engineered membrane dehalogenation process demonstrated that bimetallic Pd-Au/xGnP catalysts resisted deactivation by residual sulfide species after oxidation, and showed complete removal of gypsum during membrane filtration.

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ACKNOWLEDGMENTS

To my family, thank you for your unconditional love and support. I would not be where I am without you.

To my advisor, Dr. Volodymyr Tarabara, thank you for guidance and support. Your encouragement, advice, and insight have been and will continue to be invaluable to my successes at Michigan State University.

To my committee members, Dr. Thomas Voice, Dr. Merlin Bruening, and Dr. Rafael Auras, thank you for all of your direction and insight.

To the former and current members of my research group at Michigan State University, thank you for your endless advice, thoughtful discussions, and positive attitudes both in and out of the lab.

To Lori Larnier, Margaret Conner, Laura Taylor, Mary Mroz, Yanlyang Pan, and Joseph Nguyen, thank you for all your administrative and technical support.

To all the sources of funding that have made my research financially possible. The National Science Foundation Partnerships for International Research and Education program under Grant IIA-1243433. The Paul L. Busch award from the Water Environment. Michigan State University, the College of Engineering, the Civil and Environmental Engineering Department, and the Graduate School at Michigan State University.

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CHAPTER ONE

Hierarchical materials as a design concept for multifunctional membranes

1.1. Introduction

We are surrounded by hierarchies that manifest themselves in many ways. Examples abound in both natural and social systems from ethics to government to computer code to biology. Maslow's hierarchy of needs represents an ordered set such that the most pressing need must be met before the next highest need. Democratic systems are organized in a way that all citizens can participate in government by electing representatives at multiple levels from local municipalities to state legislatures to federal legislatures. Computer science employs the principle of hierarchy in object-oriented programming wherein simple objects or data types are elements of more complex data structures. Biology offers a beautiful example of a hierarchy – a DNA molecule – where the complexity order is descended level-by-level from the double helix of biopolymers to nucleotides to nucleic bases to the atoms of which they are made.

“There is plenty of room at the bottom”, speaking to the ability to manipulate matter at such small scales, Richard Feynman famously proclaimed in 1959 and pointed in the direction where the nanotechnology has been heading since the mid-1990s. Indeed, the advantage of such compositional hierarchies may be especially fruitful in

nanotechnology that allows us to manipulate matter at finer scales and lower levels of dimensional hierarchy. This provides the ability to assign to each level in a complex system an autonomous functionality.

In 1963, Loeb and Sourirajan developed the integrally skinned asymmetric membrane¹, a breakthrough in membrane technology that ushered in the commercial use of membranes for municipal water treatment. Asymmetry arises from the ordered hierarchy of pores, where the size of pores in the membrane “skin” are several orders of magnitude smaller than pores in the support layer (Figure 1). The asymmetric design reduces the hydraulic resistance of the membrane while maintaining its rejection capability. Recently, significant advances have been made in the design of nanocomposite membranes that show great promise for drinking water and wastewater treatment by alleviating disadvantages of membranes (e.g. membrane fouling) and enabling efficient membrane-based reactions.

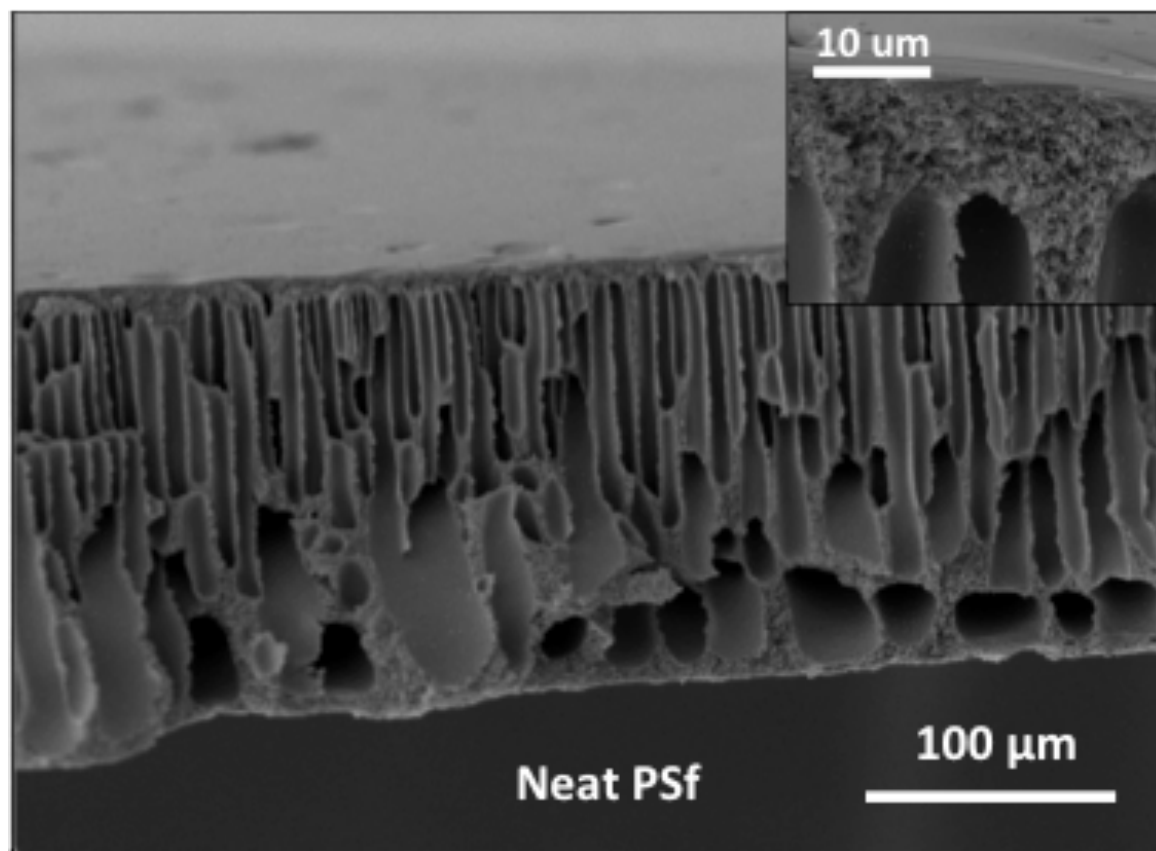


Figure 1: Cross-section of an asymmetric polysulfone membrane fabricated via phase inversion.

This chapter briefly overviews three emerging nanocomposite membrane technologies where hierarchical design of membranes is employed: 1) membranes coated with photocatalytic nanomaterials for hybrid disinfection – membrane filtration, 2) nanocomposite membranes with embedded hierarchical nanocatalysts as catalytic membrane reactors, and 3) superhydrophobic membranes for membrane distillation (MD). The examples illustrate how the hierarchical design of membrane materials can lead to improved separation properties and provide additional degrees of freedom for performance optimization.

1.2. Photocatalytic membranes and membrane reactors

Photocatalytic membrane reactor (PMR) technology combines TiO_2 membranes and UV light to enable concurrent separation and photocatalytic oxidation²⁻⁵. Most of the PMR research work has been on treating chemical contaminants with only several reports available on the application of PMR to pathogen inactivation⁶⁻¹¹. The added photocatalytic function was also shown to improve biofouling resistance of membranes (e.g. TiO_2 imbedded in polyvinylidene fluoride (PVDF) membranes¹²). In the first application of photocatalytic membranes for virus removal and inactivation. Guo et al.¹¹ showed the hybrid photocatalytic microfiltration–UV process was considerably more effective in inactivating the virus than microfiltration and UV disinfection applied sequentially (Figure 2).

Photocatalytic oxidation results when UV light strikes the surface of the catalyst, commonly TiO_2 , resulting in excited electrons and remaining electron-holes. Hydroxyl free radicals formed by holes reacting with water can degrade organic micropollutants and inactivate pathogens complementing the effect of direct UV light. Compared to its bulk counterpart, nanoscale TiO_2 is superior in the production of OH^* radicals (i.e. the photocatalytic oxidation efficiency is higher) due to a larger surface area and the quantum size effect. Consequently, significant efforts have been devoted to the fabrication and application of TiO_2 nanocomposite membranes.

Zhang et al. fabricated freestanding photocatalytic TiO_2 nanowire membranes by exploiting dimensionally different TiO_2 nanowires where separation performance and permeability were determined by the smaller nanowire dimension⁵. Hierarchical porosity, due to the use of nanowires of different diameters, presented additional degrees of freedom for controlling the membrane selectivity, where smaller (10 nm) diameter nanowires provided an excellent separation layer atop the larger (20 nm to 100 nm) diameter nanowires.

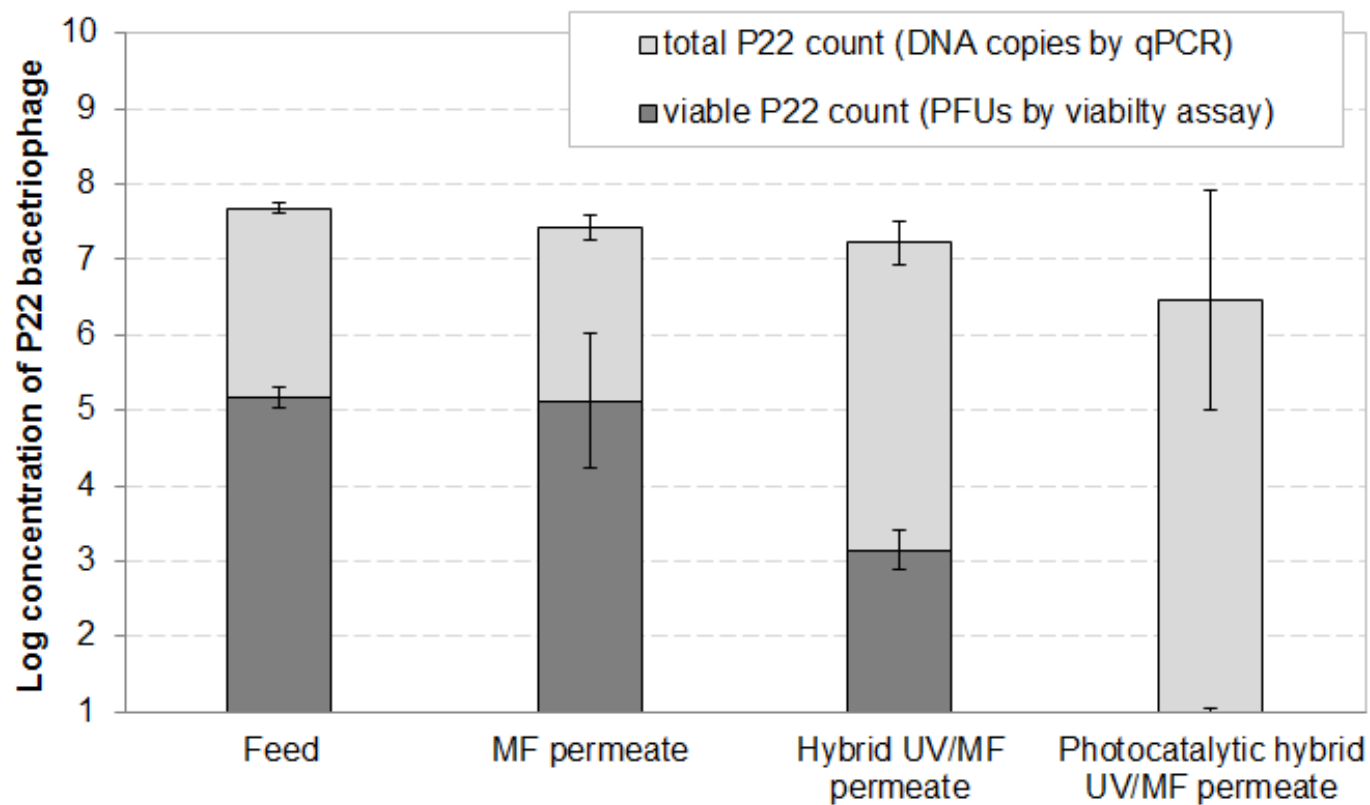


Figure 2: Log concentration of viable and total bacteriophage P22 in the feed solution and in the permeate 30 min into the filtration process. Error bars correspond to standard deviations¹¹.

A challenge in photocatalysis is the recombination of charge carriers (i.e. electron – hole pairs) responsible for redox reactions. Liu and researchers designed a multi-component photocatalyst using TiO_2 and SnO_2 , to prevent or slow down the recombination of electron – hole pairs, where SnO_2 and TiO_2 accumulate photogenerated electrons and holes, respectively¹³. For the overall reactivity to be significantly enhanced, there must be access to both the accumulated electrons and holes, therefore, both TiO_2 and SnO_2 surfaces must be freely available¹⁴. Similarly, Bai et al. fabricated photocatalytic membranes that were fouling resistant and antibacterial using ZnO nanorods grown from TiO_2 nanowires². The additional hierarchy level, ZnO nanorods, improved the photocatalytic performance by increasing the total surface area and reactive sites, and slowing the recombination of charge carriers².

By hierarchically designing photocatalysts and photocatalytic membranes their efficiency can be greatly increased. The hierarchical design can promote UV light scattering, improve separation properties, and minimize the recombination of charge carriers. Importantly, by assigning the separation and photocatalytic functions to different levels in the hierarchy, each function can be optimized separately.

1.3. Hierarchically designed nanocatalysts for catalytic membranes

Small neutral molecules and some important ions such as nitrate, nitrite, and As (V) are rejected relatively poorly even by dense membranes in the nanofiltration and reverse

osmosis range. Consequently, current conventional membrane treatment processes are poor candidates for the removal of these chemicals. By introducing nanocatalysts, however, and in the presence of reducing agents, membranes can be used as flow-through catalytic reactors that efficiently remove these chemicals with concurrent separation.

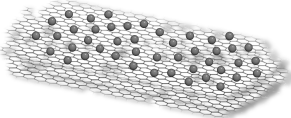
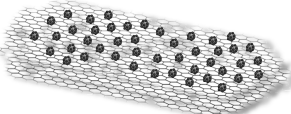
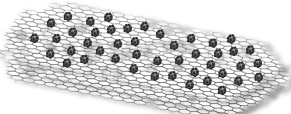
Crock et al. developed catalytic UF membranes by embedding hierarchical nanostructures – nanogold deposited on graphene – in a polymeric membrane, reducing nitrophenol to aminophenol¹⁵. The hierarchical nature of these nanocomposite membranes allowed for membrane optimization, such that graphene largely determined the membrane's separation performance and permeability, and nanogold provided catalytic functionality¹⁵. The same reaction of catalytic reduction of nitrophenol was performed by Wang et al., who used a hierarchically structured membrane wherein gold nanoparticles were attached to vertically aligned carbon nanotube arrays grown on a stainless steel mesh¹⁶.

Nutt and researchers improved the catalytic efficiency of metallic Pd for the dehalogenation of TCE by designing bimetallic Pd-on-Au nanocatalysts that were fabricated in a hierarchical nature¹⁷, where Pd (hierarchy level 1) was the catalyst and Au (hierarchy level 2) was the promoter metal. It was later shown that the degree to which Pd covered Au regulated the efficiency of catalytic TCE reduction, and, additionally, Au completely prevented chlorine poisoning and partially prevented sulfide

poisoning of the Pd catalyst¹⁸. Comparing the bimetallic Pd-on-Au catalyst to Pd catalysts supported on Al_2O_3 the first order rate constant increased from (47 to 1956) $\text{L/g}_{\text{Pd}}/\text{min}^{18}$, respectively. While tests were performed in batch reactors, application of these catalysts in a membrane reactor is promising because the high reactivity should help to negotiate the conflicting demands of throughput and sufficient detection time to complete the reaction.

Catalytic denitrification has been explored using Pd catalysts, but for nitrate to be reduced to nitrite a bimetallic catalyst consisting of a promoter metal and the Pd catalysts must be used¹⁹. The promoter metal can be thought of as level 2 in the hierarchical design of the bimetallic catalyst for denitrification. Catalysts for the denitrification of nitrate and nitrite were fabricated using supported Pd-Cu nanoparticles on PVP colloids²⁰. The Pd-Cu/PVP nanocatalyst can be viewed as consisting of three hierarchy levels: 1) the PVP support, 2) the Pd catalysts, and 3) the Cu promoter metal for the reduction of nitrate into nitrite. The relative compositions of Pd and Cu on the PVP support were manipulated, and it was determined that the highest performing catalysts was a mixture of 70% to 80% Pd and 20% to 30% Cu²⁰. By choosing different supports for Pd-Cu catalysts used in batch reactions, the reaction rate constants were in the (0.061 to 5.12) $\text{L/min/g}_{\text{metal}}$ range²⁰⁻²³.

Table 1: Examples of hierarchical catalysts for catalytic reactions

Catalytic reaction	Reactor type	Catalyst type	Hierarchy level			Reaction rate constant, k_{cat}	Nanocatalyst design	Ref.
			1	2	3			
4-nitrophenol to 4-aminophenol	flow-through	Embedded in Al_2O_3 membrane	Au NPs	-	-	18 $\mu m/s$		15
		Graphene supported; Embedded in polysulfone membrane	Graphene	Au NPs	-	2 - 12 $\mu m/s$		
TCE dechlorination	batch	Unsupported	Au NPs	Pd islands	-	1956 $L/g_{Pd}/min$		17, 18
		MgO supported	MgO	Au NPs	Pd islands	1670 $L/g_{Pd}/min$		
		SiO_2 supported	SiO_2			983 $L/g_{Pd}/min$		
		Al_2O_3 supported	Al_2O_3	Pd NPs	-	47 $L/g_{Pd}/min$		
TCE dechlorination (proposed)	flow-through	Graphene supported; Embedded in polysulfone membrane	Graphene support	Au NPs	Pd islands			
NO_3^- denitrification	batch	Al_2O_3 supported	Al_2O_3	Cu NPs	Pd islands	3.63 $L/g_{metal}/min$		21
		C supported	C	-	-	5.12 $L/g_{metal}/min$		23
		PVP supported	PVP	-	-	0.061 $L/g_{metal}/min$		20
		C supported	C	Sn NPs	Pd islands	6.08 $L/g_{metal}/min$		22
NO_3^- and NO_2^- denitrification (proposed)	flow-through	Graphene supported; Embedded in polysulfone membrane	Graphene support	Au NPs	Cu islands	-		

Exploring the design of nanocatalysts can lead to an improvement in the efficiency of the catalytic reactions. Additionally, by embedding these hierarchically designed catalysts in membranes, catalysis for water treatment is made more appealing by 1) decoupling membrane separation properties and functionality, 2) obviating the need to disperse and subsequently remove catalysts from batch reactors, and 3) improving diffusion limitations of the mass transfer of pollutants to catalysts. Moreover, membrane reactors eliminate the need to dispose of concentrate waste by transforming pollutants to nontoxic compounds, thus increasing the appeal of membrane technology for water treatment.

1.4. Superhydrophobic membranes

Superhydrophobicity results from the combination of appropriate surface roughness features and low surface energy, which can be described by the Wenzel²⁴ and Cassie-Baxter models²⁵. Mimicking natural surfaces such as that of the lotus leaf²⁶, superhydrophobic surfaces have self-cleaning characteristics and may be employed to design fouling-resistant membranes. Due to the low contact area between a water droplet and the superhydrophobic surface, water droplets roll off the surface while picking up surface foulants. The self-cleaning property can be viewed as an “additional function”, and is a strong motivation for using superhydrophobic membranes in a

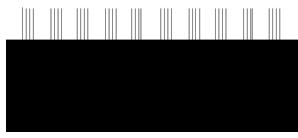
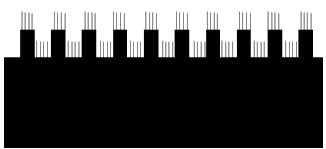
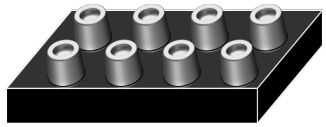
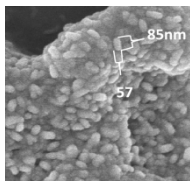
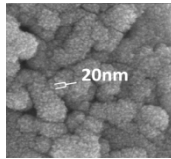
membrane distillation (MD) process where low surface energy and fouling-resistant membranes are required.

Membrane distillation benefits from having lower operating temperatures than conventional distillation technologies. Additionally, waste heat from industrial activities or solar energy can be used as an energy source to bring the feed water to temperatures appropriate for MD, thereby further decreasing energy inputs compared to other distillation technologies for desalination. An ideal MD membrane has straight pores with large pore diameters contributing to high-flux, while also having low thermal conductivity and high fouling resistance²⁷. Superhydrophobic membranes can enhance the MD process by increasing the liquid entry pressure, thus allowing for larger pore diameters, and mitigating membrane fouling. Currently, MD technology is mostly in the lab-scale phase, but there has been some work at the pilot scale²⁸⁻³⁰.

Hong et al. make use of hierarchical roughness features afforded by block copolymer micelles grafted to colloidal silica films making them superhydrophobic where the contact angle can be tuned from (122 to 171)° as a function of nanoscale surface features on silica colloids³¹. Similarly, Razmjou and researchers created hierarchical surface roughness features by coating PVDF membranes for MD with TiO₂, after which the TiO₂ was fluorinated with perfluorododecyltrichlorosilane (FTCS)³². The contact

angle (CA) of these neat PVDF membranes (CA = 125°) decreased to 98° with the deposition of TiO₂ particles that created microscale roughness features, but the PVDF membrane became superhydrophobic (CA = 163°) after fluorinating TiO₂ with FTCS to create nanoscale roughness features on the surface of TiO₂³².

Table 2: Superhydrophobic surfaces designed with surface roughness hierarchy

Morphological features		Contact angle hysteresis (θ_{adv} - θ_{rec}), °	Contact angle CA, °	Surface morphology	Ref.
microscale	nanoscale				
etched fluorocarbon coated SiO ₂ , 4.1 μm	none	8 to 28	156 to 165		33
etched fluorocarbon coated SiO ₂ , 9.5 μm	none	4 to 12	156 to 165		
CNT arrays, ~4.5 μm	CNT array surface roughness	0 to 40	154 to 165		
CNT arrays, ~9.8 μm	CNT array surface roughness	0 to 1	154 to 165		
etched fluorocarbon coated SiO ₂ , ~4.1 μm	CNT array surface roughness	0 to 1	154 to 165		
etched fluorocarbon coated SiO ₂ , ~9.5 μm	CNT array surface roughness	0 to 1	154 to 165		
fluorine coated glass micro-channels	fluorine coated glass nano-spikes	not reported	135 to 165		27
TiO ₂ coated PVDF membrane	none	47	98		32
TiO ₂ coated PVDF membrane	fluorinated TiO ₂ coated PVDF membrane	2	163		

Zheng and researchers used hierarchical roughness features afforded by nanoscale $(\text{CH}_3)_2\text{SiCl}_2/\text{CH}_3\text{SiCl}_3$ filaments on microscale PVDF aggregates to endow PVDF membranes with superhydrophobic self-cleaning properties³⁴. Ma and researchers designed superhydrophobic glass membranes for MD that resisted fouling by etching hollow-cylindrical and spiked arrays onto a glass surface²⁷.

The importance of this hierarchical nature can be described by the decrease in the interface between liquid and solid (f_s), as shown by the Cassie-Baxter model where contact angles approach 180° as f_s goes to 0. Roughening the surface at the microscale decreases f_s by introducing air gaps between the liquid-solid interfaces, but at this scale it is difficult to obtain a stable superhydrophobic surface³¹, where a stable surface could be characterized to have minimal hysteresis. Without nanoscale roughness, a receding drop on microscale roughness features can leave a layer of water behind, increasing the solid interface area³². Öner and researchers showed that the maximum scale for improving hydrophobicity for square roughness features was near $32\text{ }\mu\text{m}$ ³⁵. After introducing nanoscale roughness to the microscale features, a stable superhydrophobic surface can be achieved decreasing the contact angle hysteresis, the difference between receding and advancing contact angles, to less than

¹ 32, 33, 35.

By applying compositional hierarchy to the design of MD membranes, the combination of microscale and nanoscale roughness features (e.g.^{36, 37}) can be adjusted at each hierarchy level (i.e. the microscale and nanoscale) to impart superhydrophobicity, which can 1) increase membrane permeability due to higher LEPs, 2) mitigate fouling due to decreased water-membrane contact area, and 3) enable self-cleaning due to low contact angle hysteresis. These characteristics of MD membranes improve the likelihood of MD becoming a practical water treatment technology.

1.5. Future research

Future research on nanocomposite membranes for water treatment will be focused at the interface of materials science and membrane science. By designing nanocomposites using compositional hierarchy, the efficiency of membrane functionality and the degrees of freedom in membrane fabrication can be increased. Photocatalytic membrane reactors may benefit from multiscale design by optimizing its catalytic and separation functions independently as well by enabling finer control over the geometry of the reaction zone. In membrane reactors for reductive catalysis, incorporating additional levels in the hierarchy and optimizing the combination of the catalyst support, catalyst, and promoter metal can help achieve better catalytic performance. In

membrane distillation, multi-level surface roughness is critical for designing a superhydrophobic membrane surface that resists fouling, and promotes self-cleaning.

CHAPTER TWO

Pd and Pd-Au nanocatalysts supported on exfoliated graphite for high throughput dehalogenation by nanocomposite membranes*

*Published on Feb 22, 2016, *Env. Sci.: Nano*, DOI: 10.1039/C5EN00245A

Abstract

Exfoliated graphite nanoplatelets (xGnPs) are proposed as a support material in the design of hierarchical Pd-based nanocatalysts for reductive dehalogenation. xGnP-supported metallic (Pd) and bimetallic (Pd-Au) catalysts were synthesized and evaluated in experiments on dehalogenation of trichloroethylene (TCE) in batch and membrane reactors. The TCE removal of 96% was achieved with Pd-Au/xGnP-filled membranes operated at the specific permeate flux of 47.4 L/(m²·h·bar). Normalized reactive fluxes in flow-through dehalogenation by membranes with embedded Pd-Au/xGnP and Pd/xGnP catalysts were 14.71 ± 5.96 and 2.56 ± 1.79 (m/s)(M_{H2})⁻¹(g_{Pd}/g_{PSf})⁻¹, respectively. These values were ~80 and ~14 times higher than the normalized reactive flux obtained using membranes with embedded commercial Pd/Al₂O₃ catalyst.

To our knowledge, this is the first report on Pd and Pd-Au catalysts on a graphene-type support for hydrodechlorination and the first demonstration of high throughput TCE dechlorination in a membrane reactor. Determined for batch reactions, the second order reaction rate constants for Pd-Au/xGnP and Pd/xGnP catalysts were $26,309 \pm 6,555$ and $9,975 \pm 9,506 \text{ (M}_{\text{H}_2}\cdot\text{s)}^{-1} \text{ (g}_{\text{Pd}}/\text{L)}^{-1}$. These values were ~ 81 and ~ 31 times higher than the rate constant obtained for the commercial Pd/Al₂O₃ catalyst.

2.1. Introduction

Palladium-based catalysis has emerged as a promising approach to the reactive treatment of recalcitrant water pollutants such as halogenated organics^{38, 39}. However, several technical challenges including low catalyst activity and fouling hinder field-scale applications of this technology. Recent developments in nanocatalyst design for environmental applications have shown that catalyst support is important for highly selective and efficient reactions. Graphene-supported Pd can be an excellent catalyst choice due to its good stabilities in both alkaline and acid conditions and graphene's unique electronic properties where electron shuttling between the support and the metal could improve reactivity⁴⁰⁻⁴³. Other properties of graphene that are purported to explain its very good properties as a catalyst support include accessibility of reactants to active centers due to the graphene's 2D morphology⁴⁴ as well as various specific interactions between reactants and graphene's surface^{40, 45}. Graphene as a support has been shown to increase catalytic activity of Pd in the Suzuki reaction⁴⁶. In the electrooxidation of formic acid and ethanol, graphene-supported Pd had much higher catalytic activity and better stability than commercial Pd/carbon catalysts⁴⁷. In the dehydrogenation and hydrolysis of ammonium borane, graphene-supported Pd was also shown to be more active and stable than commercial counterparts⁴⁸. Adsorption of the reactants to the carbon surface may also be contributing to increased reactivity⁴⁹.

