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Performance Modeling of Hydrogen-Based Membrane Palladium-Film Reactors
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ABSTRACT

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Hydrogen-transfer membrane-film reactors are an emerging technology for the treatment of aqueous pollutants. Different reactor configurations have been developed to make use of the efficient and accurately controlled delivery of hydrogen through these membranes. Membrane reactors incorporating metal nanoparticles have been demonstrated to carry out the degradation of recalcitrant water pollutants. Macroscopic-level reactor modeling, which aids in mechanistic understanding and in performance improvements, has been lacking. The present work develops a Langmuir-Hinshelwood reaction modeling approach for a H₂-based membrane catalyst-film Reactor (MCfR), which evaluates performance in terms of a proposed reaction mechanism. Non-linear data fitting was performed to determine the kinetic parameters of the mechanisms developed for experimental results for the dechlorination of 2,4-dichlorophenol, 1,1,1-trichloroethane and trichloroethene, and the defluorination of perfluorooctanoic acid. The modeling analysis provides mechanistic insights for each step and correlates this to observed reactor performance, while also predicting hard to measure concentrations of adsorbed species.
Acknowledgments

It is hard to think about the person I was three years ago, when the events that have led me to finalizing this thesis began. I applied to the Fulbright Faculty Development Scholarship with hope and big dreams. In this process, I discovered the amazing work the Fulbright Program does to encourage knowledge and cultural exchange, and I am forever grateful with the people that believed in me and granted me the opportunity to be a participant.

At Rice, I have felt part of a caring community from day one. Dr. Seiichi Matsuda from the Office of Graduate Students and Dr. Adria Baker from the Office of International Students have personally ensured that my experience at Rice would be the best possible. Knowing that I had their support gave me calm in the most stressful moments and helped me remain focused on my goals throughout this time. I am thankful for their encouragement and advice throughout this process.

I would like to acknowledge my research director, Dr. Michael S. Wong, for all the lessons that he has taught me as a scientist and as a professional. His expectations for my work have been a constant motivation to push myself to improve every day. I am thankful in the trust he has placed in my potential, during my master’s and beyond.

I have also had the amazing opportunity to become a part of NEWT Center, which has allowed me to collaborate with scientists from other institutions and learn about the challenges of providing clean water. As part of this work, I had the
opportunity to work with Dr. Bruce E Rittmann, who has been supportive of my work and has given me valuable feedback. I am also grateful to have worked with Dr. Chen Zhou, Dr. Min Long, Dr. Thomas Senftle, Dr. Kim Heck and Dr. Welman Elias in the PFOA project which has been an amazing learning experience.

It would be impossible to avoid mentioning how the COVID-19 pandemic influenced my time at Rice. Being unable to be physically on the lab and in campus made the path towards a research topic obscure at times. However, this encouraged me to rely on my mathematics, engineering and programming abilities to be able to produce this work. This calamity also tested my ability to be adaptable and disciplined, skills that undoubtedly will be of great use in the future.

The isolation that the pandemic brought made me realize how valuable was to have the unconditional support and encouragement of my family. They have been the foundation of my strength and the greatest motivation to achieve my goals. I am incredibly grateful to have the love of my parents, Bernarda and Andrés, and my sister Isabel, to whom this work is dedicated.

I would also like to recognize the amazing friends that have become my surrogate family in Houston. Pedro, Erica, Ricardo, Victoria, and Elsa, thank you for being sunshine in cloudy days. I hope I can be as good friend to you as you have been to me.
Finally, I want this to be a testament to my future self, so when I reread these lines I will remember the sacrifice, the challenges, and difficulties that I had to overcome this last two years in pursuit of my goals. Let this be irrefutable proof that dreams can come true with hard work and dedication.
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<tr>
<td>MCfR</td>
<td>Membrane Catalyst-film Reactor</td>
</tr>
<tr>
<td>2,4-DCP</td>
<td>2,4-Dichlorophenol</td>
</tr>
<tr>
<td>2-CP</td>
<td>2-Chlorophenol</td>
</tr>
<tr>
<td>4-CP</td>
<td>4-Chlorophenol</td>
</tr>
<tr>
<td>P</td>
<td>Phenol</td>
</tr>
<tr>
<td>Cₜ</td>
<td>Total number of active reaction sites per unit area of catalyst (#sites/nm)</td>
</tr>
<tr>
<td>[*]</td>
<td>Concentration of vacant active reaction sites (µmol/m²)</td>
</tr>
<tr>
<td>TCE</td>
<td>1,1,1-trichloroethene</td>
</tr>
<tr>
<td>TCA</td>
<td>1,1,1-trichloroethane</td>
</tr>
<tr>
<td>PFOA</td>
<td>Perfluorooctanoic acid</td>
</tr>
<tr>
<td>PFAS</td>
<td>Polyfluoroalkyl Substances</td>
</tr>
<tr>
<td>*</td>
<td>Reactive adsorption site</td>
</tr>
<tr>
<td>FDM</td>
<td>Fused deposition modelling</td>
</tr>
<tr>
<td>ABS</td>
<td>Acrylonitrile butadiene styrene</td>
</tr>
<tr>
<td>RK</td>
<td>Runge-Kutta Method</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuously stirred tank reactor</td>
</tr>
</tbody>
</table>
## List of Equations

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Chapter 1

Background and Research Overview

Providing access to safe, uncontaminated water for every person is a global objective that has seen major advancements in the last decades but is still far from reality. The latest report from UN Water stated that there are still 2.2 billion people who still lack access to safely managed drinking water (UNESCO World Water Assessment Programme, 2020). Furthermore, as effects of climate change, pollution and population growth become evident, the need for new technologies to clean water will become increasingly important.

When discussing water treatment, the term contaminant is used broadly to define any component other than water molecules. So strictly speaking, even safe drinking water is expected to have some contaminants. However, the term is usually
used to talk about an undesirable substance that might be a health risk for the consumers. As so, water contaminants can be classified in four categories, as shown in Table 1-1. The scope of this work will focus on discussing the treatment for chemical contaminants only.

**Table 1-1: General categories of drinking water contaminants (US EPA, 2016)**

<table>
<thead>
<tr>
<th>Category</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td>sediments, clays, debris, suspended organic material</td>
</tr>
<tr>
<td>Chemical</td>
<td>nitrogen, bleach, salts, pesticides, metals, toxins, pharmaceuticals</td>
</tr>
<tr>
<td>Biological</td>
<td>bacteria, viruses, protozoan, parasites</td>
</tr>
<tr>
<td>Radiological</td>
<td>cesium, plutonium, uranium</td>
</tr>
</tbody>
</table>

**1.1. Treatment for Chemical Contaminants in Water**

The strategy to develop a water treatment system depends largely on the source of the water, the expected contaminants to be found, their concentrations, and the scale of the system. Large-scale processes will usually involve several treatment steps and might include thermal-based separation processes such as distillation or evaporation as well. These processes will not be discussed here as they deal with a
magnitude that is outside the one considered here, a review can be found in Saavedra et al., 2021.

Approaches suitable to the treatment of chemical contaminated groundwater and drinking water sources will usually fall in one of the following categories: membrane processes, adsorption and ion exchange, precipitation/coagulation, electrocoagulation, biological processes, advanced oxidation/reduction processes. Each technique will provide different benefits and drawbacks depending on the water source and the nature of the contaminants. A concise summary of these approaches can be found in Amrose et al., 2020. Background will be provided on membrane and advanced oxidation/reduction processes since these are the technologies that are involved in the modeled system.