Stacked sheets of reduced graphene, exfoliated graphite nanoplatelets (xGnP) have surface properties very similar to those of graphene, offer high surface area (up to 750 m²/g), and are more affordable than graphene with the expected cost on the order of \$5/pound^{50,51}. Ranging from 2 to 12 nm in thickness and several microns in diameter, xGnPs can be viewed as pseudo two-dimensional nanoplatelets offering the functionality of graphene at a lower cost. In contrast to activated carbon, xGnPs are not microporous; catalytic nanoparticles can be anchored on the xGnP's basal plane making them readily available to reactants. xGnPs have been used as catalyst supports in the past: Lu et al. reported on the synthesis and application of Pt and Pd nanoparticles on xGnPs for catalytic redox reactions involving H₂O₂⁵², while Maiyalagan et al.⁵³ used chemically modified xGnPs as supports for Pd and Pd-Au catalysts in formic acid oxidation. We used xGnPs modified by nanoAu as components of membrane casting mixtures and demonstrated that resulting porous asymmetric nanocomposites were permselective and catalytically active ultrafiltration membranes⁵⁴.

Table 3: Literature data on the reactivity of various Pd-based catalysts in batch dehalogenation of TCE with H₂ as the reducer.

^a Using a Pd content of 41.1 wt%

^b Designed with the optimal Pd content of 12.7 wt%

^c CMC = sodium carboxymethylcellulose

	Promoter	Support	$k_{obs}^{norm}, \frac{1}{\min} \frac{1}{\frac{g_{Pd}}{L}}$	Reference
Pd	-	-	55	Nutt et al., 2006 ⁵⁵
Pd-Au	Au	-	433 ^a and 1956 ^b	
Pd/Al ₂ O ₃	-	Al ₂ O ₃	12.2	Nutt et al., 2005 ⁵⁶
CMC ^c -capped Pd	-	-	828	Liu et al., 2008 ⁵⁷
Bio Pd	-	<i>S. oneidensis</i>	$4.0 \cdot 10^{-4} \pm 3.3 \cdot 10^{-6}$	De Corte et al., 2011 ⁵⁸
Bio Pd-Au	Au	<i>S. oneidensis</i>	$1.3 \cdot 10^{-3} \pm 1.6 \cdot 10^{-4}$	

Optimizing the materials design of catalysts can prevent catalyst poisoning and improve reaction rates. In recent studies, bi- and tri-metallic catalysts for reductive reactions were synthesized and their reactivities were measured^{55, 56, 59-63}. Pd-based metallic and bimetallic catalysts were evaluated by reductively dehalogenating TCE with dissolved hydrogen as the reducer, and in all of these studies a 1st order reaction kinetics model was used to describe the TCE dehalogenation (Table 3). Bimetallic Pd-on-Au nanocatalysts improved the catalytic efficiency due to the Au promoter and were optimized for TCE dechlorination⁵⁶. The extent of coverage of Au nanoparticles by Pd regulated the efficiency of catalytic reduction of TCE and the Au reduced sulfide poisoning of the catalyst⁵⁵. Compared to Pd catalysts supported on Al₂O₃, the Pd-on-Au catalysts with optimized Pd coverage increased the first order rate constant from 47 min⁻¹·(g_{Pd}/L)⁻¹ to 1956 min⁻¹·(g_{Pd}/L)⁻¹⁵⁵. Bimetallic Pd-Fe systems can also be used to catalytically reduce chlorinated organics wherein hydrogen is generated in situ^{62, 64-66}.

Another study successfully applied the Langmuir-Hinshelwood model to quantify TCE reaction kinetics⁶⁷; although more appropriate than simpler models, Langmuir-Hinshelwood kinetics did not apply in our case as the model relies on several assumptions (e.g. constant TCE concentration) that did not hold in the present study.

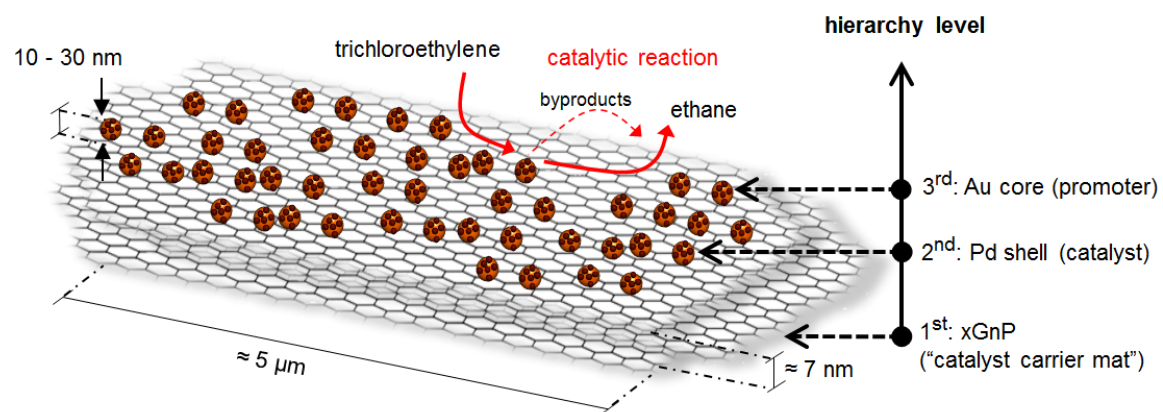


Figure 3: Conceptual illustration of a hierarchical nanocatalyst based on bimetallic (Pd-Au) as catalytic nanoparticles and exfoliated graphite nanoplatelets (xGnP) as the catalyst support. The Pd-Au nanoparticles have core-shell morphology with Au and Pd forming the core and the shell, respectively.

Using membrane reactors for catalysis can be advantageous in several aspects with respect to batch reactors, fixed bed reactors, and upflow reactors. First, in catalytic membranes the diffusional limitation is mitigated due to the small size of pores, and the rate of mass transfer of pollutants to the catalyst surface can be regulated by the rate of permeation⁶⁸. The extent to which the diffusion of TCE inside the membrane pores affects the rate of mass transfer of TCE to the catalyst can be demonstrated by estimating the diffusional distances of TCE as a function of the retention times in ultrafiltration membranes and comparing them to the typical pore sizes of ultrafiltration membranes. If the estimated diffusional distance of TCE is much greater than the typical pore sizes of ultrafiltration membranes, it can be assumed that the rate of mass transfer of TCE to the catalyst is not a limiting factor. The typical retention times, t_{det} , of a dense sublayer in an ultrafilter ranges from 0.2 to 5 s, and the diffusional distance, δ_{diff} , for TCE can be estimated by $\delta_{diff} \cong \sqrt{Dt_{det}}$. Using the diffusion coefficient for TCE, ($D = 8.16 \cdot 10^{-10} \text{ m}^2/\text{s}$ at 25 °C⁶⁹), and the retention times for an ultrafilter, δ_{diff} was estimated to range from 5 to 23 μm . In this regard, membrane reactors hold an advantage over packed bed reactors that contain pores that are several orders of magnitude larger than pores in an ultrafiltration membrane. Second, compared to batch reactors, reactive membranes obviate the need to recover the catalyst. Third, membrane reactors may eliminate catalyst poisoning or fouling by rejecting foulants at the feed-membrane interface. Immobilizing catalysts on various supports prior to

incorporating them into membranes enables better catalyst dispersion throughout the membrane^{54, 70} and may minimize catalyst loss to the permeate flow.

This chapter reports on the preparation of two novel Pd-based catalysts on an exfoliated graphite support for TCE hydrodechlorination (Figure 3). We fabricated Pd/xGnP and Pd-Au/xGnP catalysts and compared them against the commercial Pd/Al₂O₃ catalyst in a batch reactor and when embedded in polymeric nanocomposite membranes in a membrane reactor. To our knowledge, this is the first report on Pd and Pd-Au catalysts on a graphene-type support for hydrodechlorination and the first demonstration of high-throughput TCE dechlorination in a flow-through membrane reactor.

2.2. Experimental

2.2.1 Reagents

Ethylene glycol (EG) (Fluka), sodium hydroxide pellets (Fluka), 20 wt% aqueous solution of poly(diallyldimethylammonium) chloride (PDADMAC) (Sigma Aldrich), palladium chloride (PdCl_2) (Sigma Aldrich), and gold (III) chloride trihydrate ($\text{HAuCl} \cdot (\text{H}_2\text{O})_3$) (Sigma Aldrich) were used for Pd and Au nanoparticle synthesis.

Hydrogen (99.9% purity) and nitrogen (99.99% purity) gases were used to saturate TCE feed solutions. Pd on alumina (5wt% Pd) (Sigma Aldrich), and TCE (Sigma Aldrich) were used as received.

2.2.2. Synthesis of Pd/xGnP and Pd-Au/xGnP nanocatalysts and nanocomposite membranes

All chemicals were used as received. Exfoliated graphite nanoplatelets (grade M; XG Sciences) were used as a support for Pd and Pd-Au nanoparticles. The nanoplatelets were ~ 7 nm thick with the average diameter of $5 \mu\text{m}$ and surface area in the 120 to 150 m^2/g range. Pd and Pd-Au nanoparticles on the xGnP support were fabricated by thermal reduction using polyol synthesis with ethylene glycol (EG) as a reducing agent.

2.2.2.1 Au/xGnP fabrication process

To make Au/xGnP, 50 mg of xGnP was added to a mixture containing 50 mL of EG and 1 mL of a 20 wt% aqueous solution of polydiallyldimethylammonium chloride and dispersed in a sonication bath for 12 h. Next, 150 μ L of 1 M NaOH and 50 μ L of 500 mM H₂AuCl₄ were added to the xGnP suspension. NaOH was used to adjust the pH, which has been shown to control the size and morphology of the resulting Au nanoparticles⁵⁴. The suspension was mixed and heated to maintain its temperature at 195 °C (near the boiling point of EG, 197 °C) for 30 min. Finally, Au/xGnP nanoparticles were removed from EG by centrifugation, washed with acetone 3 times, and allowed to dry overnight in an oven at 100 °C.

2.2.2.2 Pd/xGnP and Pd-Au/xGnP fabrication process

To make Pd/xGnP and Pd-Au/xGnP, 50 mg of neat xGnP (or Au/xGnP) was dispersed in 18 mL of EG in a sonication bath (Aquasonic 50T, VWR Scientific) for 12 h. Next, 2 mL of 22.5 mM Pd precursor solution was added to 18 mL of the xGnP suspension in EG and stirred for 2 min. To reduce the precursor to Pd nanoparticles on the xGnP (or Au/xGnP) surface, the stirred suspension was microwaved for 50 s (900 W, 2450 MHz). Finally, Pd/xGnP (or Pd-Au/xGnP) nanoparticles were removed from EG by

centrifugation, washed with acetone 3 times, and allowed to dry overnight in an oven at 100 °C.

2.2.2.3 Characterization of Pd/xGnP and Pd-Au/xGnP catalysts by TEM, S-TEM, and S-TEM EDS

Transmission electron microscopy (TEM) imaging and scanning-TEM (S-TEM) energy dispersive X-ray spectroscopy (EDS) mapping were performed using a JOEL 2200FS microscope. Nanoparticle specimens were prepared by dispersing nanoparticles in acetone (~0.01 wt%). The nanoparticles were dispersed by bath sonication and a drop of nanoparticle suspension was placed on a 300-mesh nickel or copper grid. The grid dried for 24 h at 90 °C prior to TEM imaging and S-TEM EDS mapping. The Pd and Au contents were quantified using an atomic absorption (AA) analyzer (Perkin–Elmer 1100).

2.2.3 Preparation of nanocomposite membranes filled with Pd/xGnP and Pd-Au/xGnP catalysts

The procedure for casting polysulfone (PSf) nanocomposite membranes filled with Pd/xGnP and Pd-Au/xGnP was similar to the one described previously⁵⁴. Briefly, membranes were prepared using a combination of wet and dry phase inversion. The relative concentrations of N-methyl-2-pyrrolidone (NMP) (70 wt%), PSf (15 wt%), and

PEG400 (15 wt%) of the casting mixture were the same for all membranes. The loading of Pd/xGnP or Pd-Au/xGnP in the membrane was 2 wt% of the PSf content while the loading of Pd/Al₂O₃ was 10 wt% of the PSf content. The higher catalyst content for Pd/Al₂O₃ was chosen in order to enable TCE dechlorination in the membrane reactor.

The membrane preparation procedure included the following six steps:

- 1) Supported nanocatalysts were dispersed in NMP and sonicated for 2 h in a bath sonicator (model 50T, VWR Aquasonic).
- 2) PSf and PEG400 were added to the dispersion of xGnP-supported catalyst in NMP and the resulting mixture was stirred at 60 °C for 24 h.
- 3) The resulting mixture was cooled to room temperature and then cast onto a glass substrate using a film applicator (model 3570, Elcometer).
- 4) The cast film was exposed to air to allow NMP to evaporate for 30 s and then immersed into a water bath at room temperature.
- 5) After phase inversion was complete (as manifest by the separation of the cast film from the glass substrate) residual NMP was removed from the membrane by rinsing it with DI water for 5 min. The membrane was then soaked in DI water for 24 h to ensure complete removal of NMP.

After soaking, the water was exchanged and the membrane was stored wet at 4 °C until further use.

2.2.4. TCE dechlorination experiments

Before dechlorination experiments, controls were run to ensure that hydrogen would not leak from the batch reactor vessel and flow-through reactor feed vessel. This was done by monitoring the hydrogen concentration for 6 h in both reactor vessels, and no measureable loss of dissolved hydrogen was detected with an aqueous H₂ concentration of 0.8 mM.

2.2.4.1 TCE dechlorination experiments: batch reactor tests

Nanocatalyst reactivity for TCE dechlorination was first characterized in zero-headspace batch reactor tests. Serum vials were completely filled with 108 mL of high purity water ($> 10 \text{ M}\Omega\cdot\text{cm}^{-1}$), and the water was purged of dissolved oxygen by bubbling nitrogen gas (99.99% purity) through the water with a ceramic frit for 15 min. Because dissolved oxygen competes with TCE for H₂ it was important that all dissolved oxygen was removed, and this competition should not depend on the source of H₂. After removing dissolved oxygen, 1.25 mg of either Pd/xGnP or Pd-Au/xGnP nanoparticles, or 64 mg of

Pd/Al₂O₃ were added to the vial. The different catalyst concentration of Pd/Al₂O₃ was chosen in order to enable measurements of TCE concentration by gas chromatography. The solution in the vial was saturated (0.8 mM) with H₂ gas (99.9% purity) for 15 min at room temperature under atmospheric pressure and sealed with a Teflon septum and crimp cap. Injecting 1 mL of 1000 mg/L stirred aqueous solution of TCE started the reaction. The batch reactor was magnetically stirred. Each sample withdrawn from the reactor was passed through a 0.22 µm syringe filter to remove the catalyst and terminate the reaction. The extent of TCE reduction was measured by gas chromatography with an electron capture detector (see Supplementary Material (SM), section S1, for details). Control experiments were conducted without H₂ and it was shown that there was no observable adsorption of TCE on xGnP (see SM, Figure 8).

2.2.4.2 TCE dechlorination experiments: flow-through tests with a membrane reactor

Flow-through dechlorination experiments were conducted using a dead-end filtration system (Figure 4) that included a stirred filtration cell (model 8050, EMD Millipore), stirring plate, mass balance, stainless steel pressure vessel, and hermetic plastic bladder (High Sierra). An H₂ sensor and signal amplifier were used for H₂ monitoring. To avoid exposure of the H₂-saturated feed solution to the atmosphere and to the inner

surface of the pressure vessel, the solution was poured into a hermetic bladder, which was then placed inside the pressure vessel and pressurized while still hermetically sealed. Testing of the bladder for H₂ leakage showed no loss of H₂ and over a period of 6 h. The reactive loss of TCE should stem only from the reaction within the intrapore space of the membrane. That is because the loose ultrafiltration membranes (MWCO ~ 90 kDa) used in this work should not reject TCE and there should be no TCE concentration boundary layer at the feed face of the membrane surface. The concentration of dissolved H₂ was determined using an H₂ electrode microsensor and a picoampere-range amplifier (Unisense H2-NP).

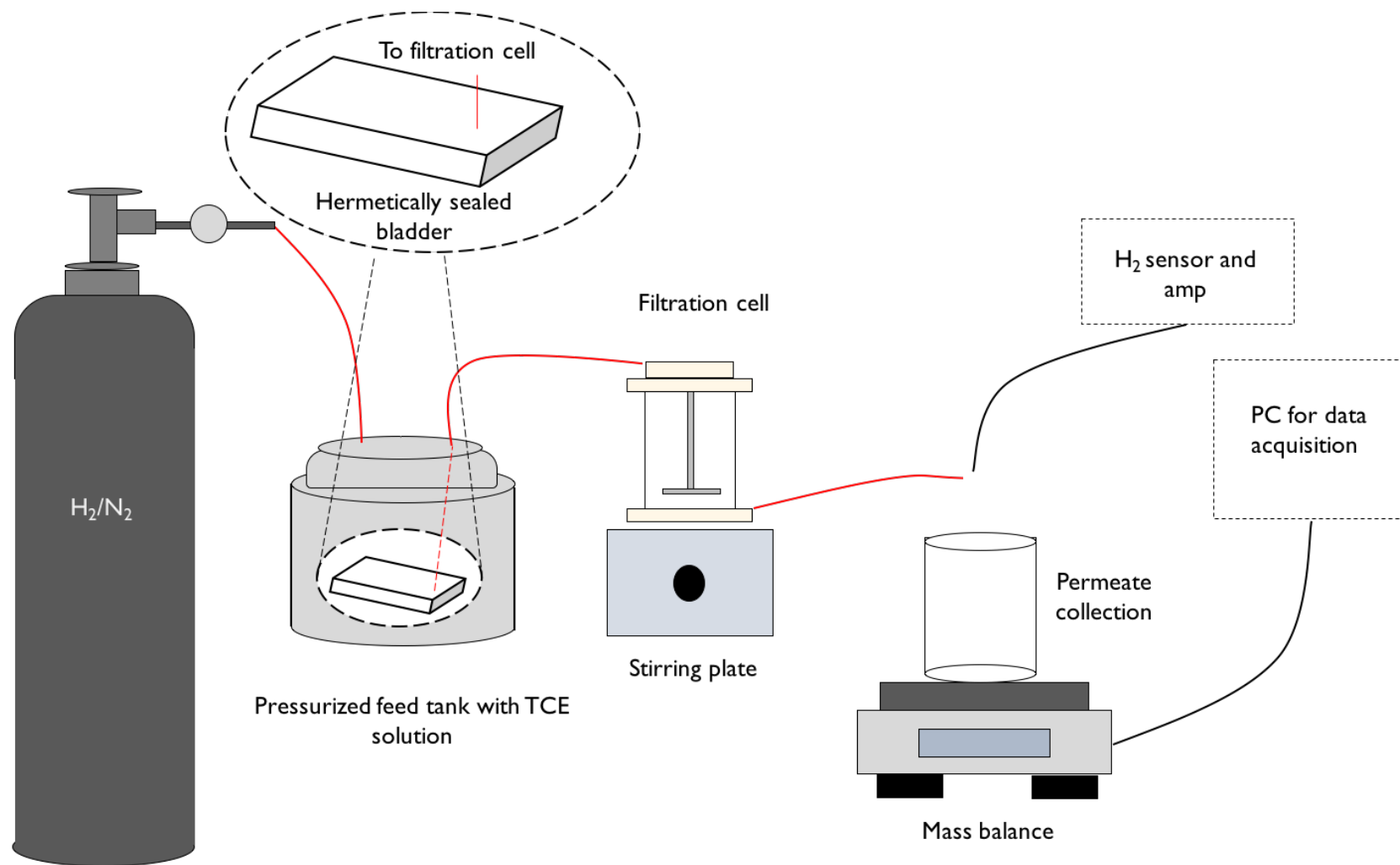


Figure 4: Schematic of the dead-end filtration system used in TCE dechlorination experiments.

Prior to measuring membrane reactivity, membrane adsorption capacity was exhausted by filtering a 9.25 mg/L TCE solution in the absence of reaction. Then, the reactivity was determined in ultrafiltration of a 9.25 mg(TCE)/L feed solution saturated with hydrogen. A survey of literature showed that TCE was typically found in groundwater at concentrations of mg/L⁷¹; the specific value (9.25 mg/L) was chosen on the basis of the preliminary screening study to determine an appropriate concentration of TCE. The determination of catalytic activity included the following steps:

- 1) 1 L of DI water was added to a plastic bladder (High Sierra) and purged with N₂(g) for 15 min.
- 2) 10 mL of 1000 mg/L TCE solution was added to N₂-purged water in the bladder, all headspace was removed, and the bladder was sealed.
- 3) The bladder was placed in a 5 L stainless steel pressure vessel (Alloy Products); the vessel was pressurized and the TCE solution was filtered through the membrane in four steps with a different transmembrane pressure at each step: 40, 30, 20, and 10 psi. The details of how the reaction rate constant for the membrane reactor can be calculated based on the results of tests with different transmembrane pressures can be found elsewhere⁵⁴.
- 4) Step 3 was repeated, except that the N₂-purged water was saturated with hydrogen prior to the addition of the TCE solution, and the aqueous hydrogen concentration was monitored in the permeate using an H₂ electrode microsensor

and a picoampere-range amplifier. The permeate was collected in glass vials that were then sealed with Teflon lined septa.

- 5) TCE concentration in permeate samples was determined using gas chromatography.

2.3. Results and Discussion

2.3.1. Pd/xGnP and Pd-Au/xGnP nanocatalysts

We evaluated several approaches to the preparation of xGnP-supported Pd and Pd-Au nanocatalysts. The most active bimetallic catalyst resulted from a hybrid procedure that combined features of two previously reported techniques^{54, 72}; the procedure included two steps: 1) decoration of the xGnP support by Au nanoparticles using thermal reduction in an oil bath, followed by 2) deposition of Pd via microwave-assisted thermal reduction. TEM images of catalyst-modified xGnPs show that most (~87%) Pd nanoparticles were in the 5 nm to 10 nm size range and that most (~85%) Pd-Au nanoparticles were in the 10 nm to 30 nm size range (Figure 5). Both metallic and bimetallic nanoparticles were distributed over xGnPs with minimal surface aggregation (see SM, section S7, for size distribution details). EDS showed that both Pd and Au were present on the xGnP support with relative atomic concentrations of 60% and 40%, respectively, and AA spectroscopy corroborated the EDS data (see SM, Figure 8, Table 5). S-TEM EDS mapping was employed to further probe the morphology of the Pd-Au nanoparticles anchored on xGnP supports and elucidate the relative distribution of the two metals in the catalyst particles. The mapping pointed to the “core-shell” morphology with Au forming the core and Pd forming the shell, where the relative strength of the Pd

signal is weaker in the center and stronger on the periphery while the Au signal is weaker on the periphery and stronger in the center of the particle (Figure 5). This morphology is expected based on the sequence of steps in the catalyst preparation procedure (i.e. formation of Au nanoparticles followed by Pd deposition). Because of the semi-quantitative nature of the S-TEM EDS technique, it was not possible to determine what shell and core thicknesses were and whether the shell was a continuous layer of Pd or “islands” of Pd decorating the Au core.

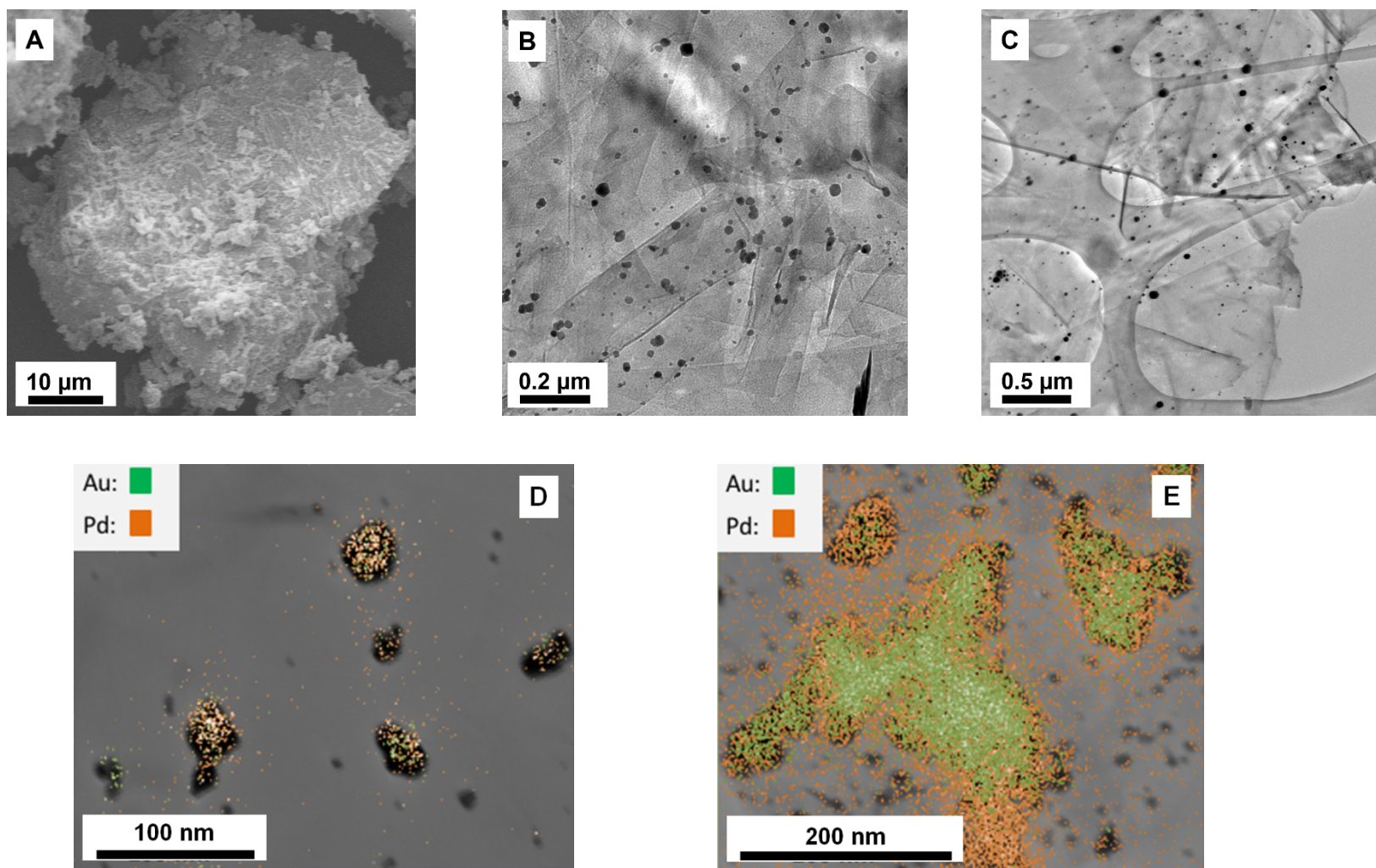


Figure 5: SEM (a), TEM (b, c) and S-TEM (d, e) images of the catalysts: (A) commercially available Pd/Al₂O₃ (Sigma-Aldrich); (B) newly synthesized Pd/xGnP; (C, D, E) newly synthesized Pd-Au/xGnP. The mapped distributions of Pd and Au (D, E) are representative of all Pd-Au/xGnP particles probed by S-TEM EDS.