1.1.1. Membrane Processes

This approach considers the removal of contaminants using a permeable barrier that separates components in water by their size or charge. The driving forces that move components through the membrane is usually applied pressure or a concentration gradient. The scope of solute sizes that can be removed by membranes varies greatly, from the macromolecular (10µm) in microfiltration membranes to the ionic (1nm) in reverse osmosis or electrodialysis, as seen in Figure 1-1. Given that this is a physical separation, these processes can remove organic, inorganic and microbial contaminants simultaneously. Membranes can also function over a wide range of pH, making this one of the most versatile separation processes. (Amrose et al., 2020)
The membranes used in the most common membrane separation technologies (micro, ultra, nano filtration, reverse osmosis and electrodialysis) are polymers with differing degrees of porosity, which can be expensive. Other limitation that comes with this technology is the fouling of the membrane which might require maintenance or replacement (Landsman et al., 2020). Therefore, these processes require
thoughtful consideration when being designed to have a balance between desired output and capital/operational costs.

When dealing with chemical contaminants, membrane processes have an additional drawback, since the retentate that does not pass through the membrane becomes concentrated in a brine that must be treated in a subsequent step. For especially harmful chemicals, this might represent an additional problem and cost in the decontamination process. Therefore, these technologies do not completely solve the problem of dissolved chemicals.

1.1.2. Advanced Oxidation/Reduction Processes

The approach of these methods relies on the creation of highly reactive oxidative/reductive species in water that will readily react with other contaminants, degrading them to more innocuous species. In order to produce the required reactants (e.g. hydroxyl and hydrogen radicals, peroxides, sulfates) a photochemical, electrochemical or chemical step is usually needed (Deng & Zhao, 2015). For this reason, the use of homogeneous or heterogeneous catalysts becomes desirable, as they can promote the efficiency of the process by reducing the required activation energies and improve selectivity towards desirable end products.

When using heterogeneous catalysis, mass transfer considerations will become important at all process scales. Since catalyst loading in a reactive system is crucial for high efficiency, the distribution and availability of the active sites will become of primary concern when designing a heterogeneous reactor. As the process
scale becomes larger, the strategies used to limit the dependance of the system on mass transfer steps will need to become more creative. The reactor design should be able to promote the contact between reactive species with the active site, while maintaining high activity, selectivity and minimizing catalyst leaching.

Traditional approaches to multiphase reactors used in heterogeneous catalysis rely on the use of a catalyst bed, where the catalyst is mounted on a porous support which is often pelletized. These beds can be fixed, as in a bubble column or trickle-bed reactors or can move with one of the material currents, as in a slurry or fluidized bed reactor. A review on several multiphase reactors and their characteristics is found on Duduković et al., 2002. While these designs have been studied extensively, they come with several drawbacks, mainly on maintaining adequate contact between phases and mass transfer limitations. Of special concern when using precious metal catalysts, is the use of a fixed support which will prevent the loss of catalyst due to leaching and avoids using a separation process afterward.

The treatment of organics and oxyanion contaminants present in contaminated water has been a research focus of the Catalysis and Nanomaterials group at Rice University. The approaches include the use of catalytic metal nanoparticles to promote the reduction of nitrate (Elias et al., 2020), nitrite (Clark et al., 2020), oxyanions (Yin et al., 2018), as well as the use of photocatalytic catalysts to treat perfluoroalkyl substances (Duan et al., 2020). As a preparation to move this research into the next step of technology readiness level, it is necessary to consider
the applicability of the proposed catalytic methods into other scale systems so that
efficiency is not compromised.

Transferring a procedure that involves nanoparticles to a scale that can be
applied for home or industrial use will present as the first design challenge the
selection of a support that will provide maximum catalyst exposure minimal losses
due to leaching. Furthermore, the continuous addition of an electron donor agent will
be required, which will impact reactor design. The goal is to produce a reactor that
satisfies these design criteria, and that can be further improved by extrapolating the
mechanistic knowledge obtained by previous studies on the activities of the selected
catalysts.

1.2. The Membrane Catalyst-Film Reactor

The emergence of the membrane catalyst-film reactor (MCfR) came as a
development on existing membrane-aerated reactors, where a porous membrane is
used to allow the bubbling or diffusion of a gas to a liquid. While many gaseous
substrates can be readily consumed by microorganisms or abiotic catalysts, their low
aqueous solubility and proclivity to strip volatile organic compounds (VOCs) from the
solution untreated has limited their use (Martin & Nerenberg, 2012).

The MCfR can be classified as a structured reactor, where the membrane
functions both as an interface between the liquid and gas phases in the reactor and as
support for the catalyst. Since the catalyst is a solid, this makes the MCfR a three phase
reactor (Comite et al., 2013). Membrane reactors were developed as a design that improves the contact and mass transfer rates of reacting species, while providing controlled delivery of reactants to the active sites. Therefore an intrinsic advantage of membrane reactors is that they offer the possibility of decoupling mass transfer phenomena and kinetics at a reactor level (Comite et al., 2013).

Figure 1-2A shows a scheme of a typical MCfR setup including several hydrophobic polymeric membranes that allow the diffusing of the gas that is pressurized on the interior of the membrane, a recirculating pump and the gas and liquid inlets and outlets. The membrane are made from a non-wettable material to avoid having liquid enter the pores at high pressures (Dittmeyer et al., 2004). The membranes used in the studies presented here are made from polypropylene. However, polyester and composite (polyethylene and polyurethane) membranes have been reported as well (Y. Tang et al., 2012). The reactor can be operated between a recirculating mode or a flow-through mode, depending on the operation of the recirculating pump.
In the cases studied hereafter, the catalyst used was Pd, although other precious metal catalysts, or a combination of metals, could be used. Pd was deposited through an in-situ method that allows the coating of the outer membrane surface under ambient conditions. Other methods for immobilizing metallic nanoparticles to polymeric membranes have been reported, by use of hydrogels (Marks et al., 2019), or by stabilizing nanoparticles through the use of polyvinylpyrrolidone (Walbrück et al., 2019). However, the in-situ method, as described in Wu et al., 2021, and Luo et al.,
was reported having the least amount of catalyst leached to the solution, an especially important feature when working with expensive precious metal catalysts. The model presented in this work will assume minimal loss of catalyst throughout the reaction.

The used reactant gas was H\(_2\) for its electron donor capabilities. The studies analyzed in the present work deal with oxidized contaminants, so a strong reducing agent is required to carry the reaction. Generally, the use of hydrogen as a reactant presents various difficulties since it has a very low water solubility (the saturation concentration of hydrogen at 1atm is 0.78mmol/L, compare for example with CO\(_2\) which is 34mmol/L), which usually means that low mass transfer rates are expected for its aqueous form, and it easily off-gases, which creates a combustible atmosphere. For this reason, when using H\(_2\), high pressures are required inside the reactor to maintain adequate concentration levels in the liquid and to reduce degassing.

The MCfR overcomes the difficulties for delivering H\(_2\) by using membranes that directly deliver hydrogen (without forming bubbles) to the catalytic metal with a rate proportional to the counter-directional diffusion direction of the incoming contaminant. This has the additional advantage that once hydrogen is delivered to the catalyst surface it is already in a reactive form, H\(^*\)\(_{ads}\). The amount of hydrogen delivered to the membranes can be regulated by controlling the gas pressure inside the lumen of the membrane, which allows treating hydrogen as an excess reactive for the reaction. This is a strong advantage of MCfR reactors over other reactor
configurations, where a balance between the reactive phases must be considered as mass transfer becomes rate limiting.

### 1.3. Langmuir-Hinshelwood Mechanisms for Surface Reactions

Surface reactions as the ones that occur in a MCfR are usually described using the Langmuir-Hinshelwood mechanism, which comprises three elementary steps: adsorption of reactants, surface reaction, and product desorption. As is the case here, a catalyst with a defined crystalline structure will be the place where the reaction will occur, and it is called the adsorbent. When an incident atom or molecule (the adsorbate) reaches the catalyst, it can interact with the surface by physical or chemical means.

Physical adsorption is usually caused by attractive dispersion forces and short-range repulsive forces, although other specific molecular interactions such as polarization or field-dipole can emerge as consequence of geometric and electronic properties of either the adsorbent or adsorbate (Thommes et al., 2015). Physical adsorption occurs at any place of the exposed surface of the adsorbent and will not produce a chemical reaction.

Chemical adsorption (chemisorption) occurs when a chemical bond or a partial chemical bond is formed between the adsorbent and adsorbate. Usually, the bond generation will limit the coverage of adsorbent to at most one chemisorbed
species that can be associated to an adsorption site at the time. However, not all sites that can chemisorb will produce a chemical reaction. There are specific places within the catalyst structure, called active sites, that is where chemical adsorption can occur and that will lead to a reaction. Not all adsorption sites will be active, so only a fraction of the total adsorption sites will also be active sites. Since the adsorption process will happen in a monolayer in the side of the adsorbent that is exposed to the adsorbate, the total amount of sites is considered constant which will be expressed as the conservation of sites.

Even though both physical and chemical adsorption modes can be modeled using a Langmuir-Hinshelwood mechanism, the focus of this work will be only in chemisorbed species as these are the ones that will produce a reaction. Additionally, the model used here assumes that the surface sites are the same, that the process is random, and no adsorbate-adsorbate interactions occur. Incoming molecules will adsorb if there is a vacant active site available (Rawlings & Ekerdt, 2004). Then, the surface count of all adsorption sites can be written as the sum of all vacant and free sites, which leads to Equation 1-1.

\[ C_t = C_v + \sum_{i=1}^{n_s} C_i \]

\textit{Equation 1-1: General form of surface site balance}
where,

$C_t$ is the total number of surface sites (#/unit area)

$C_v$ is the number of free surface sites (#/unit area)

$C_i$ is the number of surface sites occupied by species $i$ (#/unit area), and

$n_s$ is the number of adsorbent species

The usefulness of the Langmuir-Hinshelwood reaction mechanism is that it allows us to postulate a reaction mechanism that considers the reactive surface as a reactant. The production rate of species involved in heterogeneous catalysis can be defined in terms of the amount and availability of surface adsorption sites and adsorption affinity of each involved reactant.

To better understand the reaction mechanisms and derived rate expressions shown in this work, let us consider a simple surface reaction, where aqueous components A and B are adsorbed in a vacant active site (*), react to form product AB and then desorb. The overall reaction will be:

$$A + B \rightarrow AB$$  \hspace{1cm} \text{Eqn. (1.2)}

The stepwise mechanism, considering each elementary step is:

$$A(aq) + * k_1 \rightleftharpoons k_{-1} A *$$  \hspace{1cm} \text{Eqn. (1.3)}

$$B(aq) + * k_2 \rightleftharpoons k_{-2} B *$$  \hspace{1cm} \text{Eqn. (1.4)}
Eqn. (1.5)  \[ A \ast + B \ast \rightarrow AB \ast \ast \]

Eqn. (1.6)  \[ AB \ast k_4 \rightleftharpoons k_{-4} AB(aq) + \ast \]

The sum of Eqn. (1.3) to Eqn. (1.6) produces Eqn. (1.2) which is consistent with the expected overall reaction.

For illustration purposes, we consider the surface reaction Eqn. (1.5) to be the rate limiting step and the adsorption processes to be fast and in quasi-equilibrium. This is a common scenario for systems where diffusion and mass transfer rates are high. Then, the production rate for component A shown in Eqn. (1.3) we can write the forward/adsorption \((r_1)\) and reverse/desorption \((r_{-1})\) reaction rates as:

\[ r_1 = k_1[A][\ast] \quad r_{-1} = k_{-1}[A \ast] \]

which follow directly from the reaction mechanism as they are treated as elementary steps. Bracketed species are to be treated as concentrations, whether by volume for aqueous species or by area in the case of adsorbed species. The units of the rate will be mol/time-area. As the adsorption and desorption rates are considered fast and in equilibrium, we can equate them and obtain an expression for the steady-state surface adsorbed specie \(A\ast\).

\[ r_1 = r_{-1} \]

\[ k_1[A][\ast] = k_{-1}[A \ast] \]

\[ [A \ast] = \frac{k_1}{k_{-1}} [A][\ast] = K_1[A][\ast] \quad \text{Eqn. (1.7)} \]
where $K_1$ represents the adsorption constant for Eqn. (1.3). In the same manner for the adsorption step of $B$: 

$$[B \,*] = \frac{k_2}{k_{-2}} [B][\,*] = K_2[B][\,*] \quad \text{Eqn. (1.8)}$$

And a similar expression for the desorption of product $AB$:

$$r_4 = r_{-4}$$

$$k_4[AB \,*] = k_{-4}[AB][\,*]$$

$$[AB \,*] = \frac{k_{-4}}{k_4} [AB][\,*] = \frac{1}{K_4} [AB][\,*] \quad \text{Eqn. (1.9)}$$

Now, for the rate limiting step Eqn. (1.5) we will have an expression in terms of the previously defined adsorbed species, however we will still have a term that involves the number of vacant spaces $[\,*]$

$$r_3 = k_3[A \,*][B \,*]$$

$$r_3 = k_3(K_1[A][\,*])(K_2[B][\,*]) \quad \text{Eqn. (1.10)}$$

In order to be able to obtain an expression that is in terms of the measurable variables, we can use Equation 1-1 to write the site balance for all the sites in the catalyst:

$$C_t = [\,*] + [A \,*] + [B \,*] + [AB \,*]$$

Using Eqn. (1.7) -(1.9) and solving for $[\,*]$ gives:

$$C_t = [\,*] + K_1[A][\,*] + K_2[B][\,*] + \frac{1}{K_4} [AB][\,*]$$
\[
[\ast] = \frac{C_t}{1 + K_1[A] + K_2[B] + \frac{[AB]}{K_4}} \quad \text{Eqn. (1.11)}
\]

Finally, replacing Eqn. (1.11) in Eqn. (1.10) we get an expression for the irreversible reaction step that is only defined by the concentration of the observed species:

\[
r_3 = K_1K_2k_3[A][B][\ast]^2 = \frac{C_t^2K_1K_2k_3[A][B]}{\left(1 + K_1[A] + K_2[B] + \frac{[AB]}{K_4}\right)^2} \quad \text{Eqn. (1.12)}
\]

Using Eqn. (1.12) and the stoichiometry of the overall mass action statement in Eqn. (1.2) we can write the production rate for each species as:

\[
r_3 = -R_A = -R_B = R_{AB} \quad \text{Eqn. (1.13)}
\]

The reaction rate obtained in Eqn. (1.12) can better account for the role of the catalyst availability in the production of the desired product \(AB\). If the reaction mechanism that was proposed is consistent with what is happening in the reaction, then Eqn. (1.12) should correlate with observed concentrations of \(A\), \(B\) and \(AB\). This approach works best if the adsorption constants and the number of active sites is known and although this information can be extracted by running adsorption experiments, however these values are not commonly reported.