In our previous work on Au/xGnP catalysts embedded within membranes of the same formulation¹⁵, we showed that the catalyst is homogeneously distributed within polymeric UF membrane matrix. Because the catalysts are morphologically indistinguishable, Pd/xGnP and Pd-Au/xGnP should also be distributed homogeneously. Additionally, the xGnPs have a micrometer diameter; therefore, the nanoplatelets span multiple pores in the membrane and are secured in the polymer matrix.

2.3.2. Kinetics of catalytic dehalogenation of TCE in batch reactors

The catalytic reactivity of Pd/xGnP and Pd-Au/xGnP was first characterized in experiments on the reduction of TCE in a batch reactor. The concentration of H₂ decreased according to 1st order kinetics (see SM, Figure 12):

$$[H_2] = [H_2]_0 \exp(-\kappa^{batch} t) \quad (1)$$

where κ^{batch} (s⁻¹) is the reaction rate constant. For example, the average value of κ^{batch} in tests with Pd-Au/xGnP catalyst was 3.43·10⁻³ s⁻¹. Because of the decomposition of H₂, the TCE reaction data fit a 2nd order model (see SM, Figure 10) better than a 1st order model, and 2nd order reaction rate constants were extracted for Pd/Au, Pd/xGnP, and Pd/Al₂O₃ catalysts. We note that in all prior studies TCE dechlorination was modeled as a 1st order reaction⁵⁵⁻⁵⁸ (Table 3) making direct comparison with our data on 2nd order kinetics not possible. The decay of H₂ may also depend on the

concentration of TCE, but we did not test for this dependency. The batch process was modeled as a 2nd order reaction in an ideal reactor:

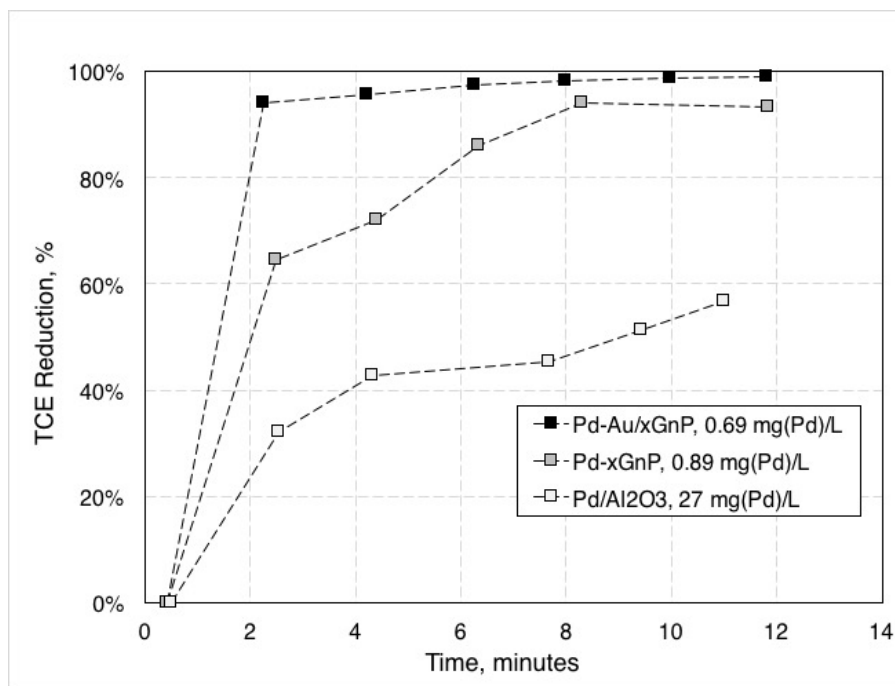
$$\frac{d[TCE]}{dt} = -k_{obs}^{batch} [TCE][H_2] \quad (2a)$$

Integration of (1) and (2a) gives:

$$\ln \frac{[TCE]}{[TCE_0]} = -k_{obs}^{batch} \frac{[H_2]_0}{\kappa^{batch}} \{1 - \exp(-\kappa^{batch} t)\} \quad (3a)$$

The normalized observed TCE reaction rate constant in batch dehalogenation, $\hat{k}_{obs}^{batch}$ ($(M_{H_2} \cdot s)^{-1} (g_{Pd}/L)^{-1}$), was computed by dividing $k_{obs}^{batch} ((M_{H_2} \cdot s)^{-1})$ by Pd content in the reactor. To our knowledge, the present study is the first description of catalytic hydrodechlorination of TCE as a 2nd order reaction.

A



B

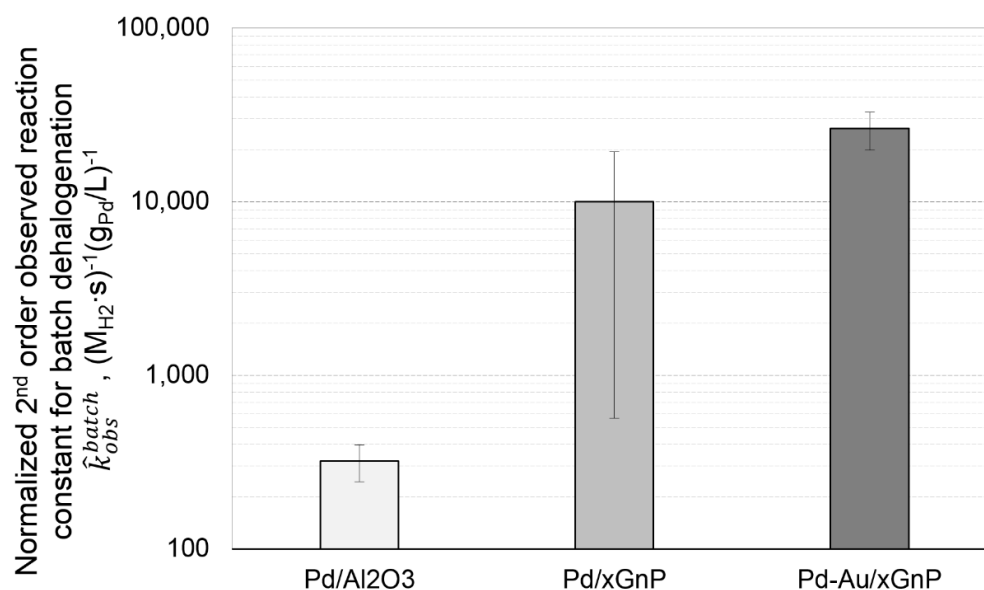


Figure 6: TCE dehalogenation performance of xGnP-supported Pd and Pd-Au catalysts and the commercial Pd/Al₂O₃ catalyst in batch reactions: A) Example data on TCE reduction. Pd content in the batch reactors is shown in the legend. B) 2nd order reaction rate constants normalized by the Pd content in the batch reactor for the three catalysts. The errors correspond to the 95% confidence interval.

We emphasize that the choice of the 2nd order kinetics to describe the reaction is necessary because the concentration of the reducing agent cannot be assumed to remain constant ($x^{batch} \neq 0$, Figure 12).

Small differences in the Pd content in tests with Pd/xGnP and Pd-Au/xGnP (0.69 mg(Pd)/L vs 0.81 mg(Pd)/L) were due to differences in the Pd content of these two catalyst types. The same mass (1.25 mg, see section 2.2.4.1) of each supported catalyst was added to batch reactors but the contents of Pd in Pd/xGnP and in Pd/xGnP were slightly different.

We extracted catalytic reaction rate constants for Pd-Au/xGnP, Pd/xGnP, and Pd/Al₂O₃ from the nearly 15 min of reaction time (Figure 6A). More than 90 % of TCE was reduced within 2 min of the reaction catalyzed by Pd-Au/xGnP. In contrast, in tests with Pd/xGnP the TCE reduction plateaued at values smaller than the values observed in tests with Pd-Au/xGnP, but higher in tests with Pd/Al₂O₃ where TCE reduction was even less complete. Figure 6B summarizes data on the reactivity of the two novel xGnP-supported catalysts and of the commercial Al₂O₃-supported Pd in a batch reactor. The 2nd order reaction rate constants for Pd/xGnP ($9,975 \pm 9,506 \text{ (M}_{\text{H}_2}\cdot\text{s)}^{-1}(\text{g}_{\text{Pd}}/\text{L})^{-1}$) and Pd-Au/xGnP ($26,309 \pm 6,555 \text{ (M}_{\text{H}_2}\cdot\text{s)}^{-1}(\text{g}_{\text{Pd}}/\text{L})^{-1}$), were ~ 31 times and ~ 81 times higher than that for the commercial Pd/Al₂O₃ catalyst ($321 \pm 77 \text{ (M}_{\text{H}_2}\cdot\text{s)}^{-1}(\text{g}_{\text{Pd}}/\text{L})^{-1}$).

While by-products of the reaction were not monitored in this study, byproduct analysis is important for ensuring the reaction is complete and no toxic by-products (e.g. dichloroethenes and vinyl chloride) remain. Such information might also provide additional mechanistic insights into reaction pathways although the effect of byproducts is likely mitigated by the fact that the reduction of TCE to DCE is the limiting reaction in the overall catalytic hydrodechlorination process ⁶⁷.

2.3.3. Dehalogenation kinetics in the batch reaction with a near-constant concentration of the reducing agent

Because of practical limits on the sampling time (i.e. finite time needed for sample withdrawal and filtration, H₂ measurement, and sample transfer to gas chromatography vials for TCE measurement), we were unable to record TCE concentration during the earliest stages (< 2 min) of the reaction. Yet for highly active catalysts such as Pd-Au/xGnP, TCE concentration decreased dramatically (~ 90%) over the first 2 min. To quantify reaction kinetics when TCE reduction was < 90%, we performed additional batch tests with a 5 times lower catalyst content. The experiments showed (see SM, section S4) that for low levels of TCE reduction, a 1st order model provided a good fit. This was because sufficiently early into the experiment ($x^{batch}_t \ll 1$), the 2nd order reaction given by eq. 1a reduced to a 1st order reaction:

$$\frac{d[TCE]}{dt} = -k_{obs}^{batch}[TCE][H_2]_0 \exp(-\kappa^{batch}t) \xrightarrow{\kappa^{batch}t \rightarrow 0} k_{1obs}^{batch}[TCE] \quad (2b)$$

where k_{1obs}^{batch} is the observed 1st order rate constant in the batch reactor. We note that for reactions where the reducing agent (H₂ in our case) is reacting sufficiently slowly, the 1st order kinetics can apply even late into the reaction, but it should be noted that

k_{1obs}^{batch} is constant only for a given initial H₂ concentration:

$$\lim_{\kappa^{batch} \rightarrow 0} \frac{1 - \exp(-\kappa^{batch}t)}{\kappa^{batch}} = t \quad (4)$$

and

$$\ln \frac{[TCE]}{[TCE]_0} = -k_{obs}^{batch} \frac{[H_2]_0}{\kappa^{batch}} \{1 - \exp(-\kappa^{batch}t)\} \xrightarrow{\kappa^{batch} \rightarrow 0} -k_{1obs}^{batch}t \quad (3b)$$

We extracted both 1st and 2nd order rate constants for batch reactors, and these constants, when normalized by Pd content, were not statistically different from respective rate constants measured in batch reactions with a higher content of Pd-Au/xGnP. Specifically, for high and low Pd-Au/xGnP contents the 1st order rate constants, $\hat{k}_{obs}^{batch}$, were 311 ± 120 and 559 ± 121 L/(min·g_{Pd})⁻¹, respectively, and the 2nd order rate constants, $\hat{k}_{obs}^{batch}$, were $26,309 \pm 6,555$ and $18,255 \pm 9,008$ (M_{H₂}·s)⁻¹(g_{Pd}/L)⁻¹, respectively. The reaction rate constant for H₂ decay where the catalyst content was 1.25 mg was observed to be 2 times greater than the reaction rate constant for H₂ where the catalyst content was 0.25 mg. Furthermore, we compared the ratio of the H₂

reaction rate constants with the respective catalyst contents, $\left(\frac{\kappa_{high}^{batch}}{\kappa_{low}^{batch}}\right)\left(\frac{m_{high}^{cat}}{m_{low}^{cat}}\right)^{-1}$, and showed that while the catalyst contents were 5 times greater the reaction rate constants were only 2 times greater for high and low loadings, respectively. The observation that reactivity did not increase in proportion to the increase in the catalyst loading indicates that there must be H₂ sinks additional to the direct H₂ consumption during the TCE reduction reaction.

Although the 1st order batch reaction model gives an inferior fit to experimental results (i.e. inferior to the fit provided by the 2nd order batch reaction model described by eq. (3)), we applied it to our batch TCE dehalogenation data in order to compare the Pd-Au/xGnP and Pd/xGnP catalytic reactivity with reaction rate constants reported in the literature (Table 3). The 1st order reaction rate constants for Pd-Au/xGnP and Pd/xGnP catalysts (311 and 140 L/(min·g_{Pd})⁻¹, respectively) are within an order of magnitude of the highest reaction rate constants reported earlier⁵⁵ even with no optimization of the Pd:Au surface coverage. We also note that because of their hydrophobicity, xGnPs could not be fully dispersed in the aqueous solution of TCE; it is likely that dispersing the xGnP-supported catalysts better can significantly enhance the efficiency of the reaction.

2.3.4. Kinetics of catalytic dehalogenation of TCE in flow-through membrane reactors

The dehalogenation of TCE by composite membranes was modeled as a 2nd order reaction in an ideal plug-flow reactor at steady-state:

$$0 = -v \frac{d[TCE]}{dx} - k_{obs}^{mem} [TCE] [H_2] \quad (5a)$$

where v (m/s) is the superficial velocity (i.e. permeate flux). As in batch tests, H_2 reacted according to a 1st order reaction in a plug flow reactor (see SM, Figure 11) so that H_2 decomposition was modeled as:

$$[H_2] = [H_2]_0 \exp(-\kappa^{mem} \ell_{eff} / v) \quad (6)$$

where $\kappa^{mem} \ell_{eff}$ (m/s) is the reactive flux of H_2 in the membrane. Integration of (5a) and (6) gives:

$$\ln \frac{[TCE]}{[TCE]_0} = -k_{obs}^{mem} \ell_{eff} \frac{[H_2]_0}{\kappa^{mem} \ell_{eff}} \{1 - \exp(-\kappa^{mem} \ell_{eff} / v)\} \quad (7a)$$

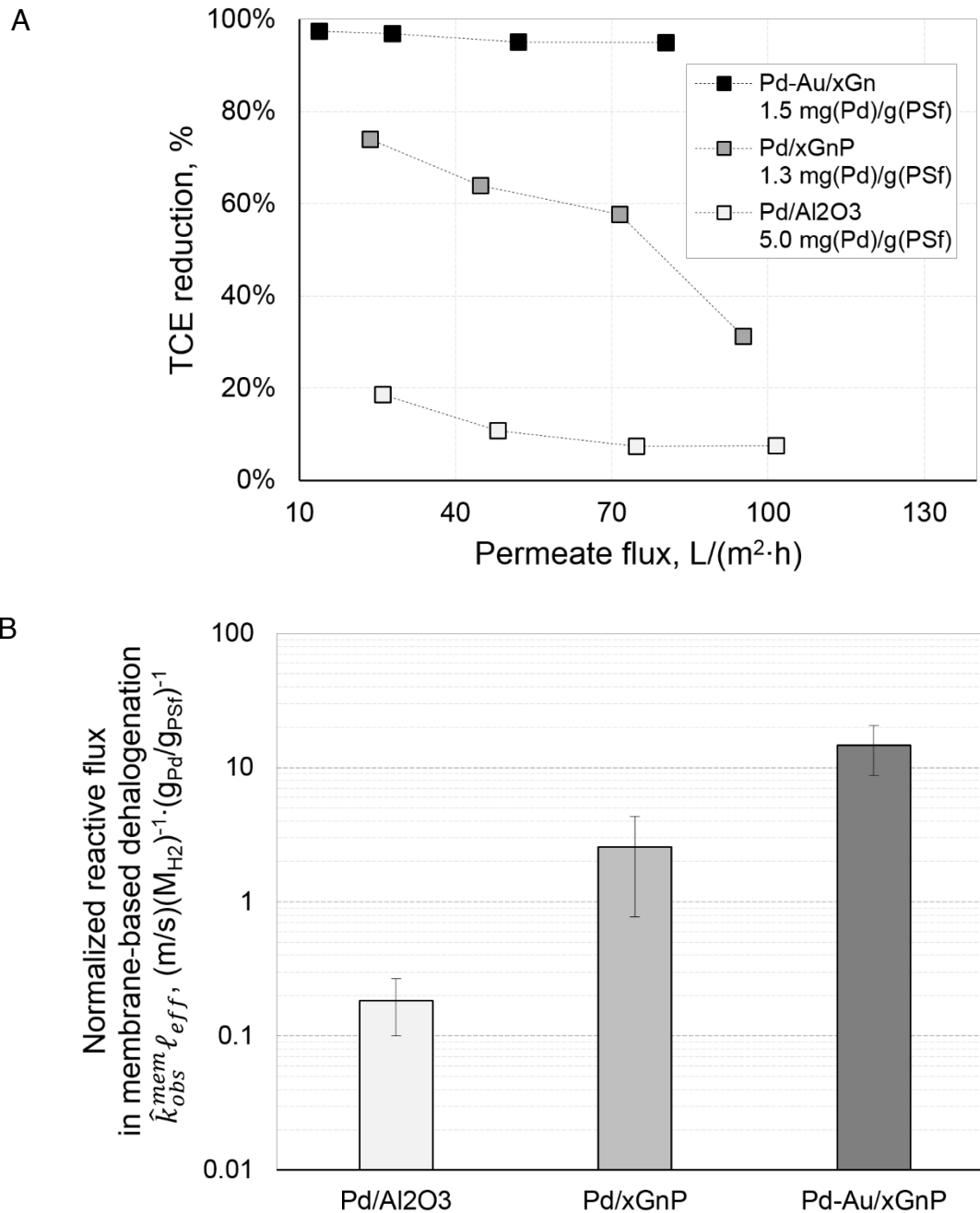


Figure 7: TCE dehalogenation performance of xGnP-supported Pd and Pd-Au catalysts and the commercial Pd/Al₂O₃ catalyst in flow-through membrane reactors: A) Example data on TCE reduction in membrane filtration tests. Pd loading in nanocomposite membranes is shown in the legend. The four points in each data set correspond to transmembrane pressure values of 10, 20, 30, and 40 psi. B) Normalized reactive fluxes in membrane dehalogenation by nanocomposite membranes with embedded catalysts. The errors correspond to the 95% confidence interval.

where ℓ_{eff} is the effective length of the reactor and $k_{obs}^{mem} \ell_{eff}$ ((m/s)(M_{H2})⁻¹) is the reactive flux of TCE in the membrane.

The reactive fluxes $k_{obs}^{mem} \ell_{eff}$ and $\kappa^{mem} \ell_{eff}$ describe the degrees to which TCE and H₂ react away in the membrane. Average values of $\kappa^{mem} \ell_{eff}$ in tests with Pd/Al₂O₃, Pd/xGnP, and Pd-Au/xGnP catalysts were determined to be 4.95, 4.10, and 7.26 $\mu\text{m/s}$, respectively.

In most membranes suitable for practical separations, the length of the reactor, ℓ_{eff} , is not known. This is in part because of the complex morphology of the pore space (pore tortuosity and connectivity) and in part because most membranes are asymmetric.

Thus, the detention time in the membrane reactor, $\frac{\ell_{eff}}{v}$ (s) is not known and computing the exact reaction rate constant k_{obs}^{mem} is not possible. For this reason, we quantify reactivity within the membrane reactor in terms of the reactive flux⁵⁴.

The normalized TCE reactive flux in membrane-based dehalogenation, $\hat{k}_{obs}^{mem} \ell_{eff}$ ((m/s)(M_{H2})⁻¹ (g_{Pd}/g_{PSf})⁻¹), was computed by normalizing the measured reactive flux, $k_{obs}^{mem} \ell_{eff}$ ((m/s)(M_{H2})⁻¹), by the mass loading of Pd in the polysulfone nanocomposite membrane (g_{Pd}/g_{PSf}). The H₂ reaction rate constants κ^{mem} and κ^{batch} are generally different; thus κ^{batch} and $\kappa^{mem} \ell_{eff}$ were determined separately.

The reactive fluxes for membranes with embedded Pd/xGnP ($2.56 \pm 1.79 \text{ (m/s)}(\text{M}_{\text{H}_2})^{-1}(\text{g}_{\text{Pd}}/\text{g}_{\text{PSf}})^{-1}$) and Pd-Au/xGnP ($14.71 \pm 5.96 \text{ (m/s)}(\text{M}_{\text{H}_2})^{-1}(\text{g}_{\text{Pd}}/\text{g}_{\text{PSf}})^{-1}$) catalysts, were ~ 14 times and ~ 80 times higher than those for the membranes with commercial Pd/Al₂O₃ catalyst ($0.18 \pm 0.08 \text{ (m/s)}(\text{M}_{\text{H}_2})^{-1}(\text{g}_{\text{Pd}}/\text{g}_{\text{PSf}})^{-1}$) (Figure 7). While $\hat{k}_{obs}^{mem}$ could not be decoupled from $\hat{k}_{obs}^{mem} \ell_{eff}$ by experimentally determining ℓ_{eff} , we can make general assumptions for PSf ultrafiltration membranes to determine ℓ_{eff} . We assumed the porosity, ϵ , and the tortuosity, τ , to be 0.5 and 5, and the membrane thickness, ℓ_{mem} , was 300 μm , where $\ell_{eff} = \ell_{mem} \cdot \epsilon \cdot \tau$. The calculated values of $\hat{k}_{obs}^{mem}$ for Pd-Au/xGnP, Pd/xGnP, and Pd/Al₂O₃ were (19613, 3412, and 244) $(\text{M}_{\text{H}_2} \cdot \text{s})^{-1}(\text{g}_{\text{Pd}}/\text{g}_{\text{PSf}})^{-1}$, respectively. The reaction rate constants, $\hat{k}_{obs}^{mem}$, from the reactive flux are in qualitative agreement with the observed reaction rate constants for batch reactions; the reaction rate constants in batch reactions differed from those in membrane –based reactions by a factor of 3 or less. Additionally, for Pd-Au/xGnP and Pd/Al₂O₃ membranes, the agreement between the calculated and observed reaction rate constants was greater, where the reaction rate constants were different by a factor of 1.5 or less.

2.3.5. Dehalogenation kinetics in a membrane reactor with a near-constant concentration of the reducing agent

Under conditions of relatively slow decomposition of the reducing agent ($-\kappa^{mem}t \ll 1$)

eq. 5a simplifies to the plug-flow model with the 1st order reaction:

$$0 = -v \frac{d[TCE]}{dx} - k_{obs}^{mem} [TCE] [H_2]_0 \exp(-\kappa^{mem}t) \quad (5b)$$

$$\xrightarrow{\kappa^{mem}t \rightarrow 0} -v \frac{d[TCE]}{dx} - k_{1obs}^{mem} [TCE]$$

where k_{1obs}^{mem} is the observed 1st order rate constant in the membrane reactor. We note that for reactions where the reducing agent is reacting sufficiently slowly ($\kappa^{mem} \rightarrow 0$), the 1st order kinetics can apply even when permeation is slow (i.e. small v) and the residence time (ℓ_{eff}/v) in the membrane is high:

$$\lim_{\kappa^{mem} \ell_{eff} \rightarrow 0} \frac{1 - \exp(-\kappa^{mem} \ell_{eff}/v)}{\kappa^{mem} \ell_{eff}} = \frac{1}{v} \quad (8)$$

and

$$\ln \frac{[TCE]}{[TCE]_0} = -k_{obs}^{mem} \ell_{eff} \frac{[H_2]_0}{\kappa^{mem} \ell_{eff}} \{1 - \exp(-\kappa^{mem} \ell_{eff}/v)\} \quad (7b)$$

$$\xrightarrow{\kappa^{mem} \ell_{eff} \rightarrow 0} - \frac{k_{1obs}^{mem} \ell_{eff}}{v}$$

Practically, high permeate fluxes are needed, which requires fast kinetics of dehalogenation to reduce the concentration of a target pollutant even at a low residence

time. Faster reduction reactions translate into faster consumption of the reducer (i.e. larger κ^{mem}), but it should be considered that the rate of consumption of H₂ may also depend on the concentration of TCE. Under these conditions, approximations (5b) and (7b) do not hold and 2nd order kinetics applies.

2.3.6. Resolving conflicting demands of throughput and reactivity within a membrane reactor

Although in the general case the plug-flow with 1st order reaction model given by eq. (7b) ⁵⁴ fits experimental results worse (see SM, section S3) than the plug flow with 2nd order reaction model described by eq. (7a), we applied the 1st order model to our membrane-based TCE dehalogenation data to elucidate the competition between mass transfer and reactivity within the membrane reactor (Table 4). The 1st order model is useful for a simple estimation of how effective different embedded catalysts are at different permeate fluxes: the 1st order reactive flux can be interpreted as the permeate flux for which the concentration of TCE is reduced in the membrane reactor by the factor of $e \cong 2.72$.

At the transmembrane pressure of 0.69 bar, the average permeate flux through membranes with embedded Pd/Al₂O₃ was 15.5 L/(m²·h), while the reactive flux was only

15.5 L/(m²·h) leading to incomplete TCE reduction (Figure 7A). In contrast, at the same transmembrane pressure, the average permeate flux through the membranes with embedded Pd-Au/xGnP was 26.4 L/(m²·h), and the reactive flux was 45.0 L/(m²·h). Thus, using the Pd-Au/xGnP catalyst makes the membrane reaction feasible at permeate fluxes in the ultrafiltration range.

Table 4: Comparison of 1st order reactive flux⁵⁴ and volumetric permeate flux for membranes filled with one of the three catalysts studied: Pd/xGnP, Pd-Au/xGnP, and Pd/Al₂O₃ (baseline).

Embedded catalyst	TCE reactive flux for 1 st order reaction model, $k_{1_{obs}}^{mem} \ell_{eff}$, $\mu\text{m/s (L}\cdot\text{m}^{-2}\cdot\text{h}^{-1})$	Average volumetric permeate flux at $\Delta P = 2.76$ bar, $\mu\text{m/s (L}\cdot\text{m}^{-2}\cdot\text{h}^{-1})$	Average volumetric permeate flux at $\Delta P = 0.69$ bar, $\mu\text{m/s (L}\cdot\text{m}^{-2}\cdot\text{h}^{-1})$
Pd/Al ₂ O ₃	1.8 (6.5)	24.9 (89.7)	4.3 (15.5)
Pd/xGnP	5.0 (18.0)	64.5 (232.2)	6.4 (23.2)
Pd-Au/xGnP	12.5 (45.0)	35.0 (125.9)	7.4 (26.4)

A comparison of batch and membrane-based reaction data (Figure 6B and Figure 7B), shows that the relative reactivity of Pd/xGnP catalyst with respect to Pd/Al₂O₃ decreased while for the Pd-Au/xGnP the ~ 80 fold advantage was maintained after catalyst incorporation into membranes. The decrease might be due to catalyst occlusion by the surrounding polysulfone matrix of the nanocomposite membrane⁵⁴. The occlusion effect can be mitigated by using a more permeable membrane⁵⁴ or by selecting a cage-type catalyst support^{73, 74} that limits or eliminates polymer access to the catalyst. It appears that the improvement in reactivity due to the addition of the promoter metal (Pd/xGnP vs Pd-Au/xGnP, Figures 6B and 7B) is sufficient to overcome the occlusion effect. Remarkably, both Pd/xGnP and Pd-Au/xGnP achieved >96% reduction of TCE while operating at 32 L/(m²·h) and 14 L/(m²·h) respectively, compared to Pd/Al₂O₃ achieving only 80% reduction while operating at 16 L/(m²·h) of TCE.