Since the measurement of adsorbed species is difficult and, in many cases, not practical, we are left with the task of using the proposed reaction mechanism and experimental data to estimate the unknown reaction constants. Since the governing
equations for this system have been established, a numerical optimization algorithm can be implemented to find the values of the independent parameters that better matches the experimental observations. Then, this information can be interpreted to insights about the reactor performance.

1.4. Non-Linear Least Squares Analysis for Parameter Estimation

When writing the governing equations for a chemical reactor it is often convenient to approximate the reaction term to a pseudo-order reaction since this will leave an equation that is simpler to solve. This can be done by having one of the reactants be present in excess, assuming that the reaction will depend on the concentration of only one reactant, continuous removal of product and consider other transport effects negligible. These reaction conditions reduce Eq. 1.12 to a pseudo-first order with respect to the limiting reactant. This will usually provide approximate results with strong correlation with experimental data that is appropriate for some cases. A shortcoming of this approach is that it does not apply when the excess reactant assumption becomes invalid during the reaction (i.e., the excess reactant depletes considerably). For a heterogeneous reaction, the supposition of first order might oversimplify the reaction mechanism and can mask other phenomena that can affect the performance of the reactor, such as mass transfer limitations, catalyst poisoning or deactivation.
For this reason, we wanted to develop an algorithm that provides a way to check the viability of a reaction mechanism and to obtain kinetic parameters and catalyst surface sites by using measured concentrations of reactant species. This approach allows using existing data on reactor performance and test it against a reaction mechanism that includes surface reactions. The mechanisms are deduced from first principles from heterogeneous catalysis steps and incorporated in the mass balance equations of the reactor.

1.4.1. Algorithm Development

Since we covered how the production rates are computed for a surface reaction, we now need to find a way to use the measured observations of the system to find the values of the unknown kinetic parameters that arise from the various elemental steps in the reaction mechanism. For any reactor we will be able to write the statement for conservation of mass for each component, which includes a generation term, where the rate expression deducted from the reaction mechanism will be incorporated.

Continuing the example reaction presented in section 1.4, a mass balance equation for a continuously stirred tank reactor can be written for the system. Since for this case the inlet and outlet flows will be zero, the equations will resemble those of a batch reactor. The mass balance equations will have the form:

\[
\frac{d(c_i V_R)}{dt} = R_i A_R
\]  
Eqn. (1.14)
\[
\frac{dc_i}{dt} = \frac{A_R}{V_R} R_i \tag{Eqn. (1.15)}
\]

where \(i=A, B \text{ or } AB\), \(V_R\) is the total reactor volume (which is assumed to be constant), \(R_i\) is the production rate for component \(i\) as defined by Eqn. (1.13). Since the production rate is defined in terms of catalyst unit area, the generation term will include the total catalyst area \(A_R\) to maintain dimensional consistency.

Now we have a system of three coupled differential equations and 5 unknown parameters \((K_1, K_2, k_3, K_4, C_i)\) which must be solved simultaneously and compared to a list of observations for the concentrations of A, B and AB. In order to do this, we will propose an algorithm which uses a first guess for the unknown parameters, uses this guess to numerically solve the differential equations, compares the results with the data, and proposes a better approximation for the parameters, repeating the cycle until a satisfactory value is obtained. Figure 1-3 shows the algorithm used to estimate the parameters.
Figure 1-3: Flowchart for the computational algorithm used to solve for the optimal value of reaction parameters
The mathematical expression for the minimization problem is presented in Equation 1.2.

\[
\text{minimize } x \quad f(x) = \sum_{i=1}^{m} f_i(x)^2
\]

**Equation 1.2: General form of the least squares minimization problem (Griva et al., 2017)**

where \( f(x) \) will be the sum of the squares of the residual, defined in terms of the auxiliary functions \( f_i \). The value of \( f_i \) will be the difference between the calculated value of concentration of a component at time \( i \), and the measured concentration at that time, summed over all the time measurements \( m \). Applying Equation 1-2 to our example system we will get:

\[
\text{minimize } K_1, K_2, k_3, K_4, C_t \quad f(K_1, K_2, k_3, K_4, C_t) = \\
\sum_{i=1}^{m} \left( C_{A \text{ calc}}(t, K_1, K_2, k_3, K_4, C_t) - C_{A \text{ meas}} + C_{B \text{ calc}}(t, K_1, K_2, k_3, K_4, C_t) - \\
C_{B \text{ meas}} + C_{AB \text{ calc}}(t, K_1, K_2, k_3, K_4, C_t) - C_{AB \text{ meas}} \right)^2
\]
Here, we are defining that we want to find the root of the function that minimizes the difference between the concentration predicted by solving the initial value system of differential equations, and the measured concentration at that time. In this model, equal weight is given to all components, however this could be adapted to give more importance to components with higher concentrations.

1.4.2. Mathematical Methods

In order to solve for the existing data, which will include dependent variables as well as many optimizable parameters, a MATLAB (MATLAB R2021a) routine was developed using the algorithms \textit{lsqcurvefit} and \textit{ode45}. The objective of the method will be to find the roots of the vector valued function \( f \) as defined in Equation 1-2 (The MathWorks, 2021). The classical method to find the root of a function is the Newton-Raphson method which is an iterative algorithm that uses the value of the function
and its slope in a point \( x_n \) to find a better approximation \( x_{n+1} \), which is closer to the root of the function. Figure 1-4 shows a scheme of the operation of this algorithm.

Figure 1-4: Scheme of the operation of the Newton-Rhapson method to determine the root of a real function

For the problem at hand, the Newton-Raphson method is insufficient to converge to a satisfactory solution while maintaining the required constraints on the optimizable parameters. Thus, the use of an advanced minimization algorithm is required. The algorithm applied in the function \textit{lsqcurvefit} is the trust-region-reflective least squares algorithm, presented in Coleman & Li, 1994. There are other available methods in the function, such as the Levenberg-Marquardt algorithm, which were not used in this work.

The trust-region-reflective method can be applied to nonlinear or linear least-squares problems and is used to minimize a smooth nonlinear multivariate function, where some (or all) of the variables have upper or lower bounds. The basis of the
method is to approximate the value of the function $f(x)$ (as shown in Equation 1-2) with a quadratic function $q$ that reasonably reflects $f(x)$ in the vicinity of $x$. The points close to the value of $x$ will be the trust region, $N$. A step of size $s$ will be calculated as:

$$\{q(s), s \in N\}$$

**Equation 1-3: Trust-region subproblem (The MathWorks, n.d.)**

The point will be updated to $x + s$ if $f(x + s) < f(x)$, otherwise another iteration is made with a smaller trust-region.