We conclude that the high reactivity of the Pd/xGnP and especially Pd-Au/xGnP catalysts enables the application of reactive membranes for TCE dechlorination by allowing for sufficient reaction time at high permeate fluxes. By normalizing k_{obs}^{batch} by Pd content in the batch reactor ($(g_{Pd}/L)^{-1}$) and normalizing $k_{obs}^{mem} \ell_{eff}$ by Pd loading in the membrane (g_{Pd}/g_{PSf}) we show that Pd-Au/xGnP and Pd/xGnP are much more cost-efficient than the commercial catalyst Pd/Al₂O₃ in dehalogenating TCE. Pd/xGnP and Pd-Au/xGnP cost \$2.79 and \$8.89 on a per gram basis, respectively, compared to \$9.23 for Pd/Al₂O₃, where the prices of all raw materials were obtained from Sigma Aldrich, 2016. The reactivity of Pd/xGnP and Pd-Au/xGnP catalysts can be further

improved by optimizing particle size (to make better use of Pd surface atoms) and Pd:Au ratio.

Supplementary Material

Pd and Pd-Au nanocatalysts supported on exfoliated graphite for high throughput dehalogenation by nanocomposite membranes

S1. TCE dechlorination experiments: analytical procedure for measuring TCE

Using a preheated (80°C) 2 mL sample from either the batch or flow-through reactor, a 50 µL sample was injected into the gas chromatograph (Perkin-Elmer) using a gas-tight syringe. The TCE peak was observed at 3.0 min, and the area under the curve was extracted for each sample. A 4-point standard calibration curve (10, 100, 1000, and 10,000 ppb) was created to convert areas to mass concentration. The GC was equipped with an electron capture detector, and N₂ was used as the carrier gas. The temperature of the oven was set to 80°C while the detector temperature was 350°C. Control experiments were conducted without H₂ and it was shown that there was no observable adsorption of TCE on xGnP (Figure 8).

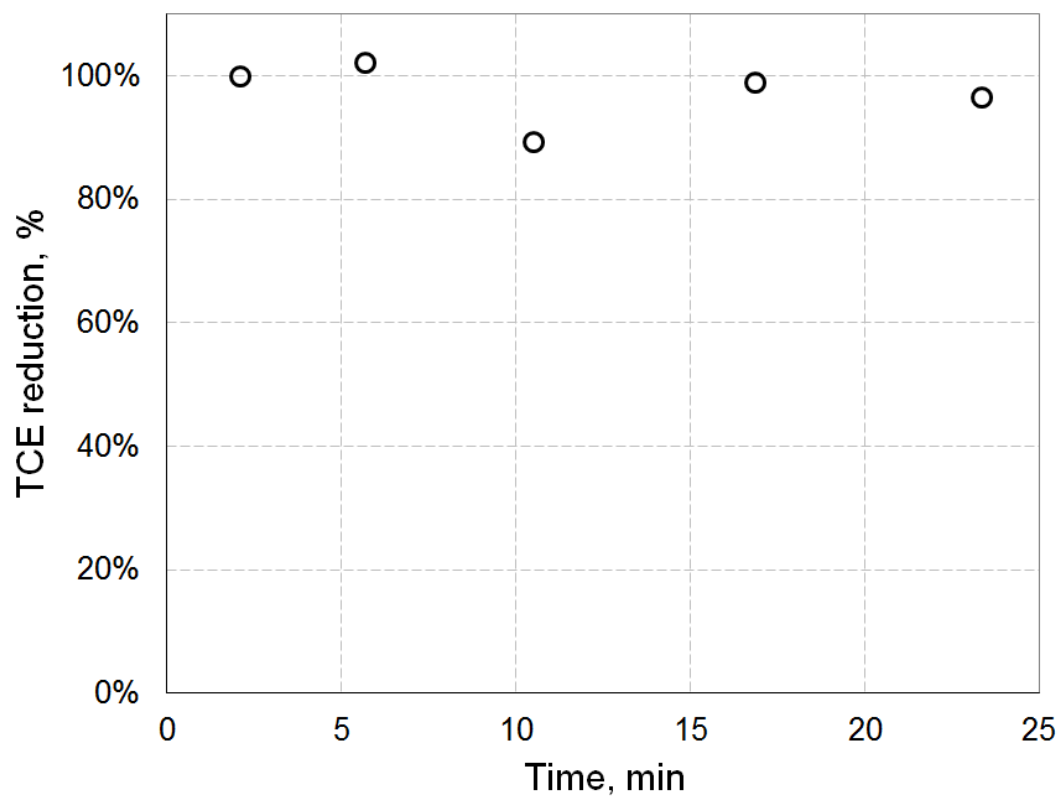


Figure 8: Results from control experiment conducted with TCE and Pd-Au/xGnP without the reducing agent H_2 present.

S2. Catalyst characterization by TEM-EDS and AA.

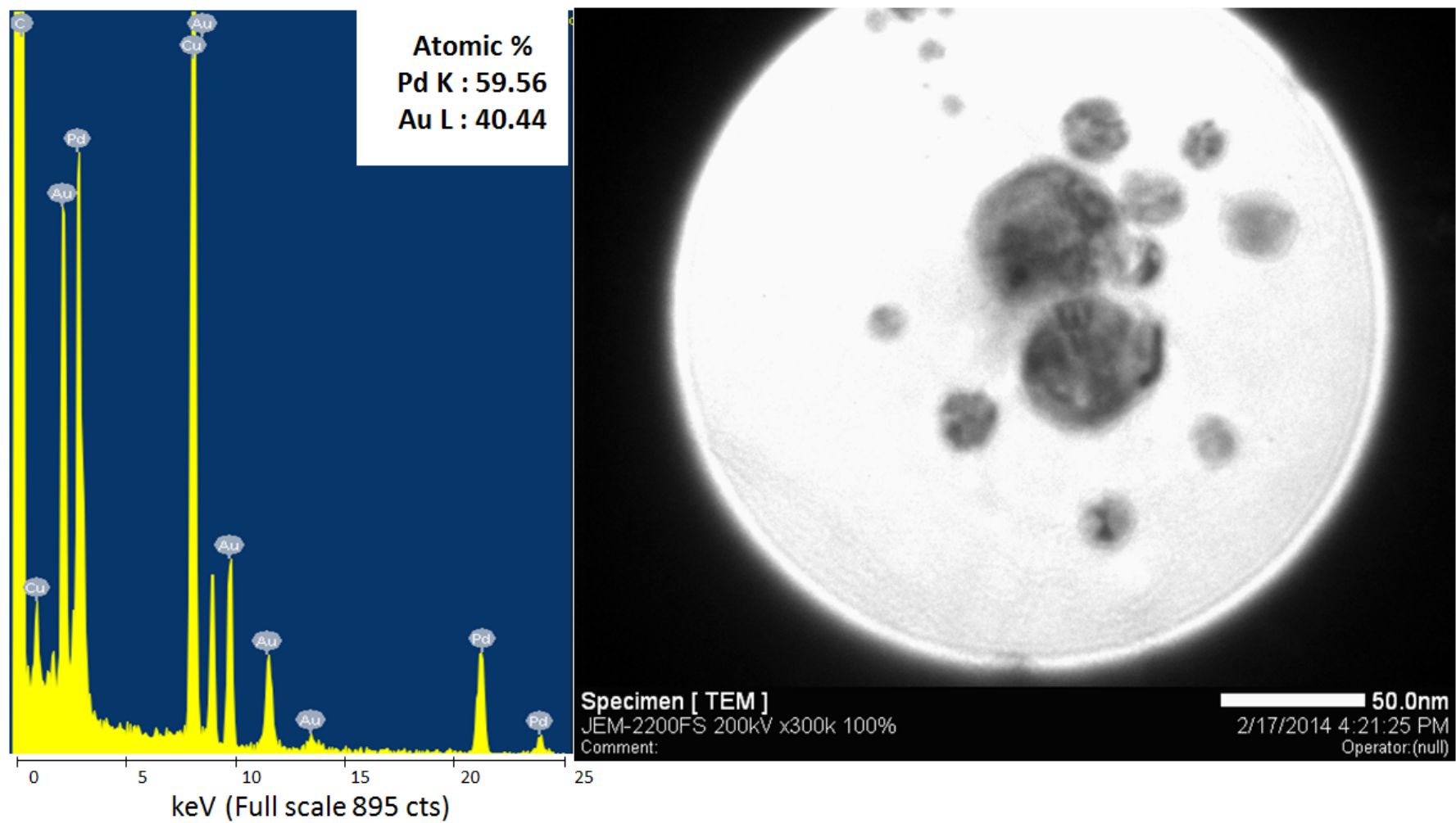


Figure 9: TEM EDS results of Pd-Au/xGnP and a TEM micrograph of Pd-Au nanoparticles supported on xGnP.

The Pd and Au nanoparticles were dissolved from the xGnP support, and the solution was filtered and analyzed using AA. AA characterization included the following four steps:

1. A sample of Pd/xGnP or Pd-Au/xGnP was weighed and heated in aqua regia ($\text{HNO}_3 + 3\cdot\text{HCl}$) at the boiling point for 1 h.
2. After heating, the suspension was sonicated (Aquasonic 50T, VWR Scientific) for 3 h.
3. The sonicated suspension was filtered through a 0.45 μm mixed cellulose ester filter (Millipore).
4. The filtrate was diluted with DI water and analyzed for Pd and Au content using AA. Because not all Au was leached from Au-xGnP, the cake on the surface of the filter was analyzed for gold content. To do that the filter was dried in a fume hood for 12 h, then was weighed, suspended in fresh aqua regia and subjected to the sequence of treatment steps 2 to 4 three times. At the end, the gold concentration in the filtrate was less than 2% of the total leached Au concentration.

Table 5: Atomic adsorption spectroscopy results of Pd and Au concentration on graphene normalized by the mass of xGnP.

Catalyst	Metal concentration normalized by xGnP mass				
Pd/xGnP	Sample A1	Sample B1	Sample C1	AVE	CI, 90%
Pd	6.54%	7.62%	4.91%	6.36%	± 1.30%
Pd-Au/xGnP	Sample A2	Sample B2	Sample C2	AVE	CI, 90%
Pd	6.54%	7.62%	7.62%	7.26%	± 0.59%
Au	7.59%	7.30%	6.20%	7.03%	± 0.70%

S3. Comparison of 1st order and 2nd order reaction kinetics

The reactivity of newly synthesized nanoparticles fit a 2nd order model (eq. (7) in the main manuscript) better than 1st order model because of the disappearance of H₂ with time. The 2nd order fits of batch (Figure 10) and flow-through (Figure 11) reaction data yielded R² values of 0.92 and 0.96, which was significantly higher than corresponding R² values (0.73 and 0.91) obtained for to 1st order models.

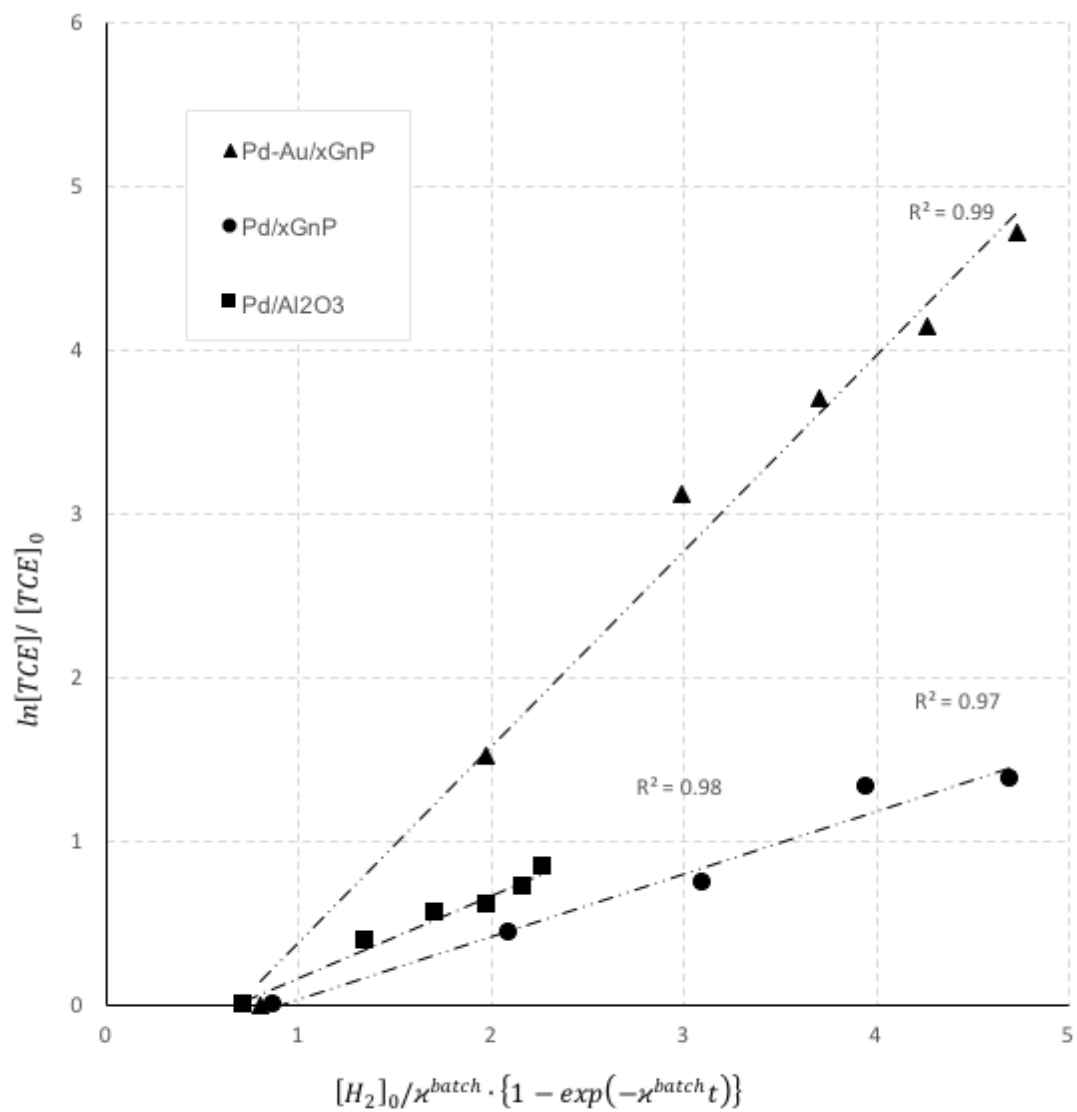


Figure 10: Example fits of batch reaction kinetics data to the 2nd order reaction model.

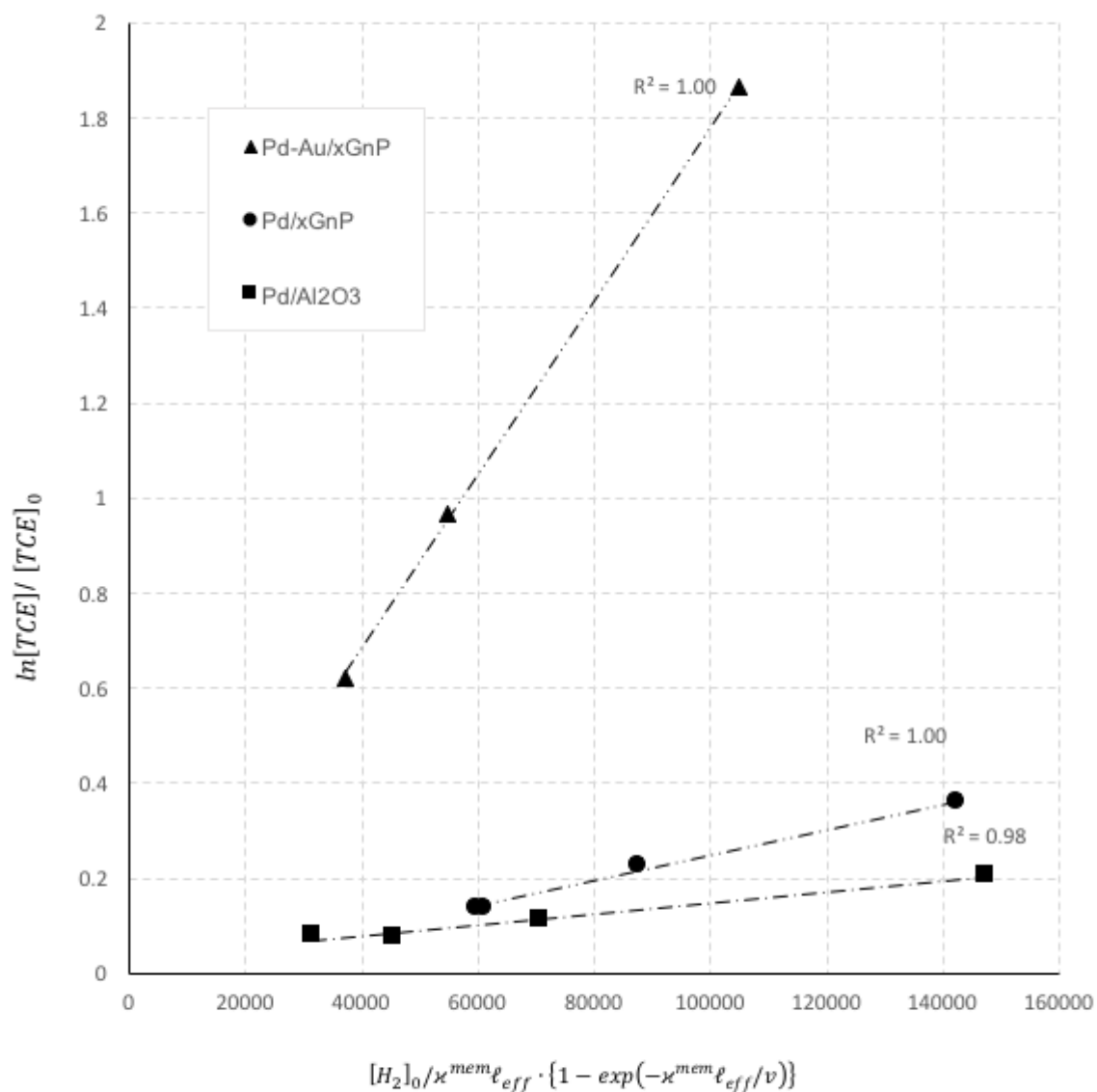


Figure 11: Example fits of flow-through reaction kinetics data to the 2nd order reaction model.

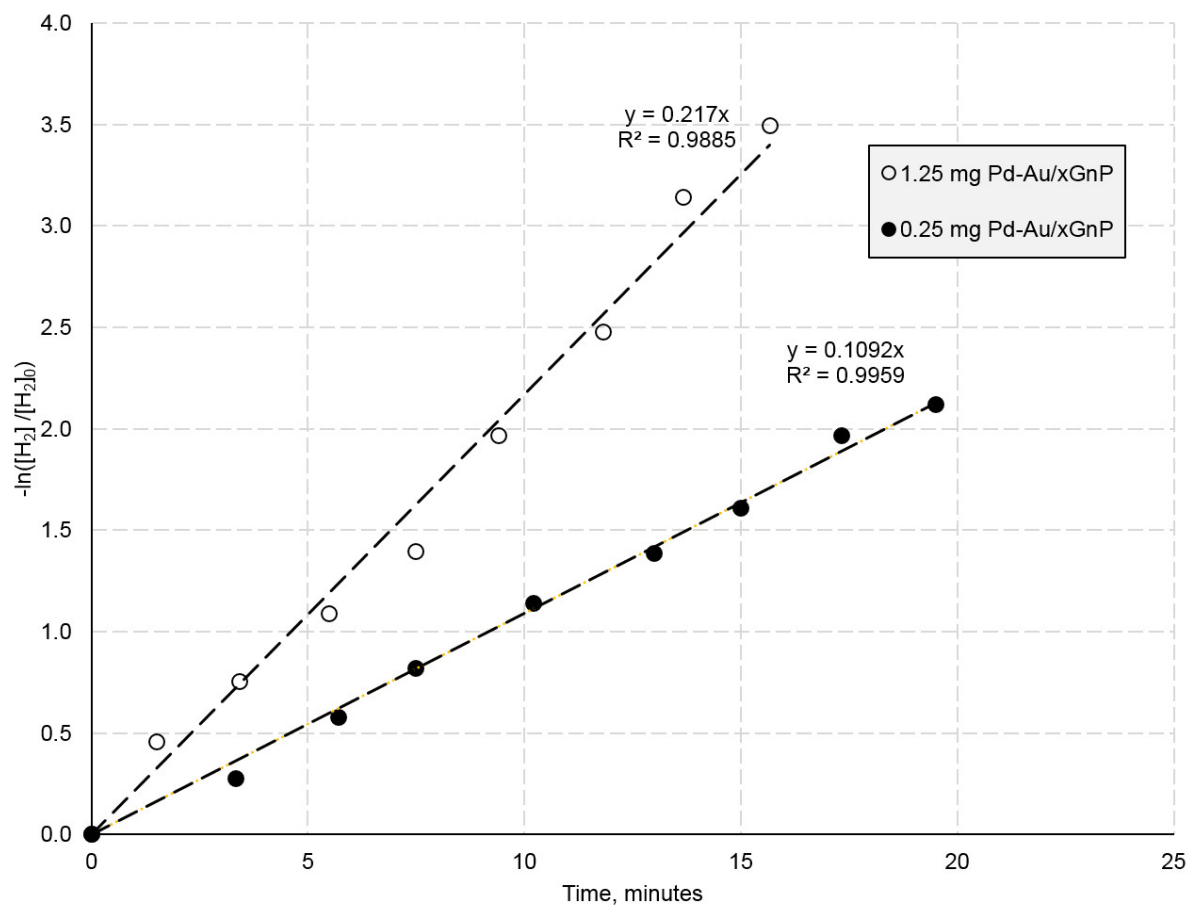


Figure 12: Example fits of H_2 decomposition kinetics data to the 1st order reaction model for TCE dehalogenation experiments with Pd-Au/xGnP catalyst at regular (1.25 mg) and low (0.25 mg) loadings.

S4. TCE dechlorination experiments using low concentrations of Pd-Au/xGnP

For dechlorination experiments with low Pd-Au/xGnP loadings, the protocol was identical to the procedure described in section 2.2.4.1 except that 5 times lower (0.25 mg) loading of the catalyst (Pd-Au/xGnP) was used. We decreased the loading in order to explore the reaction kinetics when TCE conversion was low. Based on these experiments, it was shown that TCE conversion batch reactions fit a 1st order model better than a 2nd order although the improvement was not statistically significant: the R² statistics were 0.971 ± 0.015 and 0.925 ± 0.059 ($p = 0.05$ and $n = 3$), respectively.

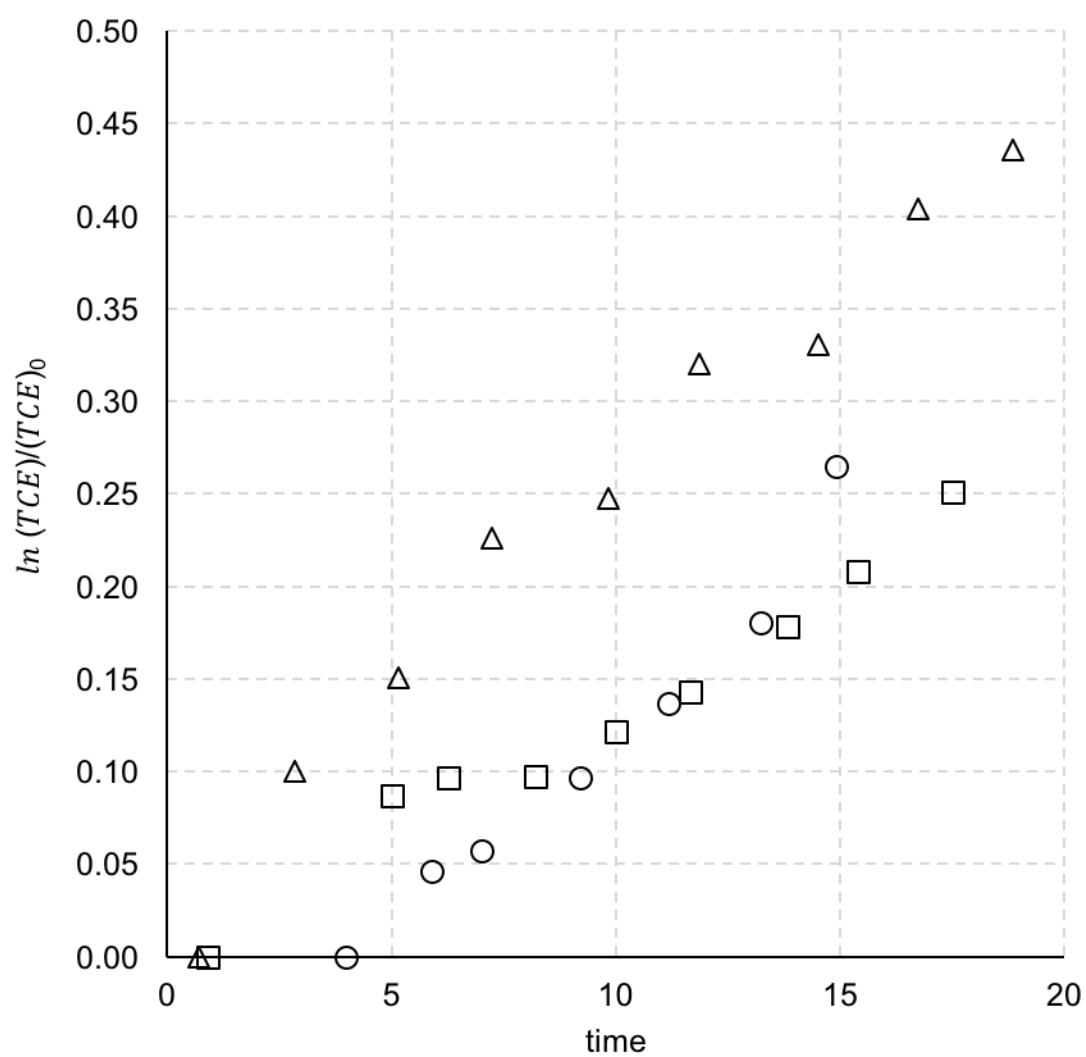


Figure 13: Fits of batch reaction kinetics data to the 1st order reaction model.