To solve the system of differential equations the function *ode45* was used since the system of differential equations is not expected to be stiff. The routine is an explicit Runge-Kutta (RK) method with adjustable step, which is an extension of Euler’s method for solving ordinary differential equations. The *ode45* routine features the use of the fourth order RK method paired with the Dormand-Prince method, presented in Dormand & Prince, 1980, which is of fifth order. Both methods can be computed with the same evaluations, thus making *ode45* a fourth- and fifth-order method.

The Runge-Kutta method is an explicit numerical method which approximates the solution of an initial value differential equation by using the value of the slope at a point $t$ to predict the value at a small interval later, $t+h$. To do so, the weighted
average of four projected slopes between $t$ and $t+h$ is calculated, to produce the value of the function at $t+h$. A visual explanation of the method can be found in Serrano, 2016. The use of the Dormand-Prince pair allows the comparison between the fourth and fifth order solutions, when a local error estimate seems too large, the algorithm recalculates the step using a smaller step size to minimize the difference between both solutions (Shampine & Reichelt, n.d.).

1.5. Research Goals and Thesis Layout

The aim of this thesis work is to create a numerical method that adequately simulates the performance of a Pd based MCfR reactor, providing insights on the reactor behavior in time while also considering reasonable reaction mechanisms occurring at the surface of the catalyst. Currently, our ability to improve the performance of these reactors is limited to the macroscopic variables that can be measured, and there is a need to bridge this information to a microscopic understanding of adsorption/reaction steps happening in the system.

When trying to produce a performance simulation of a MCfR we want a model that considers the physical dimension of the reactor and the catalytic support (total working volume, number and size of membranes, initial conditions) as well as the operation of the reactor (recirculating or flow-through). It is desirable that the model can describe the catalytic surface of the membranes as a parameter, since it would be important to optimize the number of fibers and amount of catalyst required for the reactor, as this is one of the initial capital costs of applying this technology.
Another feature of the model is that it considers adsorption/reaction mechanisms and can determine how these steps influence the observed performance of the reactor. As such, it allows the prediction of kinetic constants, the rate limiting step, and evaluate the concentration of adsorbed reactants which are difficult or impossible to determine directly. Even though further research would be needed to confirm the predicted results, these results provide a basis to build knowledge of how the reaction is happening and create strategies to allow more effective use of the catalyst.

In the application of this model, a discussion on the validity of the results it provides, as well as the cases on which it produces better results, will be presented. The underlying assumptions used will also be analyzed for consistency and applicability, considering the accuracy and completeness of the source data.

The present work shows the application of the algorithm described in the previous sections to three published studies on MCfR operation. Chapter 2 shows the model's results as applied to Figure 3 of the data presented in Wu, C., Zhou, L., Zhou, Y., Zhou, C., Xia, S., & Rittmann, B. E. ‘Dechlorination of 2,4-dichlorophenol in a hydrogen-based membrane palladium-film reactor: Performance, mechanisms, and model development’. Water Research, 2021, 188, 116465

Chapter 3 presents the model used in a recirculating configuration of the MCfR. The data used is found on Figure 3 in Luo, Y.-H., Zhou, C., Bi, Y., Long, X., Wang, B., Tang, Y., Krajmalnik-Brown, R., & Rittmann, B. E. ‘Long-Term Continuous Co-
reduction of 1,1,1-Trichloroethane and Trichloroethene over Palladium Nanoparticles Spontaneously Deposited on H₂-Transfer Membranes. Environmental Science & Technology, 2020, 55 (3), 2057-2066. For this case, a stepwise reaction mechanism was considered, expanding on the one presented on the original paper and presenting the concentration of adsorbed species.

Chapter 4 discusses the application of the model to the defluorination of perfluorooctanoic acid, a reaction which involves many elementary steps. This has been part of the discussions involved in the preparation of a manuscript with co-authors M. Long, M. Bhati, W. C. Elias, K. N. Heck, Y. H. Luo, Y. S. Lai, H. Gu, T. P. Senftle, C. Zhou, M. S. Wong and B. E. Rittmann which is currently on revision. In this chapter, the model is used to account for two modes of adsorption observed in the reactor, and to explore the extent on which non-reactive adsorption can affect the desired reaction.

As a separate line of research related to experimentation, Chapter 5 describes efforts to fabricate structured catalysts in the form of nanoparticle-immobilized 3D-printed stir bars. The intent of this work was to explore alternative fabrication methods for easy-to-handle Pd-containing heterogeneous catalyst solids. This approach to producing structured catalyst supports can be of interest in exploring how distinct geometries can be used in multiphase reactors or separators. The method presented uses a commercially available 3D printed and resin to create shapes that can adsorb Pd which can be activated as a catalyst upon reduction with hydrogen.
Mathematical Modeling for The Dechlorination of 2,4-Dichlorophenol

2.1. Chlorophenol Contamination

Chlorophenols are aromatic compounds and can be mono- to penta-chlorine substituted in a benzene ring and are commonly used as pesticides, or as intermediates in the synthesis of dyes and other biocides. They can also be produced as byproducts of the environmental degradation of other chlorinated compounds such as chlorobenzenes and phenoxyacetic acids (Gao et al., 2007).

As most of them are polar molecules, they are soluble in water and have been also detected in soil. The main concern with this family of compounds is that they are toxic, bioaccumulating and have long lasting carcinogenic effects. (World Health Organization, 2003). Although the US EPA agency has instated a health advisory for several chlorinated phenols (including 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol), they are still found in contaminated hotspots at concentrations higher
than this recommended level. The last ambient water quality criteria recommended for 2,4-dichlorophenoel by the US EPA in June 2015 was 10µg/L (US EPA, 2015). This value is intended to protect the general adult population from noncarcinogenic effects related to exposure to this chemical.

Being an oxidized compound, 2,4-dichlorophenol can be treated in the reductive environment of a H2-MCfR, as demonstrated in Wu et al., 2021, where the degradation of this molecule to its less harmful derivative, phenol, was reported. The data and procedures in this paper clearly demonstrates the working of a MCfR and because of these reasons it was used as a first approach towards the development of the performance model based on surface reactions.

2.2. Simulation Objectives

The reported data in the paper presents a developed model for the continuous dechlorination in a MCfR operated in a flow through configuration. Additionally, the paper presents a reaction mechanism and a kinetic model on which we will build on, incorporating concepts of reactions at surfaces to obtain insights on the reaction mechanism.

In addition to a model that can correlate to the concentration data, we want to demonstrate how this approach can be applied to this reactor configuration and how, by correlating the model to the obtained data, microkinetic information can be
extracted for the system. A first principles approach is used to derive the reaction mechanism and determine if reasonable new insights can be obtained from the data.