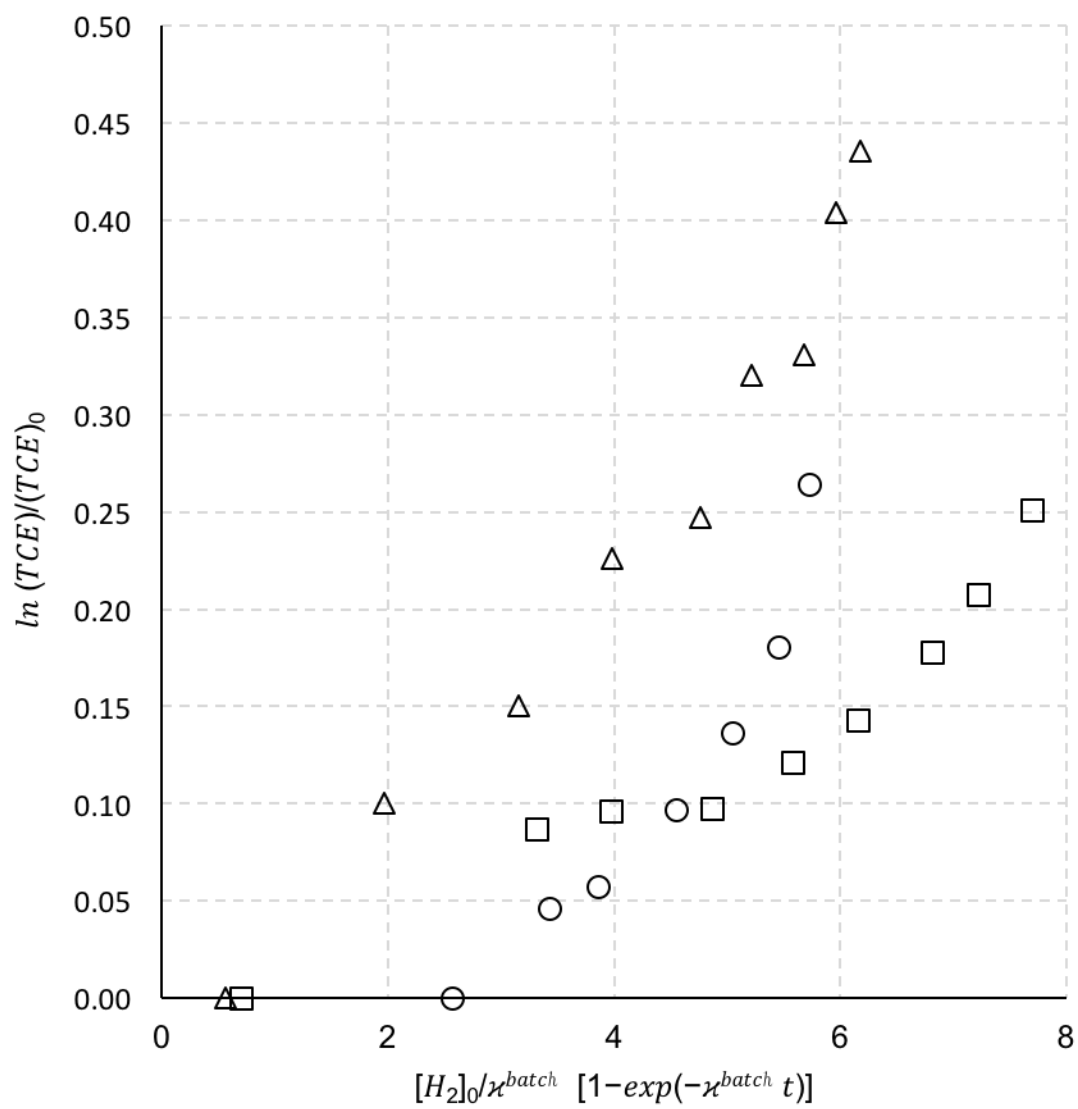


Figure 14: Fits of batch reaction kinetics data to the 2nd order reaction model.

S5. Particle size distribution of Pd and Pd-Au nanoparticles on xGnP supports

From TEM images, we could estimate the particle size distribution of Pd and Pd-Au nanoparticles using imageJ software (version java 1.6.0_65) (Figure 15). The distributions were calculated by randomly measuring the diameters of 200 nanoparticles on xGnP supports. Pd nanoparticles ranged in size from 2 to 20 nm, while ~ 87 % of these particles ranged in size from 5 to 0 nm. Pd-Au nanoparticles ranged in size from 6 to 40 nm, and 85% of these particles ranged in size from 10 to 30 nm.

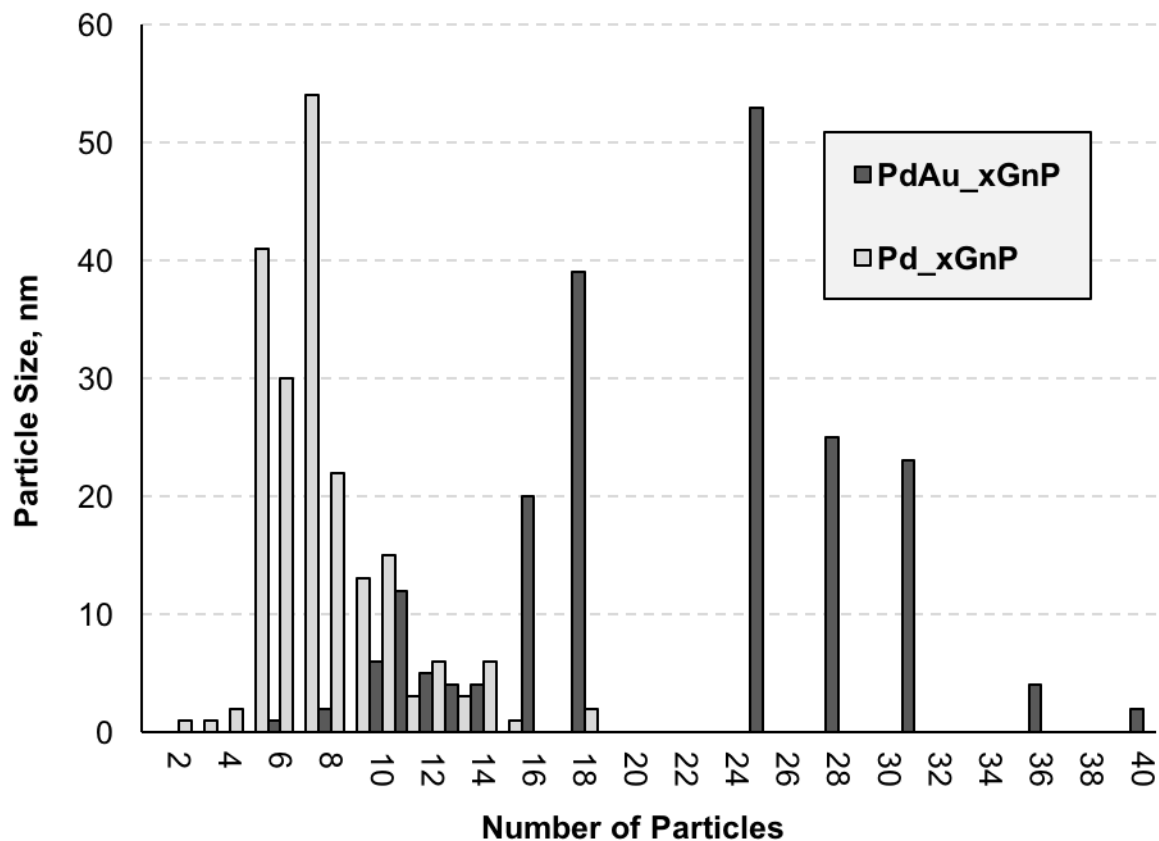


Figure 15: Size distribution of Pd and Pd-Au nanoparticles on xGnP supports. Each distribution was calculated based on 200 randomly selected nanoparticles.

CHAPTER THREE

Effects of sulfide poisoning on TCE dehalogenation reactivity for Pd/xGnP and Pd-Au/xGnP nanocatalysts

3.1. Introduction

Halogenated organics are harmful contaminants regulated by the Environmental Protection Agency, and they are linked to different human health issues such as cancer, damage to the nervous system, and damage to the liver⁷⁵. Specifically, trichloroethylene (TCE) contaminates over 800 sites listed by the EPA as National Priority List Superfund sites. The maximum contaminant level for TCE is 5 $\mu\text{g/L}$ ⁷⁶. TCE is a stable compound that is present in the environment due to a lack of proper disposal during widespread use in the past⁷⁷. Additionally, over time as TCE degrades, the byproducts are dichloroethene and vinyl chloride, which the EPA also considers as primary contaminants.

Chapter 3 showed that membranes embedded with Pd-Au/xGnP catalysts were highly efficient in catalytically dehalogenating TCE⁷⁸. The supported bimetallic catalyst, Pd-Au, had a “core-shell” morphology. The flow-through reaction was modeled as a plug-flow reactor with a second order reaction, as the reductant (i.e. H_2) significantly disappeared throughout the reaction. The significant disappearance of H_2 can be partially attributed

to the amount of H_2 reacted in the conversion of TCE, where the concentration of H_2 is 2.8 times the concentration needed to reduce 9.25 mg/L of TCE, assuming 4 moles of H_2 are reacted for every 1 mole of TCE. Compared to Pd/xGnP and commercial Pd/ Al_2O_3 catalysts, the catalytic efficiency of the bimetallic Pd-Au/xGnP catalyst imbedded in polysulfone (PSf) membranes was ~ 6 and 80 times higher, respectively. Au acts as a promoter metal to increase the efficiency of Pd catalysts in the catalytic reduction of TCE⁵. In addition to increasing the efficiency of Pd catalysts, Au as a promoter metal can prevent Cl^- poisoning and reduce the rate of catalyst deactivation by SH^- ⁷⁹.

Catalyst poisoning by sulfide, either gas-phase⁸⁰ or aqueous⁸¹ phase, results from the dissociative adsorption of H_2S or HS^- onto the Pd surface, thus forming surface hydrogen and sulfur species (i.e. Pd^*S). Low $S:Pd_{surface}$ molar concentrations resulted in unordered Pd^*S structures, but became ordered at a $S:Pd_{surface}$ ratio of 1:4 and complex at a $S:Pd_{surface}$ ratio of 2:3⁸⁰⁻⁸³. Due to the different Pd^*S structures formed for different relative concentrations of S to Pd, the extent of deactivation of Pd catalysts should depend on relative concentration of S to Pd. The Pd catalyst can be regenerated through sulfide oxidation to sulfate using water saturated with dissolved oxygen, hypochlorite, or hydrogen peroxide^{82, 84}. By using bimetallic Pd-Au catalysts as an alternative to metallic Pd catalysts for TCE dehalogenation in catalytic membrane reactors, the catalyst should resist all poisoning by Cl^- , and should slow the rate of deactivation by sulfide. The Pd-Au catalysts which are resistant to deactivation would

thus increase the lifetime of the catalysts, and decrease the frequency of catalyst regeneration.

Current methods for sulfide treatment in water are adsorption onto activated carbon (for concentrations between 50 and 300 ppb), aeration or oxidation via dissolved oxygen (for concentrations < 2 ppm), oxidation using manganese filtration (for concentrations up to 10 ppm), and chlorination (for concentrations up to 75 ppm)⁸⁵. In the chlorination of sulfide, the chlorine dosage should be nearly 2 times the concentration of sulfide with a contact time of 20 min. During treatment, H_2S and SH^- are the accepted sulfur species dominant in water, since the typical pH for water during treatment is between 6 and 8. Under basic conditions (i.e. high pH), sulfate is indicated as the favored byproduct of sulfide oxidation in chlorination⁸⁶ and in the presence of Ca^{2+} , gypsum (CaSO_4) forms and precipitates as gypsum.

The concurrent separation and reaction functions of catalytic membranes can lead to synergistic benefits in drinking water treatment applications^{87, 88}. For the catalytic treatment of TCE, membrane flow-through reactors can take advantage of this synergy between separation and reaction to prevent deactivation or fouling of the Pd catalyst. Bimetallic Pd-Au catalyst can resist deactivation by sulfide at residual molar concentrations less than 80% of the $\text{Pd}_{\text{surface}}$ concentration, and Pd-Au resisted chlorine concentrations up to 30 mM⁷⁹. To implement catalysis in TCE reduction, these concerns about catalyst deactivation must be addressed. In this study, sulfide was

used as a model “poison” in the deactivation of Pd catalyst during TCE dechlorination. The catalytic reduction of TCE was characterized in batch and flow-through reactors using Pd/xGnP and Pd-Au/xGnP catalysts in the presence of residual sulfide after oxidation by hypochlorite.

3.2. Experimental

3.2.1. Reagents

Ethylene glycol (EG) (Fluka), sodium hydroxide pellets (Fluka), 20 wt% aqueous solution of poly(diallyldimethylammonium) chloride (PDADMAC) (Sigma Aldrich), Pd on alumina (5wt% Pd) (Sigma Aldrich), palladium chloride (PdCl_2) (Sigma Aldrich) and gold (III) chloride trihydrate ($\text{HAuCl} \cdot (\text{H}_2\text{O})_3$) (Sigma Aldrich) were used in Pd and Au nanoparticle synthesis. Hydrogen (99.9% purity) and nitrogen (99.99% purity) gases were used to saturate TCE feed solutions. Polysulfone (PSf, Udel P-3500 MB8 pellets), N-methyl-2-pyrrolidone, and poly(ethylene glycol) (PEG400) with a MW of 400 Da were used to fabricate flat sheet membranes. TCE (Sigma Aldrich), sodium sulfide nonahydrate (Sigma Aldrich), and CaCl_2 (Sigma Aldrich) were used in solutions for TCE dechlorination experiments.

3.2.2 Synthesis of Pd/xGnP and Pd-Au/xGnP catalysts

Pd/xGnP and Pd-Au/xGnP catalysts were synthesized in the same manner as described in Chapter 2 using a modified polyol method. For Pd/xGnP catalysts, PdCl_2 was used as the Pd nanoparticle precursor. The precursor solution was reduced to metal nanoparticles on xGnP supports in ethylene glycol by heating the precursor solution using a microwave. For bimetallic Pd-Au/xGnP catalysts, first Au was deposited on the xGnP supports in ethylene glycol by heating using a hot oil bath. Subsequently, Pd was deposited on the Au/xGnPs.

3.2.3 Synthesis of residual sulfide solution

The residual sulfide solution was synthesized in order to model the treatment process of sulfide before dechlorination using chlorine oxidation. To model the treatment process of sulfide oxidation, sodium hypochlorite was the source of free chlorine. The sulfide solution was prepared by oxidizing 0.1 mM sulfide using sodium hypochlorite to make up 0.2 mM of free-chlorine in the presence of 0.1 mM Ca_2Cl . After 20 min of contact time, gypsum formed and was removed by filtering the sulfide solution through xGnP nanocomposite membranes, and the sulfide concentration of the filtered solution was determined using an H_2S sensor equipped with a picoampere amplifier. To determine the concentration of sulfide using an H_2S sensor, the sulfide solution had to be buffered first at a pH of 4 to ensure all sulfide species were in the form of H_2S .

3.2.4 Fabrication of Pd-Au/xGnP membranes

Membranes were prepared with a combination of dry and wet phase inversion. The composition of the casting mixture included 15wt% PSf, 70wt% NMP, 15wt% PEG400, and 2% (Pd-Au/xGnP)/(PSf). This composition was chosen because the permeability of these membranes are typical for ultrafiltration membranes as previously shown⁷⁴. The casting mixture was prepared by first dispersing Pd-Au/xGnP catalysts in NMP using bath sonication for 12 hours. Next, PSf pellets and PEG400 were added to the NMP with dispersed Pd-Au/xGnP catalysts. The solution was mixed for 24 hours or until the casting mixture reached homogeneity. After 24 hours, the casting mixture was spread as a thin film on a glass support using a doctor blade equipped with a micrometer at 300 μm in thickness. The thin-film was allowed to evaporate for 15 s to start dry phase inversion and then immersed in a water bath to start wet phase inversion. The membranes were rinsed with DI water for 20 min and then residual NMP was removed by storing the membranes in DI water for 24 h.

3.2.5 TCE dechlorination experiments in batch reactors

Dechlorination batch experiments were conducted in the same manner as dechlorination experiments in Chapter 2, except for when sulfide was used as a model poison for Pd-Au/xGnP and Pd/xGnP catalysts. First, the nanocatalysts reactivity for

TCE dechlorination was characterized in batch reactor tests conducted in zero-head space reactors.

For sulfide free experiments, high purity water ($> 10 \text{ M}\Omega\cdot\text{cm}^{-1}$) was purged of DO by aerating the water with nitrogen through a ceramic frit. Next, 1.25 mg of either Pd/xGnP or Pd-Au/xGnP was added to the water and dispersed, after which the water was saturated with H_2 by bubbling H_2 gas through the water for 15 min and sealed with a Teflon septum. Next, TCE was added to the sealed reaction vessel to initiate the reaction, and the solution was stirred throughout the duration of the experiment. Samples were withdrawn from the reactor and transferred to GC vials to determine the TCE concentration. The H_2 concentration was monitored throughout the entire reaction, using a hydrogen sensor equipped with a picoampere amplifier. For experiments with sulfide as a poison to the catalyst, a solution of either $0.7 \mu\text{M}$ or $2 \mu\text{M}$ of residual sulfide after oxidative treatment was used.

3.3. Results and Discussion

3.3.1. Catalytic reactivity of Pd/xGnP and Pd-Au/xGnP

The catalyst for Pd/xGnP was deactivated completely in the presence of sulfide, while Pd-Au/xGnP catalysts were significantly deactivated in the presence of TCE. The observed second-order reaction rate constants for Pd-Au/xGnP in the presence of 0.7

μM and $2\ \mu\text{M}$ sulfide were $(469 \pm 35$ and $192 \pm 38)$ $(\text{M}_{\text{H}_2\text{S}})^{-1}(\text{g}_{\text{Pd}}/\text{L})^{-1}$, respectively.

Compared to the reactivity of Pd/xGnP and Pd-Au/xGnP for dechlorination experiments with no sulfide, Pd/xGnP catalysts were completely deactivated for $0.7\ \mu\text{M}$ and $2\ \mu\text{M}$ sulfide solutions, and Pd-Au/xGnP catalysts were deactivated by factors of 56 and 137, respectively (Figure 16).

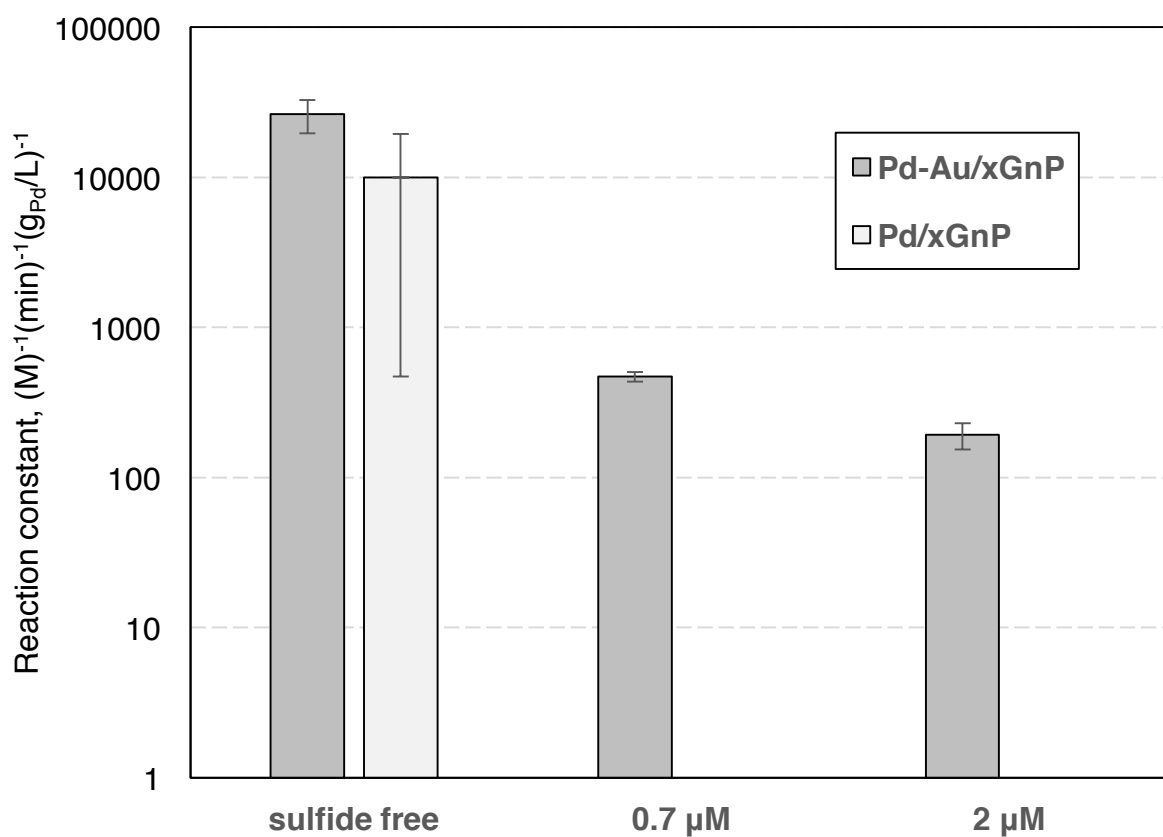


Figure 16: Comparison of batch reaction constants in the 2nd order for Pd/xGnP and Pd-Au/xGnP catalysts for sulfide free, 0.7 μM , and 2 μM sulfide concentrations.

3.4. Conclusions

Pd/xGnP and Pd-Au/xGnP catalysts were characterized for reactivity in the dechlorination of TCE in the presence of sulfide in batch reactors. Metallic Pd/xGnP catalysts were completely deactivated in the presence of sulfide at 0.7 μM and 2 μM . The reactivity of bimetallic Pd-Au/xGnP was significantly lower when employed in solutions with 2 μM of sulfide compared to 0.7 μM of sulfide due to increased deactivation, with second-order reaction rate constants of $(192 \pm 38$ and $469 \pm 35)$ $(\text{M}_{\text{H}_2\text{S}})^{-1}(\text{g}_{\text{Pd}}/\text{L})^{-1}$, respectively.

CHAPTER FOUR

Hollow fiber nanocomposite membranes with Pd and Pd-Au nanocatalysts supported on exfoliated graphite for TCE dechlorination*

*Hollow fiber membranes were fabricated and characterized in collaboration with MEM-TEK at Istanbul Technical University in Istanbul, Turkey.

Abstract

Hollow fiber membrane reactors were fabricated by embedding Pd/xGnP and Pd-Au/xGnP nanocatalysts in the polymer matrix, and the morphological and structural properties were characterized and compared with xGnP-free hollow fiber membranes and hollow fiber membranes embedded with neat xGnPs. The reactive fluxes of Pd-Au/xGnP filled membranes spun at 0 cm and 2.5 cm gap widths (7.2 ± 1.1 and 6.5 ± 1.2) $(\text{m/s})(M_{\text{H}_2})^{-1}(g_{\text{Pd}}/g_{\text{PSf}})^{-1}$ were significantly higher than reactive fluxes of Pd/xGnP filled membranes spun at 0 cm and 2.5 cm gap widths (2.0 ± 1.1 and 2.5 ± 0.6) $(\text{m/s})(M_{\text{H}_2})^{-1}(g_{\text{Pd}}/g_{\text{PSf}})^{-1}$. Hollow fiber membranes (xGnP-free, neat xGnP, Pd/xGnP, and Pd-Au/xGnP) spun at 2.5 cm gap widths demonstrated a significant increase in permeability ($\alpha = 0.1$) compared to hollow fiber membranes spun at 0 cm gap width, where permeabilities increased from (34 to 57, 18 to 37, 27 to 67, and 31 to 53) $\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}\cdot\text{bar}^{-1}$, respectively.

4.1. Introduction

Reductive catalysis is a promising strategy for removing drinking water contaminants that can elude conventional treatment methods, such as adsorption, ion exchange, chemical oxidation, or air-stripping. In particular nitrogen, bromine, and chlorine oxyanions; a number of halogenated organics; and aromatics are primary contaminants as listed by the U.S. EPA that can be transformed using Pd-based reductive catalysis. A major advantage of reductive catalysis as compared with conventional water treatment technologies is that the target contaminant is chemically transformed instead of merely transferred from one phase to another (e.g. water to solid, or water to air). While chemical oxidation by ozone, peroxide, or chlorine also destroys contaminants, toxic byproducts can form in the presence of dissolved organic matter.

Compared to up-flow and batch reactors, catalytic membrane reactors have confined pores where catalysis takes place. In confined pores, diffusion has a limited effect on the catalytic reaction kinetics, which are instead limited by rate of the reaction and convective flow through the membrane⁸⁹. Additionally, the polymer matrix can secure the catalysts, removing the need for catalyst recovery. Moreover, ultrafiltration membranes can remove dissolved organic matter that otherwise could foul the Pd-based catalyst. Ultrafiltration membranes are commercially produced in both flat sheet and hollow fiber configurations. Hollow fiber membrane modules are less prone to

clogging by foulants, and have much higher packing densities compared to flat sheet modules, improving the overall efficiency of water treatment.

In chapter 2 we showed that flat-sheet ultrafiltration membranes embedded with Pd-Au/xGnP and Pd/xGnP nanocatalysts acted as a flow-through catalytic reactor for TCE dechlorination achieving >90% TCE removal⁷⁸. To the best of our knowledge, this was the first report of TCE dechlorination in a polymeric membrane flow-through reactor. We built on this earlier work by fabricating hollow-fiber ultrafiltration membranes with embedded nanocatalysts for the flow-through dechlorination of TCE.

4.2. Experimental

4.2.1. Reagents

Ultrapure water (> 18 MΩ·cm) was used for membrane storage, nanoparticle synthesis, and in dechlorination experiments. Gold(III) trihydrate (HAuCl₄•3H₂O) (Sigma-Aldrich, >99.9%), palladium(II) chloride (PdCl₂) (Sigma-Aldrich, >99%), exfoliated graphene nanoplatelets (xGnP) (xG Sciences, Grade M), ethylene glycol (EG) (Fluka), sodium hydroxide (NaOH) (ACS, analytical reagent grade), polysulfone (PSf) (Udel, P3500), N-methyl-2-pyrrolidinone (NMP) (Sigma-Aldrich, >99%), polyethyleneglycol (PEG 4400) (Sigma-Aldrich, MW = 4400 da), and

poly(diallyldimethylammonium) chloride (PDADMAC) (Sigma-Aldrich) were used as received.

4.2.2. Synthesis and characterization of xGnP supported nanocatalysts

For Au nanoparticles, a solution of gold salt precursor solution was prepared by dissolving HAuCl_4 in water to make a concentration. 500 mM aqueous HAuCl_4 served as the gold salt precursor solution. Secondly, 50 mg of xGnP was suspended in 1 mL of PDADMAC and 50 mL of ethylene glycol in a round bottom flask using bath sonication (Aquasonic 50T, VWR Scientific) to disperse xGnPs. The round bottom-flask containing the xGnP in ethylene glycol was immersed in the oil bath and heated to 195° C. Next, 50 μL of gold precursor and 150 μL of 1 M NaOH were added to the solution and stirred. The reaction took place for 30 minutes under stirred conditions at 195° C. The prepared Au/xGnP particles were removed from solution by centrifugation, pouring off the supernatant, and then the separated Au/xGnPs were washed with acetone three times.

For Pd nanoparticles, a 22.5 mM solution of palladium salt precursor was prepared by dissolving PdCl_2 in ethylene glycol. Secondly, 50 mg of xGnP was suspended in 18 mL of ethylene glycol using bath sonication (Aquasonic 50T, VWR Scientific) for 12 hours to disperse the xGnP. Next, 2 mL of 22.5 mM PdCl_2 solution was added to the suspended xGnP in ethylene glycol and stirred for 2 minutes. After stirring, the solution was heated

in a microwave (900 W, 2450 MHz) for 50 seconds. The Pd/xGnP catalysts were separated from solution and washed in the same manner as Au/xGnP.

For bimetallic Pd-Au/xGnP nanoparticles, Au deposition occurred first using the Au/xGnP protocol described above. Next, Pd was deposited using the same procedure as described in the Pd/xGnP protocol except that Au/xGnP was used in place of neat xGnP. The Pd-Au/xGnP catalysts were separated from solution and washed in the same manner as Au/xGnP.

The concentration of Au and Pd was characterized using atomic absorption spectroscopy (Perkin–Elmer 1100). Au and Pd were stripped off xGnPs by leaching, and the concentration of Pd and Au was measured in the leachate. A weighed amount of Au/xGnP, Pd/xGnP, and Pd-Au/xGnP was heated in aqua regia near its boiling point (109° C). After boiling the aqua regia solution for 1 hour, the solution was sonicated in a bath sonicator for 3 hours. The sonicated solution was then filtered through nitrocellulose membranes and was diluted with water. The diluted filtrate was analyzed for Pd and Au content using atomic absorption analysis.

4.2.3. Preparation of nanocomposite hollow fiber membranes and membrane modules

Hollow fiber membranes were fabricated at MEM-TEK in Istanbul, Turkey using a pilot-scale hollow fiber machine (PHILOS) with the following spinning parameters. The dope solution composition for all membranes was 15% PSf, 16% PEG 4400, 69% NMP, and the bore solution was NMP. In catalyst filled membranes, the concentration of catalyst was 1.25 wt% of the PSf content. The dope and bore speeds were adjusted using control settings of 38 and 16 Hz on the spinning control panel, respectively, while no outside solution was applied. The temperature of the first and second coagulation bath was 30° C with a take up speed adjusted to 8.82 Hz on the spinning machine control panel.

For catalyst filled membranes, Pd/xGnP or Pd-Au/xGnP was suspended in NMP using bath sonication. After dispersing the nanocatalysts in NMP, PSf and PEG 4400 were added and stirred for 24 hours until the solution became homogenous. Prior to all hollow fiber spinning for different solution compositions, the machine was cleaned with a neat solution of PSf, NMP, and PEG 4400 with the same composition described above. All hollow fibers were rinsed in water for 24 hours, and were stored in water until used in dechlorination experiments. The only parameter adjusted during spinning was the gap width. Gap widths of 0 cm and 2.5 cm were used to determine the effect of dry phase inversion on reactivity and permeability (Figure 17).

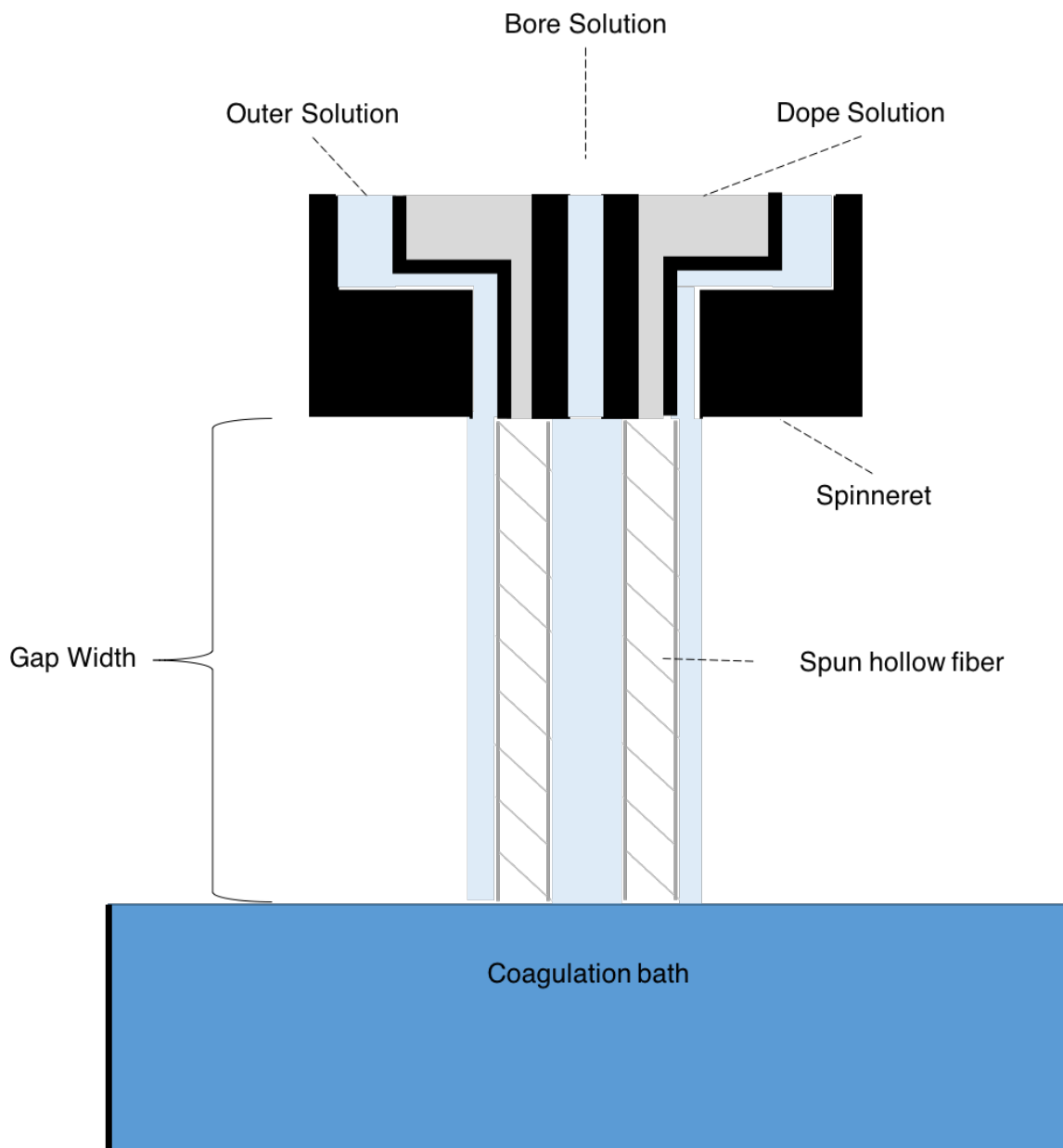


Figure 17: Schematic showing the hollow fiber spinneret where the bore solution and dope solution consisted of NMP and the nanocomposite polymer solution, respectively. The extrusion speed of the bore and dope solution can be controlled in the machine control panel.

To fabricate dead-end hollow-fiber modules, three spun fibers were secured end-to-end in tubing (diameter = 1.4 ± 0.2 mm, length = 300 ± 40 mm) using epoxy (Loctite Quick Set Epoxy). After drying for 24 hours, each module was pressure tested for leaks in water. The total outer active fiber surface area for each module is 40.3 ± 10.9 cm².

4.2.4. Membrane characterization

4.2.4.1 Membrane permeability

Membrane flux was determined by recording the mass of the filtrate collected on a mass balance interfaced with a computer. All membranes were compacted at 2.76 bar until steady state flux was reached. Following compaction and at $22 \pm 2^\circ$ C, permeability was calculated by using the linear regression of permeate flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$) versus pressure (bar) for (2.76, 2.07, 1.38, and 0.69) bar.

4.2.4.2 Mechanical properties

Young's modulus was determined for hollow fiber membranes using mechanical analysis with SII DMS 6100 Exstar. Every 3 s force data was collected in 250 N increments for 20 steps. The sample cross-sectional surface area of the hollow fiber was used to calculate the Young's modulus for each of the membranes.

4.2.4.3 TEM and SEM imaging

Membrane cross-section samples were prepared for SEM imaging by freeze fracturing hollow fibers in liquid nitrogen and coating the cross-sections with gold by sputtering. The specimens were mounted on aluminum stubs using carbon tape, and all images were recorded on an FEI Quanta FEG 200 SEM. Catalytic nanoparticles were imaged using a JOEL 2200FS TEM microscope. All samples were prepared by drop casting nanoparticles dispersed in acetone (~0.01 wt%) on 300-mesh nickel or copper grids. The grid was dried for 24 h at 90° C prior to imaging.

4.2.4.4 Catalytic reactivity

Dechlorination experiments were conducted in flow-through mode using dead-end hollow fiber modules with zero headspace in a pressurized hermetic bladder (High Sierra) contained in a stainless steel pressure vessel (Figure 18). To monitor H₂ concentration a sensor and signal amplifier (Unisense) were used. There was no loss of H₂ when testing for leakage over a 6-hour period. Before measuring membrane reactivity, adsorption capacity was exhausted by filtering 9.25 mg/L of TCE solution in the absence of reaction. After exhaustion experiments, the reactivity was determined using 9.25 mg/L TCE solution saturated with H₂ (0.8 mM). The catalytic activity for hollow fiber membranes was determined using the following steps:

- 1) 1 L of DI water was added to a plastic bladder (High Sierra) and purged with

N₂(g) for 15 min with the hollow fiber module secured inside.

- 2) 10 mL of 1000 mg/L TCE solution was added to N₂-purged water in the bladder, all headspace was removed, and the bladder was sealed.
- 3) The bladder was placed in a 5 L stainless steel pressure vessel (Alloy Products); the vessel was pressurized and the TCE solution was filtered through the membrane in four steps with a different transmembrane pressure at each step: 40, 30, 20, and 10 psi.
- 4) Step 3 was repeated, except that the N₂-purged water was saturated with H₂ prior to the addition of the TCE solution, and the aqueous hydrogen concentration of the permeate was monitored using an H₂ electrode microsensor and a picoampere-range amplifier. The permeate was collected in glass vials that were then sealed with Teflon lined caps.
- 5) TCE concentration in permeate samples was determined using gas chromatography

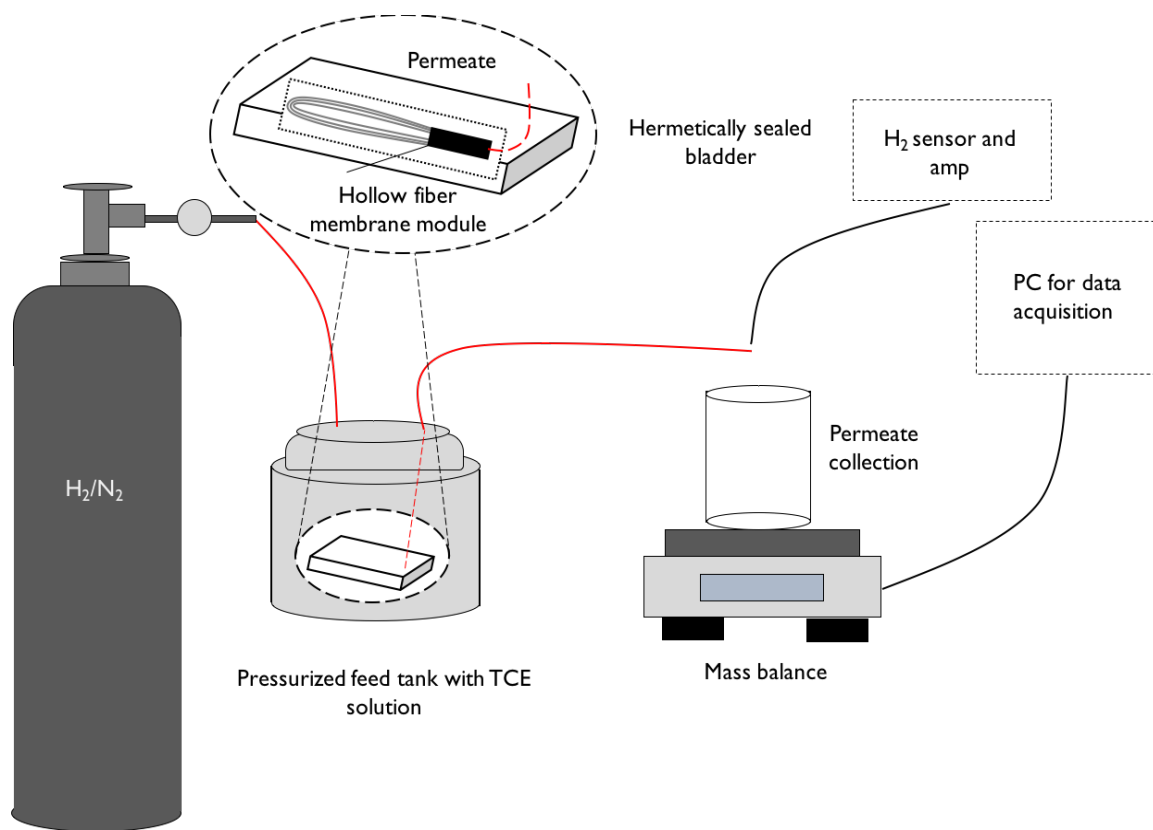


Figure 18: Schematic of experimental setup for TCE dechlorination experiments.

4.3. Results and Discussion

4.3.1. Properties of Pd/xGnP and Pd-Au/xGnP nanoparticles

To decorate xGnPs with Pd and Au nanoparticles, the polyol method was chosen based on our previous research¹⁵. This method is convenient because it allows for the synthesis of Pd/xGnP and Pd-Au/xGnP using a “one-pot” approach. The method combines two previously modified versions^{72, 87} of the polyol method⁹⁰. The initial stage of nanoparticle formation starts with the reduction of metal-salt precursor to metal ions, after which nucleation of ions occurs at the carbon surface of xGnPs⁷². Donor-acceptor complexes form between the π -electron rich regions on the carbon support and the metal ions supporting nucleation and metal nanoparticle formation.

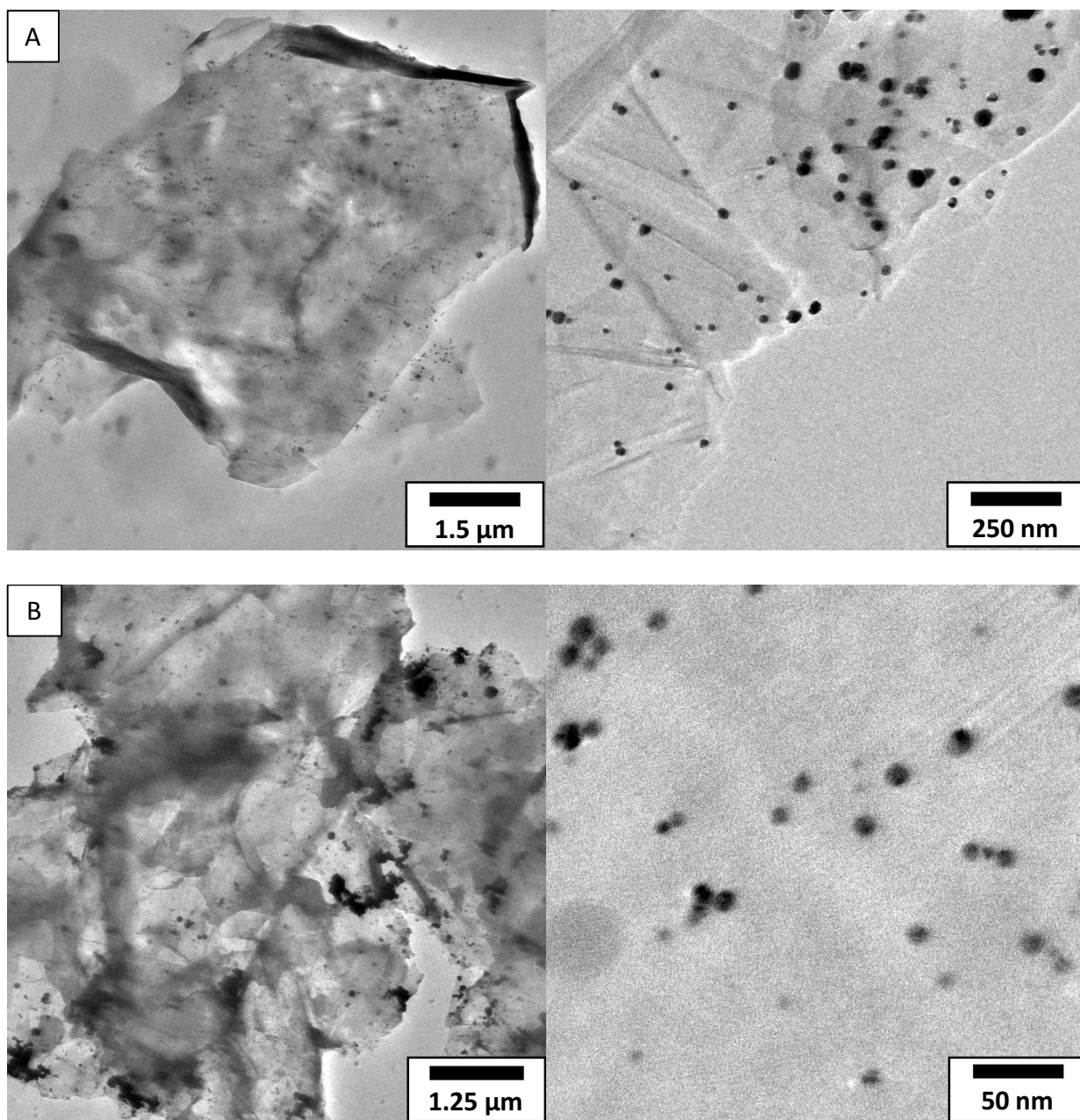


Figure 19: TEM images of Pd supported on xGnP (image A) and Pd-Au supported on xGnP (image B) used as nanofillers for nanocomposite hollow fiber membranes.

The average diameters of Pd nanoparticles and Pd-Au nanoparticles supported on xGnPs were 15 nm and 30 nm, respectively (Figure 19). Pd-Au nanoparticles formed a “core-shell” type morphology on the graphene support where the shell contains Pd and the core contains Au⁷⁸. The concentration of Pd on xGnPs for Pd/xGnP and Pd-Au/xGnPs was 10.3 and 12.4 wt%. The variability in Pd concentration for Pd/xGnP and Pd-Au/xGnP catalysts can be attributed to the formation of different sizes of nanoparticles formed for Pd nanoparticles on neat xGnPs compared to on Au decorated xGnPs.

4.3.2. Morphology and permeability of nanocomposite membranes

The cross-sectional morphology of all hollow fiber membranes was similar with a thin “dense layer” on a support layer that included large macrovoids. The cross-sectional morphologies of hollow-fiber membranes embedded with xGnPs and free of xGnPs were not noticeably different (Figure 20). For all nanocomposite and neat PSf membranes, there was a significant difference in permeability between membranes prepared with 0 cm gap width and 2.5 cm gap width ($\alpha = 0.1$). The permeability of Pd-Au/xGnP, Pd/xGnP, neat xGnP, and xGnP free membranes increased from (31.2 to 53.4, 26.7 to 66.7, 18.1 to 37, and 34.3 to 56.7) $\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}\cdot\text{bar}^{-1}$ respectively between 0 cm gap width to 2.5 cm gap width (Figure 21). The increase in membrane permeability can be attributed to a thinner “dense layer” resulting from the delayed onset of demixing for the thin selective layer of the membranes spun with a 2.5 cm air gap. During the

time of delayed onset of demixing, skin formation can occur slowly, thus forming a thinner “dense layer” compared to a “dense layer” formed during instantaneous demixing.

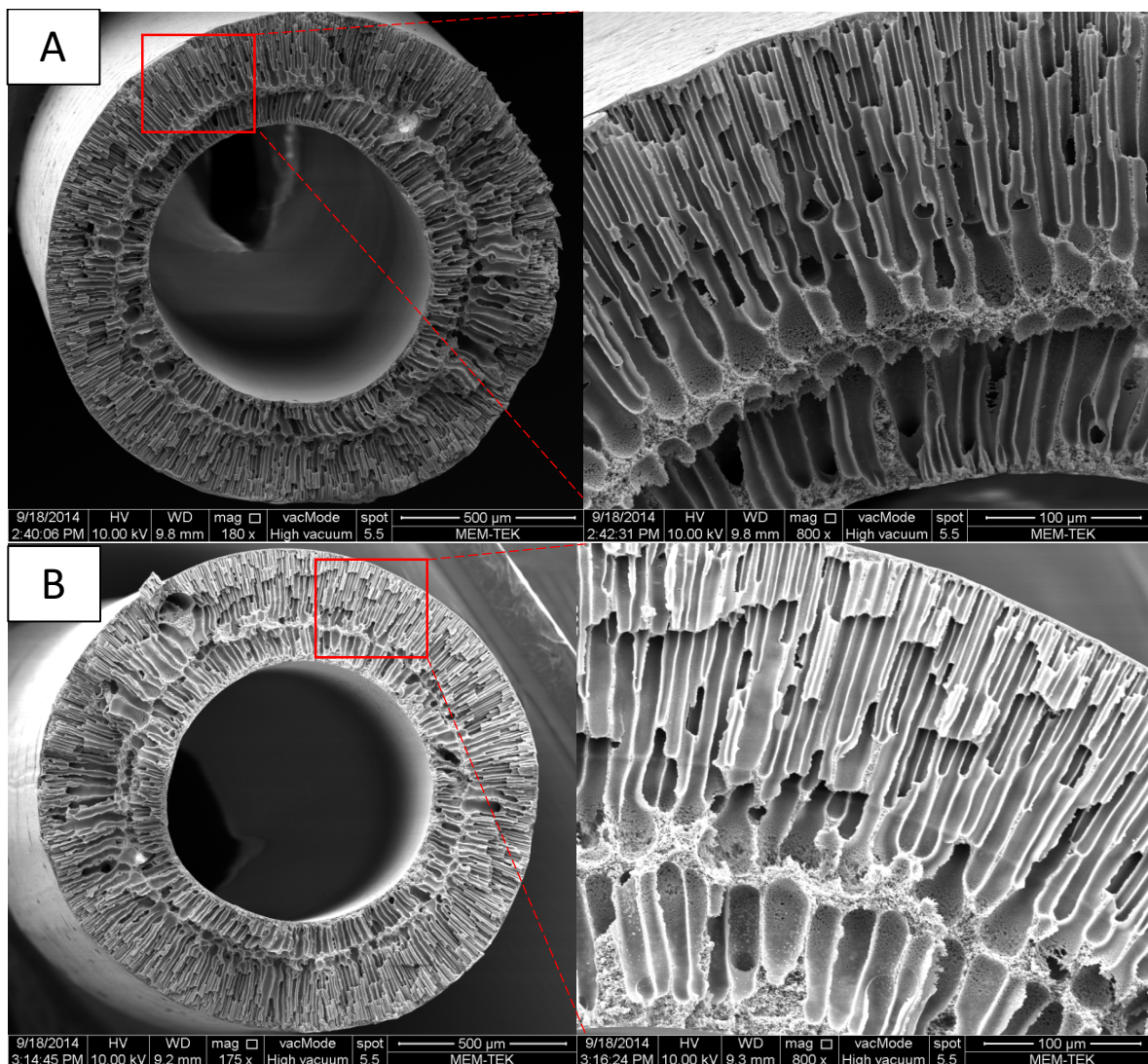


Figure 20: SEM images of cross-sections of xGnP-free hollow fiber membranes (A) and hollow fiber membranes filled with xGnPs (B).

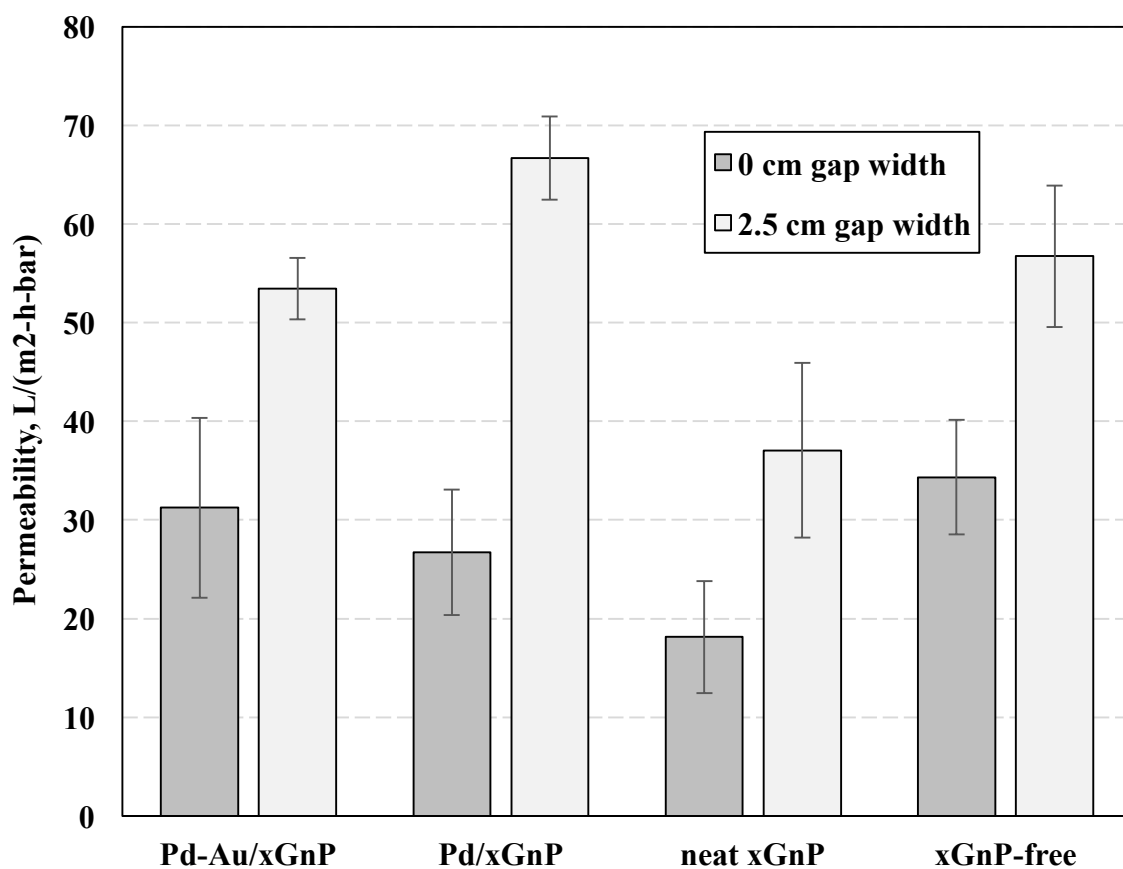


Figure 21: Permeability of hollow fiber membranes embedded with Pd-Au/xGnP, Pd/xGnP, neat xGnP, nanofillers; and without nanofillers. Error bars correspond to a 90% confidence interval for 3 measurements.

Dynamic mechanical analysis showed that there was no significant difference between the Young's modulus for membranes spun with 0 cm gap width and 2.5 cm gap width. The Young's moduli were 100 ± 22 MPa and 122 ± 14 MPa for 0 cm and 2.5 cm gap widths, respectively. Additionally, comparing nanocomposite membranes spun with 0 cm gap widths and 2.5 cm gap widths showed no significant difference in Young's moduli where the average moduli were 109 ± 16 and 132 ± 18 MPa, respectively.

4.3.3. Catalytic reactivity of nanocomposite membranes

The catalytic activity of membranes was quantified by conducting experiments where TCE was reduced with H_2 using Pd as the catalyst. The Pd catalyzed reduction of TCE is well studied^{79, 91-94}. The concentration of TCE in the permeate was determined using gas chromatography.

The nanocomposite hollow fiber membranes can be modeled as a plug-flow reactor with a pseudo-second order reaction. While the pseudo-first order decay model for Pd catalyzed TCE reduction is most commonly used for modelling, we used a second order model, which the data fit better (equation 9), where v (m/s) is the superficial velocity, $k_{obs}^{mem} \ell_{eff} ((m/s)(M_{H_2})^{-1})$ is the reactive flux of TCE in the membrane, and $\kappa^{mem} \ell_{eff}$ (m/s) is the reactive flux of H_2 in the membrane. Additionally, a significant decrease (>40% decrease) of H_2 was detected.

$$\ln \frac{[TCE]}{[TCE]_0} = -k_{obs}^{mem} \ell_{eff} \frac{[H_2]_0}{\kappa^{mem} \ell_{eff}} \{1 - \exp(-\kappa^{mem} \ell_{eff} / v)\} \quad (9)$$

Equation 9 was derived by integrating equation 10 where the decomposition of H_2 can be described by equation 11.

$$0 = -v \frac{d[TCE]}{dx} - k_{obs}^{mem} [TCE][H_2] \quad (10)$$

$$[H_2] = [H_2]_0 \exp(-\kappa^{mem} \ell_{eff} / v) \quad (11)$$

By plotting $-\ln \frac{[TCE]}{[TCE]_0}$ against $\frac{[H_2]_0}{\kappa^{mem} \ell_{eff}} \{1 - \exp(-\kappa^{mem} \ell_{eff} / v)\}$ and fitting the dependence using a linear regression, $k_{obs}^{mem} \ell_{eff}$ were determined (Figure 22). The complex porous structure (porosity and tortuosity) of the hollow fiber membranes made it impossible to determine k_{obs}^{mem} and ℓ_{eff} separately. The extent of the reaction can be described by the reactive flux, $k_{obs}^{mem} \ell_{eff}$, however.