Specifically, the aim is to recreate the results in Figure 3 presented in Wu et al., 2021, which is replicated here in Figure 2-1. These plots represent the effluent concentrations obtained from the dechlorination of 2,4-DCP, starting with initial concentrations of 25, 55, 95 and 195µM. The data points used as measured concentrations were obtained by extracting the data by means of the tool WebPlotDigitizer (Version 4.4, available at: https://automeris.io/WebPlotDigitizer)
Figure 2-1: Effluent concentrations of 2,4-DCP, 2-CP, 4-CP, and P over time at different influent concentration of 2,4-DCP, during initial 6 h. This figure was published in Water Research, Vol 188, C. Wu, L. Zhou, Y. Zhou, C. Zhou, S. Xia, B. E. Rittmann, Dechlorination of 2,4-dichlorophenol in a hydrogen-based membrane palladium-film reactor: Performance, mechanisms, and model development, 116465, Copyright Elsevier 2021.
2.3. Proposed Reaction Mechanism

The overall mass action statement found for this system can be summarized as:

$$3Cl_2C_6H_3OH + 8H_2 \rightarrow ClC_6H_4OH(o) + ClC_6H_4OH(p) + C_6H_5OH + 4Cl^- + 4H^+$$

Equation 2-1: Overall reaction for the reduction of 2,4-DC

where $Cl_2C_6H_3OH$ is the incoming 2,4-Dichlorophenol (hereafter abbreviated as 2,4-DCP) which can be partially dechlorinated to either the ortho (2-CP) or para (4-CP)
configurations \( (ClC_6H_4OH(o) \text{ and } ClC_6H_4OH(p), \text{ respectively}) \) and the final dechlorinated product, phenol \( C_6H_5OH \) (abbreviated as P). The reaction mechanism proposed on the paper includes the formation of the intermediaries 2-CP and 4-CP as well as a direct reaction from 2,4-DCP to P.

The stepwise mechanism that will be proposed builds on this mechanism but includes the adsorption steps that are characteristic of a heterogeneous reaction at a surface. The mechanism is summarized in Steps. (2.1) - (2.10):

\[
\begin{align*}
2,4 - DCP(aq) + * k_1 & \rightleftharpoons k_{-1} 2,4 - DCP * & \text{Step (2.1)} \\
2,4 - DCP * + H * k_2 & \rightarrow 2 - CP * + H * & \text{Step (2.2)} \\
2 - CP * k_3 & \rightleftharpoons k_{-3} 2 - CP(aq) + * & \text{Step (2.3)} \\
2 - CP * + H * k_4 & \rightarrow P * + Cl * & \text{Step (2.4)} \\
2,4 - DCP * + H * k_5 & \rightarrow 4 - CP * + H * & \text{Step (2.5)} \\
4 - CP * k_6 & \rightleftharpoons k_{-6} 4 - CP(aq) + * & \text{Step (2.6)} \\
4 - CP * + H * k_7 & \rightarrow P * + Cl * & \text{Step (2.7)} \\
P * k_8 & \rightleftharpoons k_{-8} P(aq) + * & \text{Step (2.8)} \\
Cl * + H * k_9 & \rightleftharpoons k_{-9} Cl^-(aq) + H^+(aq) + 2 * & \text{Step (2.9)} \\
H_2 + 2 * k_{10} & \rightleftharpoons k_{-10} 2H * & \text{Step (2.10)}
\end{align*}
\]

where an active reaction site is labeled as *, and surface-bound species are differentiated by this notation as well.
Additionally, the desorption of chloride ions was considered irreversible and fast, primarily because the concentration of dissolved chloride was not reported, which prevents using this as a parameter to evaluate reaction progress. However, this assumption might be valid considering that evidence of reaction of adsorbed chloride with H* has been reported to happen at near room temperature though thermal desorption spectroscopy as reported in Hunka et al., 2002. Additionally, DFT calculations on another dechlorination reaction over Pd (111) show that the reaction rate of this desorption step can be several orders of magnitude faster than the rate limiting step (Xu et al., 2016). Since the Pd surface will be rich in electron donor H*, this might further promote the formation of Cl⁻ ion in solution. Therefore, Step (2.9) becomes:

\[ \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl}^- (aq) + \text{H}^+ (aq) + 2 \ast \]  \hspace{1cm} \text{Step (2.11)}

Even though chloride is a known Pd catalyst poison, the expected concentrations in the experiments shown here and in Chapter 3 are below a threshold where substantial deactivation starts to occur. On the work done by Heck et al., 2009, Pd nanoparticles showed a small change of catalytic activity for concentrations of chloride less than 1mM, and the highest expected concentration for the experiment shown in section 2.5.4 would be 0.58mM.

The proposed reaction mechanism considers that the 2 possible dechlorination reactions (leading to 2-CP and 4-CP, respectively) are possible, although they will happen at different rates due to the different reactivities the
chlorine atoms can have depending in their position on the ring. Figure 2-2 and Figure 2-3 illustrate the pathways from which 4-CP can be reduced to P.

Figure 2-2 and Figure 2-3 were drawn assuming a pH of 5.8-7.4 for the reaction, because although there is no explicit reference to this on the text, the use of a phosphate buffer is stated. At this pH 2,4-DCP will be protonated (pKa =7.9). The adsorption configuration depicted is the one found to be most thermodynamically favorable by DFT calculations in Jiang et al., 2018.
Figure 2-2: Reaction scheme for the dechlorination of 2,4-DCP via the production of 2-CP (purple lines represent adsorption/desorption processes, blue lines represent irreversible reactions)
Figure 2-3: Reaction scheme for the dechlorination of 2,4-DCP via the production of 4-CP (purple lines represent adsorption/desorption processes, blue lines represent irreversible reactions)
As the dechlorination reactions are considered the slow steps, the reaction rate will be determined by the speed of Steps (2.2), (2.4), (2.5) and (2.7). Since these are elementary steps, their rate can be written as shown in Eqn. (2.1) - (2.4).

\[ r_2 = k_2 [2,4 - DCP \, *] [H \, *] \] \hspace{1cm} \text{Eqn. (2.1)}

\[ r_4 = k_4 [2 - CP \, *] [H \, *] \] \hspace{1cm} \text{Eqn. (2.2)}

\[ r_5 = k_5 [2,4 - DCP \, *] [H \, *] \] \hspace{1cm} \text{Eqn. (2.3)}

\[ r_7 = k_7 [4 - CP \, *] [H \, *] \] \hspace{1cm} \text{Eqn. (2.4)}

As the above reaction rates are defined in terms of adsorbed components, the approach presented in section 1.3 will be used to evaluate the concentration of adsorbed components in terms of measured species. This will use the previously presented assumption that the adsorption reactions are rapidly equilibrated.

Equating the forward and reverse speeds for Steps (2.1), (2.3), (2.6), (2.8) and (2.10) will provide expressions for adsorbed species in terms of measured variables and the number of available active reaction sites (*). The expressions obtained are shown in Eqns. (2.5) - (2.7). Substitutions of terms have been applied where applicable and adsorption equilibrium constants are defined as \( k_{\text{forward}}/k_{\text{reverse}} \) for all equilibrium reactions.

\[ [H \, *] = \frac{k_{10}}{k_{-10}} [H]^{1/2} [\ast] = K_{10} [H]^{1/2} [\ast] \] \hspace{1cm} \text{Eqn. (2.5)}

\[ [2,4 - DCP] = K_1 [2,4 - DCP] [\ast] \] \hspace{1cm} \text{Eqn. (2.6)}

\[ [2 - CP \, *] = \frac{1}{K_3} [2 - CP] [\ast] \] \hspace{1cm} \text{Eqn. (2.7)}
\[ [4 - CP \; *] = \frac{1}{K_6} [4 - CP][*] \quad \text{Eqn. (2.8)} \]

The inclusion of an additional equation will be needed to account for the number of active sites, which will be derived from the surface site balance as stated in Equation 1-1.