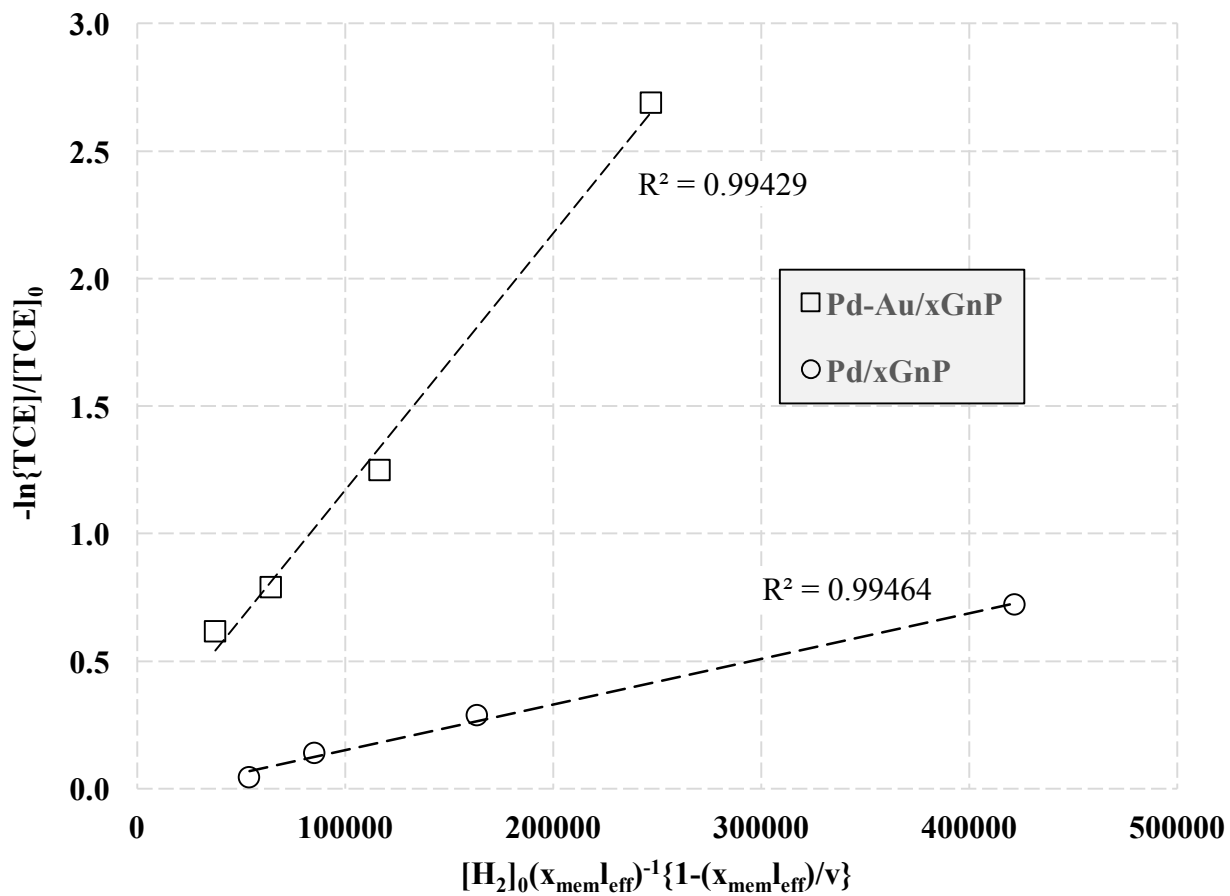


Figure 22: Example fits of experimental data for Pd-Au/xGnP and Pd/xGnP to determine the 2nd order reactive flux, $k_{obs}^{mem} \ell_{eff}$.

For xGnP-free and neat xGnP hollow fiber membranes, no reduction of TCE occurred, and for Pd/xGnP and Pd-Au xGnP membranes the average reactive flux for 0 cm and 2.5 cm gap widths was $(2.0 \pm 1.1$ and $7.2 \pm 1.1)$, and $(2.5 \pm 0.6$ and $6.5 \pm 1.2)$ $(\text{m/s})(M_{\text{H}_2})^{-1}(\text{g}_{\text{Pd}}/\text{g}_{\text{PSf}})^{-1}$, respectively. For Pd-Au/xGnP membranes the reactive flux was significantly greater than the reactive flux for Pd/xGnP membranes. However, there was no statistically significant difference between different gap widths for the same catalyst (Figure 23).

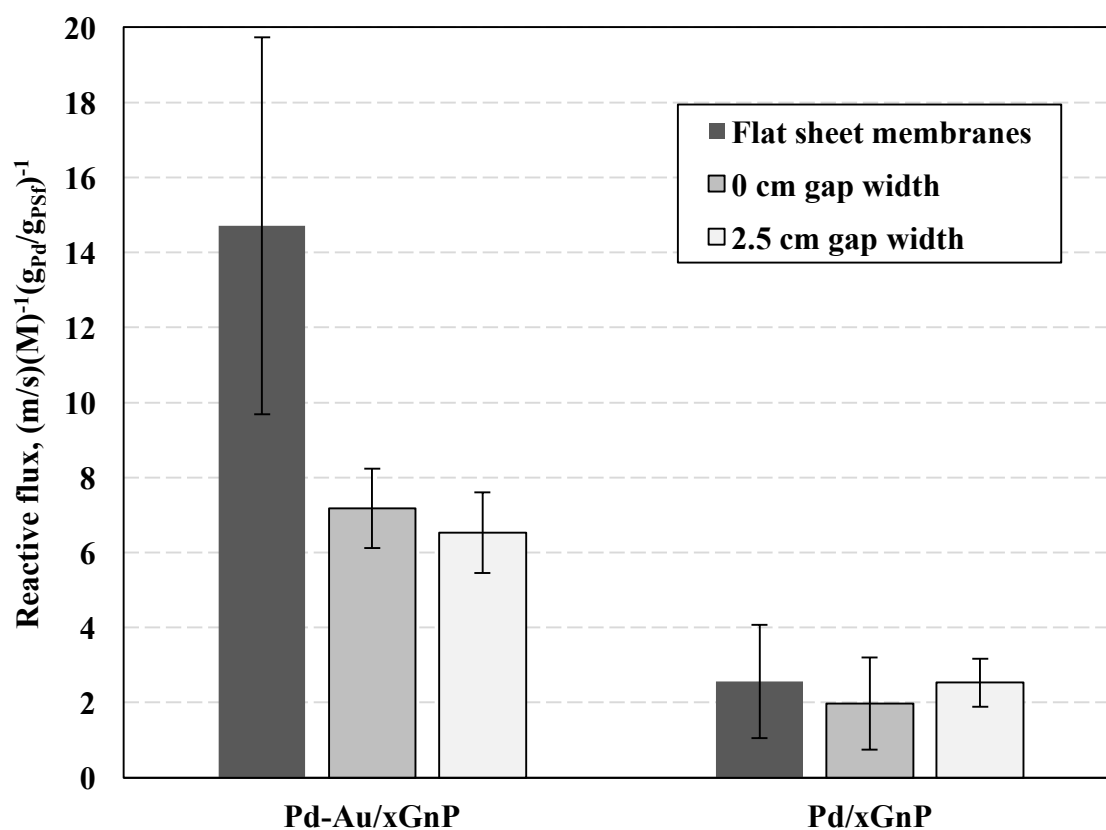


Figure 23: Reactive flux (i.e. 2^{nd} order reaction rate constants normalized by Pd content in hollow fiber membranes) for Pd-Au/xGnP and Pd/xGnP hollow fiber membranes where error bars correspond to a 90% confidence interval with 3 measurements. The hollow fiber membranes were compared with flat sheet nanocomposite membranes characterized in Chapter 2.

4.4. Conclusions

Metallic Pd/xGnP and bimetallic Pd-Au/xGnP were used as catalyst for the dehalogenation of TCE in hollow fiber membranes, extending on the use of these catalysts in flat-sheet membranes. The extended use of Pd/xGnP and bimetallic Pd-Au/xGnP filled membranes to hollow fiber membranes shows promise for industrial and municipal use of catalytic membranes for TCE dehalogenation. It was shown that the reactive fluxes for Pd-Au/xGnP in hollow fiber membranes spun at 2.5 cm and 0 cm gap widths were significantly higher than reactive fluxes for hollow fiber membranes embedded with Pd/xGnP. Additionally, it was shown that hollow fiber membranes spun at 2.5 cm gap width has significantly higher permeabilities than hollow fiber membranes spun at 0 cm gap width.

CHAPTER FIVE

Future work: Using self-assembled block-terpolymer membranes for flow-through catalytic reactions to improve modelling of reaction kinetics

5.1. Introduction

The integrally skinned asymmetric membrane developed in 1963 by Loeb and Sourirajan ushered membranes into commercial use for water treatment. While membranes have evolved dramatically since their early development, research presses forward in the advancement of materials science, pushing separation and permeability nearer to the thermodynamic limits^{95, 96}. However, as more permeable and selective membranes approach the practical thermodynamic limit for demixing there will be diminishing returns in energy consumption versus permeability⁹⁶. As a result of these practical limits on further improving permeability and selectivity, it is important to find other ways to improve the efficiency of membrane separations, such as developing hybrid membrane processes that combine membrane separations with some other treatment process.

Recent nanocomposite membrane research gives promise to new hybrid membrane processes being developed for water treatment applications. By embedding catalytic

nanoparticles into a membrane matrix, membranes can perform catalytic reactions in addition to physical separation^{87, 97}. Anti-fouling membranes can be fabricated by imbedding biocidal nanoparticles that could reduce biofouling and bacterial growth⁹⁸⁻¹⁰⁰. Photocatalytic membranes that provide virus disinfection can be fabricated by depositing titanium dioxide nanoparticles onto the outer surface of inorganic membranes^{10, 88, 101, 102}. Such hybrid processes can greatly enhance membrane performance, benefitting from synergistic functionality. These developments in hybrid membrane processes have led researchers to push for a more comprehensive understanding of the interface of nanomaterial science and membrane science.

The limits of understanding hybrid membrane processes on a fundamental level illustrate a critical deficiency in our current knowledge as it relates to membrane science. This lack of understanding about hybrid membrane processes hinges on the fact that the structures of these membranes are not well defined. It has been shown that membranes fabricated from polymeric and inorganic matrices can be used for flow-through catalysis^{87, 97}. For polymeric membranes, it was difficult to model high-throughput catalytic reactions for Au/xGnP, Pd/xGnP, and Pd-Au/xGnP supported membranes to the extent at which the reaction constant could be quantified for the catalyst^{78, 87}. Instead, an aggregate reaction constant was developed by combining the reaction constant of the catalysts with the effective length of the reactor (i.e. the pore characteristics), resulting in the aggregate constant, reactive flux, for describing the observed membrane reactivity. Titania membranes were used to support anatase TiO₂

nanoparticles for photocatalytic deactivation of viruses, however, the photocatalytic reaction and virus deactivation could not be modeled comprehensively because of the complexity of the membrane structure^{88, 103}. Track-etched membranes with Au nanoparticles supported on the pore walls enabled researchers to model 4-nitrophenol to 4-aminophenol, but tracked-etched membranes with such low pore densities were impractical for high throughput catalysis⁹⁷. For self-assembled block terpolymer membranes, it has been demonstrated that the pore size, length, and packing structure can be controlled through the self-assembled nonsolvent induced phase separation (S-NIPS) fabrication process¹⁰⁴⁻¹⁰⁶. A membrane with such tunable pore structures that are well-defined would make an exceptional matrix for flow-through catalysis and would enable researchers to model the kinetics of flow-through reactions better than with membranes with complex, undefined matrices.

The limited understanding of how membrane pore structure affects the performance of hybrid membrane processes leads to the following research objectives, questions, and hypotheses

Objective 1: Evaluate the effects of size, shape, morphology and placement of nanoparticles embedded in self-assembled membranes.

Q1: What incorporation routes for nanoparticles into self-assembled membranes leads to the best catalytic membrane for the optimal control of size, shape, and morphology of

nanoparticles during synthesis; the placement of nanoparticles inside the membrane; and the pore characteristics of self-assembled membranes after incorporating nanoparticles?

H1: The **a1)** size, shape, morphology of the nanoparticles; **b1)** placement of nanoparticles embedded inside self-assembled membranes, and; **c1)** pore characteristics, contribute to the extent of the catalytic reaction by changing the available catalyst surface area manifested by changes of **a1)** and by changing the amount of time the reactants are in contact with catalysts manifested by changes in **b1)** and **c1)**.

Objective 2: Evaluate the optimal pore characteristics and operating conditions for catalytic flow-through reactions in self-assembled membranes.

Q2: What are the effects of the pore characteristics (i.e. pore diameter, porosity, and pore length) and the membrane operating parameters on the performance of the catalytic membrane?

H2: The pore characteristics and operating conditions of self-assembled membranes can induce changes in membrane reactivity by changing the extent in which convective transport, diffusive transport, and residence time of the reactants inside the membrane affect the membrane reactivity.

Objective 3: Construct models to simulate and predict the effects discussed in objective 1 and objective 2 on the performance of the membrane reactor.

Q3: How can these parameters be used to build models that simulate and predict the effects studied in **Q1** and **Q2** on membrane performance? With these research questions in mind, I propose to fabricate self-assembled catalytic membranes with highly controllable pore characteristics and model how such pore characteristics affect membrane reactivity and performance.

H3: Self-assembled membranes embedded with catalytic nanoparticles as compared to conventional phase inversion membranes can preserve the high reactivity of catalytic membranes, and additionally, can be modeled more completely as a result of well-defined pore characteristics and well-characterized shape, size, morphology and placement of catalytic nanoparticles embedded in the membrane.

Answering these research questions would significantly advance the field of membrane science and technology.

5.2. Functionalization of self-assembled block terpolymer membranes with Au nanoparticles

I propose that self-assembled terpolymer membranes be functionalized with Au nanoparticles to support high-throughput catalysis of 4-nitrophenol to 4-aminophenol, allowing researchers to fully elucidate the fundamental mechanisms affecting performance in membrane reactors for high-throughput reactions. Membrane functionalization can be achieved using three different methods: **1)** incorporating Au nanoparticles into the terpolymer solution that favorably interact with core of the poly(4-vinylpyridine) (P4VP) micelles in the terpolymer solution¹⁰⁷⁻¹⁰⁹, **2)** reducing Au precursor solution to form nanoparticles selectively within the core of the P4VP micelles in the terpolymer solution^{110, 111}, or **3)** depositing Au nanoparticles on the pore walls (i.e. the P4VP block) of the formed terpolymer membrane using a layer-by-layer approach.

Using method **1)**, researchers have shown that both modified and neat nanoparticles could be included in the P4VP block of a copolymer/terpolymer system. In a block terpolymer and tetrahydrofuran/dioxane system, TiO₂ nanoparticles were incorporated in the P4VP block of the terpolymer due to preferential interactions¹⁰⁷. Using atom-transfer radical polymerization, researchers grafted P4VP branches on Au nanoparticles that were subsequently included in the P4VP block of a copolymer solution and cast as a thin film^{108, 109}. This method is a “one-pot” approach to fabricate self-assembled membranes functionalized with Au nanoparticles, and the shape, size, and morphology

of Au nanoparticles can be easily controlled due to ex-situ synthesis of the nanoparticles. However due to the high surface energy of metal nanoparticles, it is difficult to precisely control the placement of metal nanoparticles within the membrane and maintain the self-assembly of ordered pore structures¹¹².

Using method **2**), it was shown that nanoparticles can be fabricated in-situ by reducing a metal precursor solution selectively inside the microphases of block copolymer and solvent solutions. Pd nanoparticles were synthesized in both homopolymer (poly(4vinylpyridine), P2VP) and block copolymer (poly(4-vinylpyridine-b-isoprene), P2VP-b-PI) solutions, where nanoparticles preferentially remained in the P2VP blocks¹¹⁰. The resulting Pd nanoparticles were mixed and cast with neat block copolymer solutions (P2VP-b-PI) such that the Pd nanoparticles were included only in the P2VP block for nanoparticles modified with the homopolymer, and at the P2VP-b-IP interface for nanoparticles modified with the copolymer¹¹⁰. Similarly, a system of terpolymer (poly(isoprene-b-styrene-b-2-vinylpyridine), PI-b-PS-b-P2VP) and toluene/hexane was used to selectively incorporate a gold metal precursor (i.e. gold(III) chloride) into the P2VP microphases and was subsequently reduced forming Au nanoparticles after plasma treatment¹¹¹. Unlike method **1**), this method gives precise control of nanoparticle placement within the terpolymer solution while maintaining the self-assembly of a controlled porous structure. However, in-situ synthesis of metal nanoparticles lacks much of the control that would be present in method **1**).

Using method **3**), it was shown that polycarbonate track etched membranes were functionalized with Au nanoparticles using layer-by-layer deposition of polyelectrolyte solutions containing Au nanoparticles⁹⁷. Knowing that polyelectrolyte multilayers (PEMs) can immobilize metal nanoparticles, one could functionalize block terpolymer membranes with Au nanoparticles using a layer-by-layer approach for depositing PEMs, containing Au nanoparticles, on the pore walls of self-assembled terpolymer membranes. Similar to method **1**), metal nanoparticles are synthesized ex-situ, hence, enabling a high degree of control of the size, shape, and morphology of metal nanoparticles. However, the polyelectrolytes would effectively change the pore size and surface charge of the P4VP pore walls.

5.3. Approach to modelling hybrid membrane catalysis and separation using self-assembled block terpolymer membranes functionalized with Au nanoparticles

Fundamentally understanding the parameters that affect hybrid membrane processes depends on the ability to comprehensively model them. The complex pore structure of traditional phase-inversion polymeric membranes makes structural characterization such as determining pore size, length, and overall porosity, difficult, which in turn makes comprehensively modelling of the hybrid membrane process difficult. Self-assembled block terpolymer membranes with well-defined pore characteristics can be

functionalized and used to support flow through catalysis, which can be modeled to elucidate the fundamental mechanisms affecting flow through reactions.

To comprehensively model the catalytic reduction of 4-nitrophenol in functionalized self-assembled membranes, the following protocol is proposed. First, the catalytic nanoparticles will be characterized. Second, diffusional studies will be conducted on 4-nitrophenol passage through the membrane. Third, the pore structure of the membrane will be characterized. Finally, the membrane operating parameters will be optimized. The characterization of nanoparticles gives the reaction parameters, which include particle diameter and surface area, the concentration of reactive surface sites, and catalyst loading. The diffusivity and partitioning coefficient of 4-nitrophenol determined from diffusion studies of the membrane can be used to bolster the flow-through reaction model by incorporating diffusional effects. Membrane parameters such as pore size, length, and porosity will serve as the physical parameters of the membrane reactor. Finally, the feed concentration of 4-nitrophenol, volumetric flux, and permeability are the operating parameters that will be used in modeling the performance of the membrane reactor. Using these modeling parameters, the intrinsic reaction constants and concentration profile of 4-nitrophenol in the membrane can be calculated, which can be used to predict and simulate the effects that the reaction rate constant, membrane parameters, and 4-nitrophenol diffusivity have on the catalytic reduction of 4-nitrophenol.

In the catalytic reduction of 4-nitrophenol to 4-aminophenol, borohydride is the reducing agent, and Au nanoparticles are the catalyst. The extent of this reaction can be quantified using ultraviolet-visible spectrophotometry. To determine the rate constant of the catalytic reaction, it can be modeled as a plug-flow reactor, accounting for advective and diffusive transport of 4-nitrophenol to the catalyst in a two-dimensional model. Separation properties, such as the molecular weight cutoff and permeability, can be characterized by challenging the membrane with solutions of dextran or poly(ethylene glycol) of different molecular weights. Characterization of pore size, length, and porosity can be conducted using electron microscopy, while rejection and permeability studies can corroborate conclusions from microscopy.

The ability to comprehensively model a hybrid catalytic membrane enables us to have better control of membrane and catalyst parameters that affect the performance of the membrane reactor. For example, knowing at what operating flux advective transport of 4-nitrophenol can no longer be assumed to dominate diffusive transport would be critical in optimizing the hybrid process. Being able to model the effects of the pore size (i.e. the plug-flow reactor width) on the membrane reactivity is crucial in optimizing and understanding this hybrid process. Finally, being able to model the extent of the reaction as a function of catalyst loading is important in balancing the reactivity of the membrane with the cost of the membrane.

5.4. Merit of work

The hybridization of membrane separations with other processes such as disinfection, or catalysis can benefit from combining two processes into one, as compared to the processes being operating distinctly on their own. The benefits can arise from reducing the footprint of the combined processes or synergistic effects resulting from combining two processes. The extent to which these processes are understood relies on the ability to model them. For catalytic membranes, it is difficult to determine parameters such as pore size, length, and porosity because of the complicated pore structure of traditional polymeric membranes, thus, models of these processes are often incomplete. Modelling self-assembled block terpolymer membranes with embedded catalytic nanoparticles as a flow-through reactor eliminates this complication because of the well-defined pore characteristics of this membrane, allowing for a more complete model and characterization of the flow-through reaction. While track-etched membranes can also have well-defined pore structures, these membranes have low porosities. The high porosity of self-assembled membranes, however, allows for high-throughput reactions, not limiting their use to small lab scale operation.

It is important to fully understand how the reaction parameters, membrane parameters, and operation parameters affect the efficiency of the catalytic reactor. Using a well understood reaction such as the catalytic reduction of 4-nitrophenol to 4-aminophenol will allow for exhaustive modelling. This work can be extended to optimize the

performance of current catalytic membranes, or perform feasibility studies on new catalytic membranes, such as membranes for catalytic denitrification. This research can also be used as a framework to delve into modelling other hybrid membrane processes such as combining disinfection or photocatalysis with membrane filtration in place of catalysis. Finally, practical limitations of catalytic membrane reactors can be recognized and overcome as a result of this study. For example, catalytic reaction constants, residence time, pore characteristics, and operating flux all are parameters that can be used in modelling the reactivity of the membrane, the separation properties of the membrane, and the total cost of the membrane.

APPENDICES

APPENDIX I

Derivation of 1st and 2nd order reaction kinetics for plug-flow reactors

The following describes the plug-flow model with a first and second order reaction for flow through reactors.

List of terms:

$[TCE]_0$ = Initial feed concentration of TCE in the reactor

$[TCE]$ = Concentration of TCE in the reactor at distance, x

E = Dispersion term in the reactor

x = Distance in the reactor

v = Superficial velocity of flow across the membrane

k_{obs} = Observed reaction rate constant for the dechlorination of TCE

l_{eff} = Effective length of the plug flow reactor

$[H_2]_0$ = Initial concentration of hydrogen in the reactor

$[H_2]$ = Concentration of hydrogen in the reactor at distance x

κ^{obs} = Observed reaction rate constant for the consumption of H_2

Advection-dispersion equation with a first order reaction in one dimension

$$\frac{\partial [TCE]}{\partial t} = E \left[\frac{\partial^2 [TCE]}{\partial x^2} \right] - v \frac{d[TCE]}{dx} - k_{obs}[TCE] \quad (12)$$

The concentration profile of TCE along the reactor's length was assumed to achieve steady state. This means that the partial derivative of concentration with respect to time is 0

$$0 = E \left[\frac{\partial^2 [TCE]}{\partial x^2} \right] - v \frac{d[TCE]}{dx} - k_{obs}[TCE] \quad (13)$$

It was assumed that dispersion could be neglected.

$$0 = 0 - v \frac{d[TCE]}{dx} - k_{obs}[TCE] \quad (14)$$

To solve the differential equation, the variables are separated and both sides of the equation are integrated.

$$v \frac{d[TCE]}{dx} = k_{obs}[TCE] \quad (15)$$

$$\frac{d[TCE]}{[TCE]} = k_{obs} \cdot \frac{1}{v} \cdot dx \quad (16)$$

The limits of integration for the concentration are from the feed concentration, $[TCE]_0$, at $x = 0$ to the effluent concentration $[TCE]$ at effective length, l_{eff} .

$$\int_{[TCE]_0}^{[TCE]} \frac{d[TCE]}{[TCE]} = k_{obs} \cdot \frac{1}{v} \cdot \int_0^{l_{eff}} dx \quad (17)$$

$$\ln \frac{[TCE]}{[TCE]_0} = -\frac{1}{v} k_{obs} l_{eff} \quad (18)$$

The solved equation describes the plug-flow at steady state with a first order reaction and no dispersion.

$$[TCE] = [TCE]_0 \cdot \exp \left[-\frac{1}{v} k_{obs} l_{eff} \right] \quad (19)$$

Advection-dispersion equation with a second order reaction in one dimension

$$\frac{\delta [TCE]}{\delta t} = E \left[\frac{\delta^2 [TCE]}{\delta x^2} \right] - v \frac{d[TCE]}{dx} - k_{obs} [TCE] [H_2] \quad (20)$$

The concentration profile of TCE along the reactor's length was assumed to achieve steady state. This means that the partial derivative of concentration with respect to time is 0.

$$0 = E \left[\frac{\delta^2 [TCE]}{\delta x^2} \right] - v \frac{d[TCE]}{dx} - k_{obs} [TCE] [H_2] \quad (21)$$

It was assumed that dispersion could be neglected.

$$0 = 0 - v \frac{d[TCE]}{dx} - k_{obs} [TCE] [H_2] \quad (22)$$

To solve the differential equation, the variables are separated and both sides of the equation are integrated.

$$v \frac{d[TCE]}{dx} = k_{obs} [TCE] [H_2] \quad (23)$$

$$\frac{d[TCE]}{[TCE]} = k_{obs} \cdot \frac{1}{v} \cdot [H_2] \cdot dx \quad (24)$$

The hydrogen concentration was determined to follow a first order plug flow model (Equation 17), and was inserted into the differential equation before integration (Equation 18).

$$\frac{d[H_2]}{dt} = \kappa_{obs}[H_2] \quad (25)$$

$$\frac{d[H_2]}{[H_2]} = -\kappa^{obs} \cdot dt \quad (26)$$

$$\int_{[H_2]_0}^{[H_2]} \frac{d[H_2]}{[H_2]} = \int_0^t -\kappa^{obs} \cdot dt \quad (27)$$

$$[H_2] = [H_2]_0 \exp(-\kappa^{obs} t) \quad (28)$$

$$\frac{d[TCE]}{[TCE]} = k_{obs} \cdot \frac{1}{v} \cdot [H_2]_0 \exp(-\kappa^{obs} t) \cdot dx \quad (29)$$

$$\int_{[TCE]_0}^{[TCE]} \frac{d[TCE]}{[TCE]} = k_{obs} \cdot \frac{1}{v} \cdot [H_2]_0 \cdot \int_0^{l_{eff}} \exp\left(\frac{-\kappa^{obs} x}{v}\right) \cdot dx \quad (30)$$

After integration the plug flow reaction can be modeled by equation 31, and after multiplying by $\frac{l_{eff}}{l_{eff}}$ equation 32 expresses the hydrogen and TCE reaction constants as reactive fluxes, $-k_{obs}l_{eff}$ and κl_{eff} .

$$\ln \frac{[TCE]}{[TCE]_0} = -k_{obs} \frac{1}{\kappa^{obs}} \cdot [H_2]_0 \cdot \left\{ 1 - \exp\left(\frac{-\kappa^{obs} l_{eff}}{v}\right) \right\} \quad (31)$$

$$\ln \frac{[TCE]}{[TCE]_0} = -k_{obs} l_{eff} \frac{1}{\kappa^{obs} l_{eff}} \cdot [H_2]_0 \cdot \left\{ 1 - \exp \left(\frac{-\kappa^{obs} l_{eff}}{v} \right) \right\} \quad (32)$$

APPENDIX II

Fabrication of TFC polyamide membranes and semipermeable CA membranes with xGnPs as a nanofiller

1. Introduction

The first reverse osmosis membranes were fabricated in 1963 via phase inversion of cellulose acetate (CA) polymer¹. CA membranes continue to be employed as ultrafiltration, nanofiltration, and reverse osmosis membranes. With more than 50 years of research on cellulose acetate membranes, researchers have exhaustively characterized the different properties of these membranes. As the acetylation of cellulose acetate increases, membranes can be made more selective^{113, 114}. The phase inversion of CA produces a very smooth surface with greatly decreased the propensity of membrane fouling¹¹⁵. By changing the parameters involved in membrane synthesis (e.g. polymer content, solvent, non-solvent, coagulation bath temperature, etc.), the pore size and density can be controlled relatively easily. The limits of operation of cellulose acetate membranes, however, is usually restricted to temperatures less than 30 °C and pH between the range of 4-8.