\[ C_t = [\; *] + [2,4 - DCP] + [2 - CP \; *] + [4 - CP] + [P \; *] + [H \; *] \quad \text{Eqn. (2.9)} \]

Replacing the expressions obtained in Eqn. (2.5) - (2.8) in Eqn. (2.9) gives an expression for the number of vacant sites:

\[ [\; *] = \frac{C_t}{\left( \frac{K_1[2,4 - DCP]}{K_3} + \frac{[2 - CP]}{K_6} + \frac{[4 - CP]}{K_8} + \frac{[P]}{K_{10}[H]^2} \right)} \quad \text{Eqn. (2.10)} \]

With this, there is enough information to write the reaction speed of the slow steps, which will depend on the aqueous concentration of measured components. The last step is to determine the rate of formation for each component. For this, the reaction rates and the stoichiometry of Equation 2-1x will be used to define the rate for each component as shown in Eqns. (2.11) - (2.15).

\[ R_{[2,4 - DCP]} = -r_2 - r_5 \quad \text{Eqn. (2.11)} \]
\[ R_{[2 - CP]} = r_2 - r_4 \quad \text{Eqn. (2.12)} \]
\[ R_{[4 - CP]} = r_5 - r_7 \quad \text{Eqn. (2.13)} \]
\[ R_{[P]} = r_4 + r_7 \quad \text{Eqn. (2.14)} \]
\[ R_{[H_2]} = 0 \quad \text{Eqn. (2.15)} \]

An important assumption is implicit in Eqn. (2.15), which implies that hydrogen concentration will be constant in the liquid, and it will be at the saturation
concentration of hydrogen in water. This assumption is made since hydrogen is diffusing from the membrane to the liquid in a counter-diffusional direction, and also serves as a way to simulate the high availability of hydrogen being supplied through the membrane. This mathematical statement allows to imply that the availability of hydrogen in the surface will only be hindered by other species occupying available slots. This is also corroborated by the fact that a high pressure of hydrogen was used in the membranes, which according to previous studies (Y. Tang et al., 2012) would assure that enough hydrogen is supplied for the reactions to occur.

2.4. Mass Conservation Equations

The data to be modelled resulted from the operation of the MCfR operating in a flow-through regime, with internal recirculation. The calculated hydraulic retention time for the reactor is 25.9 min, which suggests that the components will be thoroughly mixed, thus the approximation to a continuously stirred tank reactor is reasonable. As such, we will start from the general equation for a CSTR:

\[ V_R \frac{dC_i}{dt} = QC_{i0} - QC_{ie} + A_m R_i \]  
Eqn. (2.12)

where \(i=2,4-DCP,2-CP,4-CP, P, H_2\), \(V_R\) is the total liquid volume in the reactor, \(A_M\) is the total external surface area of the membranes, \(C_{i0}\) and \(C_{ie}\) are the inlet and outlet concentrations of component \(i\) (mol/volume) and \(R_i\) is the rate of production for component \(i\) (mol/time-area).
The following suppositions are included, following the method presented in the paper: inlet and outlet volumetric flow rates are equal ($Q=\text{constant}$), the concentration for any aqueous component inside the reactor is equal to the outlet concentration ($C_i=C_{ie}$), and the catalyst is evenly distributed throughout the outside of the membranes. Additional parameters used in the simulation are presented in Table 2-1.

**Table 2-1: Reactor conditions used in the simulation (adapted from (Wu et al., 2021))**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$</td>
<td>$2.7\times10^{-3}$</td>
<td>L/min</td>
</tr>
<tr>
<td>$V_R$</td>
<td>$7\times10^{-2}$</td>
<td>L</td>
</tr>
<tr>
<td>$A_M$</td>
<td>$5.4\times10^{-3}$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$[H_2]$</td>
<td>780</td>
<td>$\mu$M</td>
</tr>
</tbody>
</table>

2.5. **Results and Discussion**

2.5.1. **Simulation Results for Influent 2,4-DCP Concentration=25$\mu$m**

For this and the remaining cases, the concentration at $t=0$ was assumed to be 0 for all components except for 2,4-DCP, which was considered according to the case
presented. Figure 2-4 shows the data fitted by solving Eqn. (2.12) for the 4 reported components when applying the algorithm presented in Section 1.4 to obtain the values for the kinetic constants that best fit the data.

Figure 2-5 shows the calculated concentration of adsorbed components in the membrane. The sum of concentrations of adsorbed components always equals $C_t$. $\text{Ct}_{\text{max}}$ was bounded at 13/nm$^2$ for a Pd FCC crystalline structure as per the calculations shown in Appendix 1. The values and comparison of calculated parameters are presented in section 2.5.5.

![Graph showing concentration over time](image)

**Figure 2-4:** Simulated results for concentration of aqueous components for initial 2,4-DCP Concentration =25µM. Simulated data is shown with straight lines.
Figure 2-5: Simulated results for concentration of adsorbed components for initial 2,4-DCP Concentration =25µM

2.5.2. Simulation Results for Influent 2,4-DCP Concentration=55µm

The same routine was implemented for the second case, where the initial concentration is 55µm. Figure 2-6 and Figure 2-7 present the aqueous and adsorbed concentrations calculated for this case.
Figure 2-6: Simulated results for concentration of aqueous components for initial 2,4-DCP Concentration = 55µM. Simulated data is shown with straight lines.

Figure 2-7: Simulated results for concentration of adsorbed components for initial 2,4-DCP Concentration = 55µM.
2.5.3. Simulation Results for Influent 2,4-DCP Concentration=95µm

In the same way, the model was applied to the case where the initial concentration of 2,4-DCP was 95µM. Figure 2-8 and Figure 2-9 present the aqueous and adsorbed concentrations calculated for this case.

Figure 2-8: Simulated results for concentration of aqueous components for initial 2,4-DCP Concentration = 95µM. Simulated data is shown with straight lines.
Figure 2-9: Simulated results for concentration of adsorbed components for initial 2,4-DCP Concentration =95µM

2.5.4. Simulation Results for Influent 2,4-DCP Concentration=195µm

This case is particular in the sense that it is the only one where 4-CP was detected in the outlet stream. This implies that the reaction favors the formation of 2-CP more strongly, which is confirmed in the results presented in section 2.5.5. Resulting simulations are shown in Figure 2-10 and Figure 2-11.
Figure 2-10: Simulated results for concentration of aqueous components for initial 2,4-DCP Concentration = 195µM. Simulated data is shown with straight lines.

Figure 2-11: Simulated results for concentration of adsorbed components for initial 2,4-DCP Concentration = 195µM
2.5.5. Parameter Comparison and Observed Trends

For all the above results, and the results provided hereafter, the solver had a fixed tolerance of $1 \times 10^{-6}$. The solver was allowed to iterate as many times as needed until the relative sum of squares was less than the tolerance described above. Since the tolerance value was strict, no further repetitions were made with a smaller tolerance. The solver converged quickly, averaging a computing time of 5 seconds.