Thin film composite (TFC) reverse osmosis membranes are fabricated via interfacial polymerization of two monomers on an ultrafiltration membrane support. The first TFC

membranes were fabricated in 1980¹¹⁶ and became popular as the permeability and rejection are nearly 50% higher than CA membranes and greater than 99% rejection of monovalent ions, respectively. While TFC membranes are superior in permeability, selectivity, and operating at more extreme parameters (i.e. pH and temperature) compared to CA membranes, they have a very low tolerance to chlorine and are structurally fragile. Additionally, the process of fabrication is complex since the formation of the thin film separation layer is extremely sensitive to factors such as curing temperature and method, support layer morphology, monomer concentration, etc¹¹⁷⁻¹²¹.

The solution diffusion model emerged as a highly debated way to describe reverse osmosis as compared to flow through a porous medium in the late 1960's and early 1970's. This model describes the process of how different permeants partition in the membrane and diffuse across the membrane. The mechanisms that induce separation of different permeants through the membrane are described in the model by the different partition coefficients and rates of diffusion across the membrane for different permeants. The solution diffusion model is a unified approach used to model reverse osmosis membranes and applications.

In this study, two methods of fabrication, phase inversion and interfacial polymerization (i.e. TFC), were used to synthesize semipermeable membranes with CA and polyamide. The effects of xGnP nanofiller in CA membranes were studied, and the effects of support membranes were studied for TFC membranes.

2. Experimental

2.1. Reagents

Dioxane, acetic acid, acetone, methanol, cellulose diacetate (CDA), cellulose triacetate (CTA), xGnPs, phenylenediamine (2%wt, MDP), trimethylamine (2%wt, TEA), camphorsulfonic acid (4%wt, CSA), trimeoyl chloride (0.1% wt), polysulfone (PSf), n-methyl-2-pyrrolidone (NMP), and polyethylene glycol (MW400, PEG400) were all used as received.

2.2 Fabrication of PA TFC membranes

2.2.1. Ultrafiltration support membrane

PSf ultrafiltration membranes were used as a support membrane for the thin-film PA layer and were cast using the phase inversion technique. PSf pellets were dissolved in NMP at a known composition (Table 6) at 60 °C to help with dissolution. After PSf completely dissolved (~ 24 h), PEG400 was added and stirred until a homogenous mixture was reached. A thin film was cast on either a glass support or a non-woven support taped to a glass support using a micrometric film applicator (Model 3570, Elcometer). Immediately after casting the film, the film was immersed in a water bath, initiating phase inversion. After the membrane detached from the glass support, it was

rinsed with DI water for 15 minutes. The ultrafiltration membrane soaked in DI water for 24 h to remove any residual NMP, after which the water was exchanged with fresh DI water.

2.2.2. Interfacial polymerization of PA on the ultrafiltration support

A template of the support membrane was cut using a sharp razor blade and taped to the outside of a petri dish with the dense side facing up. The edges of the membrane template were sealed with tape to prevent any monomer solutions from coming in contact with the permeate side of the ultrafiltration membrane. MPD solution was prepared by dissolving 4 g of CSA in 2.754 mL of TEA. The solution was mixed for 20 minutes. After CSA was completely dissolved, 2 g of MPD was added and dissolved by agitation for 5 minutes. After MPD was dissolved, 100 mL of DI water was added and stirred for 15 minutes. TMC solution was prepared by mixing 0.336 mL of TMC in 250 mL of hexane. After the feed side of the ultrafiltration template was completely dry, the template taped on the outside of the smaller petri dish was immersed for 15 s in the larger petri dish containing the MPD solution. The MPD saturated membrane was removed from the larger petri dish and dried with forced air for 2 min. In a separate larger petri dish, 40 mL of TMC solution was added. The dried membrane template that was saturated with MPD solution was immersed in the petri dish containing TMC solution for 15 seconds initiate the polymerization. Again, the membrane template was removed and dried with forced air for 2 min. The TFC composite membranes were then

heat treated for 10 min at 50C. Finally, the membrane was rinsed with DI water for 15 minutes and soaked in DI water for 24 hours.

2.3 Fabrication of CA nanocomposite membranes

For nanocomposite membranes, a desired amount of xGnP was dispersed in 12.59 mL of dioxane using a sonication bath for 1 hour. After xGnP was fully dispersed, 1.2 g of CTA was dissolved in the dioxane containing xGnP and 6.32 mL of acetone. The solution was mixed for 24 hours or until the solution reached homogeneity. After CTA was fully dissolved, 2.29 mL of acetic acid was added and 2.8 g of CDA was dissolved in the CTA solution by slowly adding 250 mg of CDA at a time. Finally, methanol, a non-solvent, was slowly added using a burette to prevent localized inhomogeneity in the polymer solution. One drop was added every second until 5.06 mL of methanol was added to the polymer solution. After homogeneity was reached (~24 h), a thin film (250 μm) of the polymer solution was spread on a glass support using micrometric film applicator (Model 3570, Elcometer). Dry phase inversion was initiated first by allowing the solvent to evaporate from the film for 15 s. Next, wet phase inversion was initiated by immersing the thin film into a coagulation bath of DI water with a temperature of 4C. After nearly 2 hours, the thin film detached from the glass support. The membrane was rinsed with DI water for 20 minutes. After removing any residual solvent or non-solvent, the CA membrane was annealed in water at 80C for 15 minutes.

2.4 Compositions of semipermeable membranes

For TFC membranes, all monomer solutions were kept the same, but the support membranes varied by thickness and whether the ultrafiltration support membrane was cast with or without a non-woven support. For CA membranes, the solution compositions were all kept the same, except for the nanofiller content. Table 6 and 7 describes the compositions of all membranes.

Table 6: Compositions of TFC PA solutions and support membranes

Compositions of TFC PA semipermeable membranes for reverse osmosis									
Monomer solution components					Support membrane components				
Membrane	MPD wt%	TEA wt%	CSA wt%	TMC wt%	Non-woven support	Thickness, μm	PSf wt%	PEG400 wt%	NMP wt%
UF1	2	2	4	0.1	Yes	300	20	15	65
UF2					Yes		24	0	76
UF3					No	200	20	0	80
UF4					Yes		18	0	72
UF5					No		18	0	72

Table 7: Compositions of semipermeable CA membranes

Compositions of semipermeable CA membranes for reverse osmosi							
Membrane	Dioxane wt%	Acetic acid wt%	Acetone wt%	Methanol wt%	CTA wt%	CDA wt%	xGnP/PSf, %
CA							0
CA1%	45.7	8.5	17.6	14.1	4.2	9.9	1
CA2%							2

2.5 Characterization of membrane permeability and selectivity

To characterize membrane permeability, dead-end filtration was used with a stainless steel high pressure filtration device (Sterlitech HP4750) pressured under nitrogen. First, all membranes were compacted at the highest pressure (600 psi) to be used in filtration experiments. Compaction ended after steady-state flux was achieved. Membrane flux was measured at four different pressures (27.6, 20.7, 13.8, and 6.9 bar) by collecting mass data with a balance connected to a computer. The flux was then plotted against pressure, and a linear regression was used to determine the membrane permeability in $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$.

The selectivity of membranes was evaluated in terms of solute rejection of NaCl using dead-end filtration. The feed concentration of NaCl was 2000 mg/L, and all selectivity experiments were conducted at 27.6 bar. The concentration of NaCl was monitored using an ion selective electrode probe.

3. Results and discussion

3.1. Permeability and selectivity of TFC membranes

For TFC PA membranes, the highest NaCl rejection observed was for TFCs where the interfacial polymerization was conducted on an ultrafiltration membrane without a non-

woven support. Additionally, a denser support membrane, UF3, provided the best support for the PA TFC with the highest NaCl rejection at 78%. With less than 15% NaCl rejection, PA TFC membranes synthesized with ultrafiltration membranes cast on a non-woven support, such low selectivity could result from defects in the PA layer. While the defects in these membranes with non-woven supports prevented PA TFC membranes from being highly selective, it does not seem that the defects were great enough to significantly affect the water flux through the membrane. The complexity of TFC PA membrane fabrication resulted in few membranes that performed consistently in terms of permeability and selectivity (Figure 24).

For CA membranes, all three membrane compositions (0% xGnP/PSf, 1% xGnP/PSf, and 2% xGnP/PSf) produced membranes that rejected more than 70% NaCl (Figure 24). In terms of selectivity, CA membranes with 1% xGnP/PSf loading were most selective with NaCl rejection of $(94 \pm 1)\%$ compared to 0% xGnP/PSf and 2% xGnP/PSf loadings with NaCl rejections of $(72 \pm 8)\%$ and 90%, respectively. The most permeable CA membrane was observed with 2% xGnP/PSf at $(1.09 \pm 0.19) \text{ L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}\cdot\text{bar}^{-1}$ compared to 1% and 0% xGnP/PSf at $(0.53 \pm 0.08) \text{ L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}\cdot\text{bar}^{-1}$ and at $0.71 \text{ L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}\cdot\text{bar}^{-1}$, respectively.

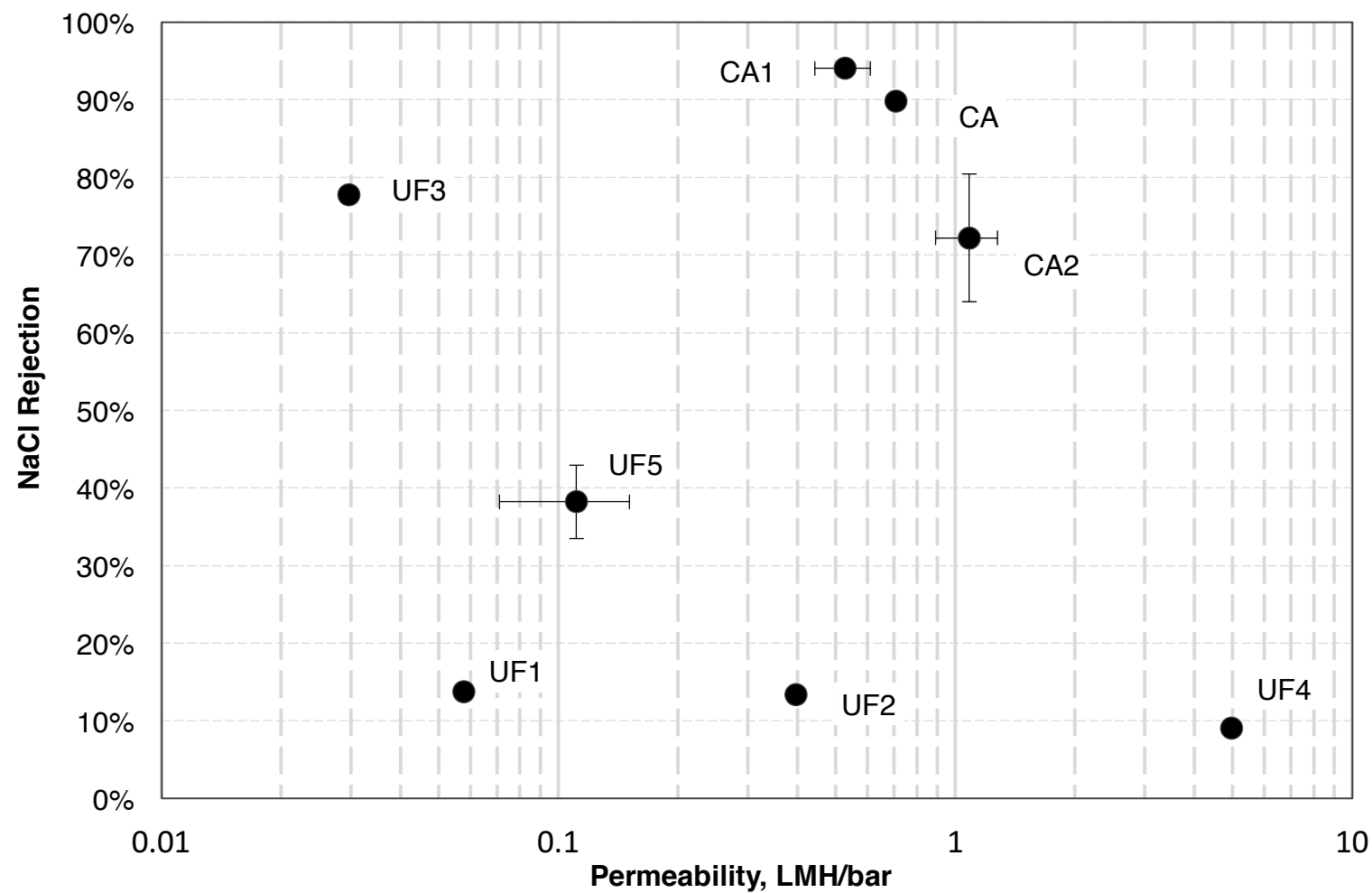


Figure 24: Performance of semipermeable TFC PA and CA membranes. All error bars correspond to a 90% confidence interval.

4. Summary

Semipermeable membranes were fabricated using two different methods – TFC interfacial polymerization with PA and phase inversion with CA. The complexity and sensitivity of TFC PA membrane fabrication resulted in membranes with PA layers with defects and inconsistent NaCl rejection. For TFC PA membranes, NaCl rejection ranged from <10% to ~80%. While interfacial polymerization was complex and produced inconsistent semipermeable membranes, phase inversion CA membranes performed much better in terms of consistency, selectivity, and permeability. All CA membranes rejected >70% NaCl and up to 94%. With the addition of 1% xGnP, the selectivity increased to 94% while the permeability decreased to $0.53 \text{ L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}\cdot\text{bar}^{-1}$, compared to 90% and $0.71 \text{ L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}\cdot\text{bar}^{-1}$ for neat CA membranes.

APPENDIX III

Synthesis of Pd/xGnP and Pd-Cu/xGnP catalysts for the denitrification of nitrate and nitrite

1. Introduction

Elevated nitrate and nitrite levels pose a risk to public health as they form nitosamines in the human body and can cause methemoglobinemia in infants¹²². In 2101 the U.S. EPA reported 1,093 violations of the nitrate/nitrite MCL in 561 community water supplies, which corresponds to 11.0% of total MCL violations. For private wells, the number of drinking water sources with elevated nitrate/nitrite levels is even more staggering at nearly 250,000¹²³. Current methods of nitrate and nitrite removal are biological denitrification, ion exchange, reverse osmosis, and catalytic denitrification. Of these treatment methods, ion exchange, reverse osmosis, and catalytic denitrification are least complicated as the treatment processes can be automated and require minimal operational expertise.

Catalytic denitrification has been explored using Pd catalysts, but for nitrate to be reduced to nitrite a bimetallic catalysts consisting of a promoter metal and Pd catalyst must be used¹²⁴. Nanocatalysts for the denitrification of nitrate and nitrite were fabricated using Pd-Cu nanoparticles supported on polyvinylpyrrolidone (PVP) colloids¹²⁵.

The relative compositions of Pd and Cu on the PVP support were manipulated, and it was determined that the highest performing catalyst was a mixture of 70% to 30% Pd to Cu. By choosing unique supports for Pd-Cu catalysts used in batch reactions, reaction rates varied from (0.061 to 5.12) L/min/g_{metal}¹²⁵⁻¹²⁸. In this study Pd/xGnP catalysts were fabricated for the catalytic denitrification of nitrite in batch reactors, and such catalysts were compared with commercial Pd/Al₂O₃ catalysts.

2. Experimental

2.1. Pd/xGnP catalyst fabrication

Pd nanoparticles were fabricated using the microwave assisted polyol method. A 22.5 mM solution of palladium salt precursor was prepared and 2 mL of the precursor solution was added to 18 mL of ethylene glycol containing 50 mg of xGnP. After stirring, the solution was heated in a microwave (900 W, 2450 MHz) for 50 seconds. The Pd/xGnP catalysts were separated from solution and washed in the same manner as Au/xGnP.

The concentration of Pd was characterized using atomic absorption spectroscopy (Perkin–Elmer 1100). Au and Pd was stripped off xGnPs by leaching, and the concentration of Pd and Au was measured in the leachate. A weighed amount of Au/xGnP, Pd/xGnP, and Pd-Au/xGnP was heated in aqua regia near its boiling point

(109° C). After boiling, the aqua regia solution for 3 hours the solution was sonicated in a bath sonicator for 1 hour. The sonicated solution was then filtered through nitrocellulose membranes and was diluted with water. The diluted filtrate was analyzed for Pd and Au content using atomic absorption analysis.

2.2. Catalytic denitrification experiments in batch reactors

The reactivity of nanocatalysts for nitrite denitrification was characterized in zero-headspace batch reactor tests. The experiments used serum vials filled with 108 mL of high purity water ($> 10 \text{ M}\Omega\cdot\text{cm}^{-1}$), and the water was purged with N_2 gas for 15 min. After all dissolved oxygen was removed, 64 mg of Pd/xGnP or Pd/ Al_2O_3 was added to the reactor, and the water was saturated with H_2 gas for 15 minutes. Nitrite was added to the reactor to make up 60 ppm nitrite as the initial concentration. The batch reactor was magnetically stirred at room temperature. Samples were withdrawn with a syringe and filtered through a $0.22 \mu\text{m}$ syringe filter to remove the catalyst and terminate the reaction. The nitrite concentration was monitored in withdrawn samples using ion chromatography.

3. Preliminary results

It was shown that Pd/xGnP catalysts performed better than commercial Pd/ Al_2O_3 . Using atomic absorption analysis, the Pd content of Pd/xGnP was determined to be 5.04%

using atomic absorption analysis, and the content of Pd on commercial catalysts was 5% Pd/Al₂O₃. The Pd nanoparticles agglomerated into > 100 nm particles on the support, but the agglomerations were made up of relatively monodisperse nanoparticles with a diameter of 10 nm (Figure 25). While the catalytic denitrification of nitrite is modeled as a pseudo-first order reaction usually, the data from 50 min of denitrification did not fit the model well. In the future, it would be useful to monitor the H₂ concentration during the extent of the reaction to determine a model that the data fit better. After 50 min, the extent of denitrification reached 78% for commercial catalysts and 98% for Pd/xGnP catalysts (Figure 26).

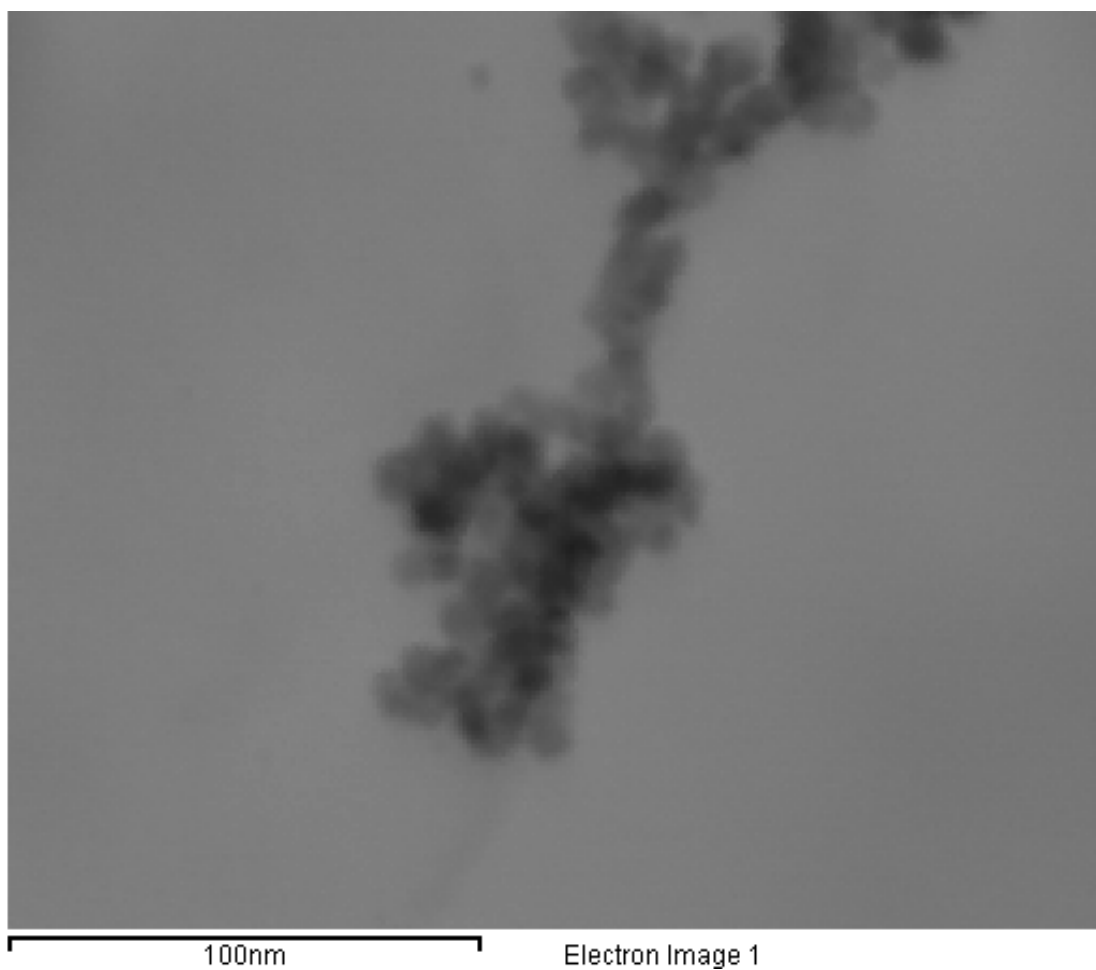


Figure 25: TEM image of Pd NPs supported on xGnP.

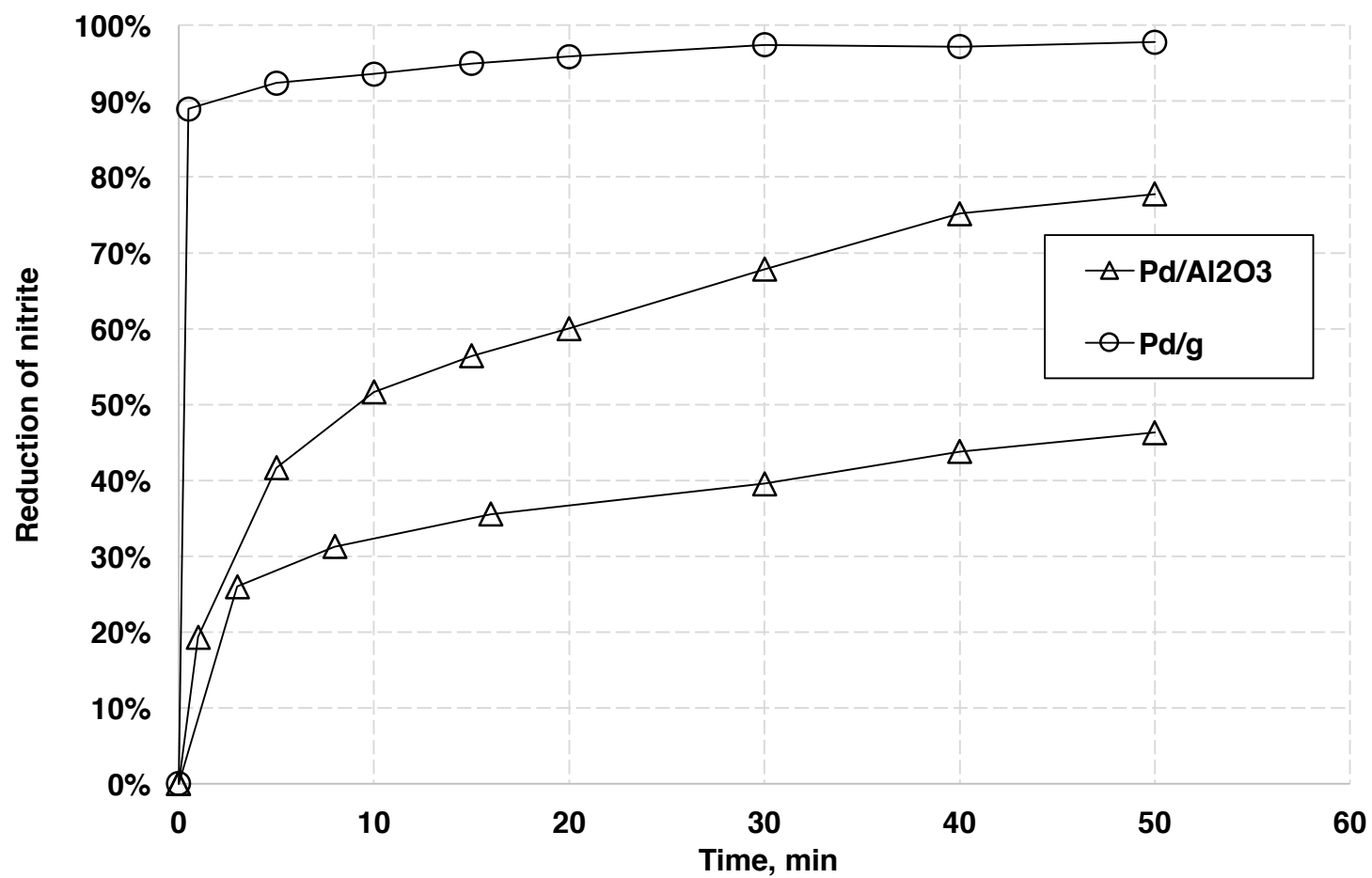


Figure 26: Reduction of nitrite in batch reactors using Pd/xGnP and Pd/Al₂O₃ catalysts

4. Summary

Pd/xGnP catalysts were synthesized and used in the catalytic denitrification of nitrite. These catalysts were compared with commercial Pd/Al₂O₃ catalysts. It was shown that Pd/xGnP catalysts were more active than commercial Pd/Al₂O₃ catalysts in preliminary studies. In future studies, the concentration of H₂ should be monitored in order to better fit the reaction data with an appropriate reaction model. Also, for future studies, bimetallic Pd-Cu/xGnP catalysts should be looked at for the denitrification of nitrate in addition to nitrite.

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