A summary of the obtained parameters for each initial condition is presented in Table 2-2. The overall trends observed in all experiments will be discussed and compared to the conclusions found in the original paper. The obtained parameters will also allow us to discuss the validity of the assumptions, as well as making reasonable new assumptions found in the data.
Table 2-2: Comparison between reaction parameters obtained for each initial condition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>([2,4\text{-DCP}]_0 = 25\text{µM})</th>
<th>([2,4\text{-DCP}]_0 = 55\text{µM})</th>
<th>([2,4\text{-DCP}]_0 = 95\text{µM})</th>
<th>([2,4\text{-DCP}]_0 = 195\text{µM})</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_1)</td>
<td>0.54</td>
<td>1.03</td>
<td>0.75</td>
<td>1.28</td>
<td>-</td>
</tr>
<tr>
<td>(k_2)</td>
<td>8.93</td>
<td>2.96</td>
<td>6.94</td>
<td>4.18</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>(K_3)</td>
<td>0.04</td>
<td>0.08</td>
<td>0.09</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>(k_4)</td>
<td>1.28</td>
<td>2.66</td>
<td>4.15</td>
<td>3.84</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>(k_5)</td>
<td>0.08</td>
<td>0.41</td>
<td>0.38</td>
<td>0.37</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>(K_6)</td>
<td>0.52</td>
<td>0.03</td>
<td>0.31</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>(k_7)</td>
<td>0.16</td>
<td>0.36</td>
<td>0.47</td>
<td>0.48</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>(K_8)</td>
<td>3.09</td>
<td>6.68</td>
<td>5.94</td>
<td>3.86</td>
<td>-</td>
</tr>
<tr>
<td>(K_{10})</td>
<td>0.25</td>
<td>0.73</td>
<td>0.71</td>
<td>1.80</td>
<td>-</td>
</tr>
<tr>
<td>(C_t)</td>
<td>5.77</td>
<td>7.20</td>
<td>7.33</td>
<td>12.19</td>
<td>#sites/nm²</td>
</tr>
</tbody>
</table>

The first observed trend for the parameters that are involved in surface reactions (\(k_2, k_4, k_5, k_7\)) is that in all four experiments the dechlorination of chlorine in the para position is the fastest (\(k_2 \gg k_5\)). This was a conclusion reached by the original authors as well, and it is supported on the fact that the chlorine atom located in position 4 has less steric constraints caused by the hydroxyl group in position 1 (Wu et al., 2021).
A second conclusion can be drawn from comparing the speed at which 2,4-DCP and the intermediaries (2-CP and 4-CP) react. The trend shows that the reactions were 2,4-DCP is involved ($k_2$, $k_5$) are faster than the second dechlorination step ($k_4$, $k_7$). This observation contradicts the conclusions that the authors reached, since in their publication the second dechlorination was determined to be faster.

However, in other studies that are cited in the paper as well, this was not the case. In the publications by Shin & Keane, 1999 and Wei et al., 2006, the observed trend was that the first dechlorination step was faster. It is important notice that all these studies assumed a pseudo-first order kinetic dependence on 2,4-DCP. In our model we could suggest that the second reaction will happen at a lower rate since the required H* might not be as readily available to react as the first one.

It is important to point out that the model predicts some 4-CP being produced in the cases where the inlet concentration of 2,4-DCP is lower when this was not observed in the experimental data. This is because the parameters were constrained to be non-zero. The mechanism could have been modified by setting $k_5$, $K_6$ and $k_7$ to zero to avoid any change in the concentration of 4-CP, however this was not done to maintain consistency between the experiments and to assess the importance of the reaction pathway that has 4-CP as an intermediary.

Regarding the adsorption equilibrium constants, the general trend seems to suggest that the adsorption equilibrium of 2,4-DCP favors the formation of the adsorbed species. For the intermediaries, their equilibrium constants do not favor
desorption, which could explain why the concentration of 2-CP and 4-CP is low compared to the initial concentration of 2,4-DCP. This is also congruent with P adsorption equilibrium tilted towards the desorption of phenol. The adsorption kinetics of all of these components was presented in the paper as well (Wu et al., 2021), and all of the species showed similar affinity to the Pd coated membranes. However, the experiments were conducted in a hydrogen-free MCfR, and one component at a time, so the competition for the adsorption in active sites between different molecules and hydrogen was not considered.

The last observed trend is the increase of $C_t$ as the concentration of 2,4-DCP in the reactor is higher. This would seemingly contradict our supposition that this value should be a constant, however we are considering * to be a reactive adsorption site. Since the adsorption constant for 2,4-DCP ($K_i$) is also large in comparison to the other components, the fact that $C_t$ becomes larger might suggest that there is some diffusion or mass transfer resistance that could be hindering the probability of a molecule to find an active site, thus increasing the aqueous concentration increases the reactivity of the catalytic film.

An important point to address is the fact that the value of $C_t$ could not be set as a fixed parameter since this information was unavailable for the system. When this value was set to be 13 sites/nm$^2$ (as shown in Annex A), the simulations did not converge. This could be due to unaccounted surface species being prevalent at lower concentrations of 2,4-DCP or because in lower concentrations fewer active sites are available for reaction. It would be helpful for the development and validation of the
model to experimentally measure the site concentration and have a fixed value for this parameter.

It is important to observe that the conclusions drawn here are based on parameters that were independently obtained for each experiment, in contrast to using a fixed set of values for all experiments. Since this was the case, the solver can take advantage of the large number of degrees of freedom and iterate the parameters until reaching the specified tolerance. This observation will hold true for the results shown in the next chapters as well.

This condition was required since experimental data was limited to the sets shown here. Additional suppositions were made about the catalytic surface (uniform coverage of membrane surface, constant number of active sites, non-deactivation of sites) to be able to use the available information on the reactor dimensions. Some recommendations on how to validate and improve the existing assumptions of the reactor are presented in Chapter 6.

2.6. Conclusions

The results shown in this Chapter show that the algorithm developed in this model can adequately simulate the experimental data. This confirms that the programmed routine works as intended in finding a convergent, non-negative, non-trivial solution for the required parameters. Additionally, the results obtained for the adsorbed concentrations seem in line with the expected behavior, although the
calculation at early times is sometimes erratic, this is stabilized when the reactor has reached steady state.

The values obtained for the reaction rates give us information on how the reaction is likely to be advancing. It is noteworthy that the model does not presuppose a particular reaction to be the rate limiting step, so this is an insight that is obtained from the data. The results show that the first dechlorination was faster than the second, making the steps that produce phenol rate limiting. This observed trend is consistent throughout the different initial conditions.

In this case the assumption of chloride not being adsorbed was needed since no data was presented on aqueous Cl\textsuperscript{-} concentration. The quality of the experimental data in this publication is very consistent and the model would have greatly benefited from having an additional data set to reduce the degrees of freedom of the calculated parameters. So, the results shown here would exclude any interaction or effect that chloride can have either on the availability of active sites or on the mass transfer to and from the aqueous phase to the catalytic surface.
Mathematical Modeling for the Dechlorination of 1,1,1-Trichloroethane and Trichloroethene

3.1. Chlorinated Solvents Contamination

Several industries, as well on many consumer and household products, take advantage of the highly polar nature of chlorinated organic compounds to be used as cleaners and solvents. These compounds have a long story of use and their effect on the environment is now notorious, since the detection of chlorinated compounds is common on groundwater resources all across the United States (Moran et al., 2007).

Compared to other volatile organic compounds, chlorinated species usually present a higher vapor pressure, high density and low viscosities (Moran et al., 2007). These properties make them easier to remain in solution and slowly deposit in groundwater reservoirs, creating a dense non-aqueous phase liquid which might require long-term continuous treatment of groundwater ex-situ. Furthermore, the
long-term exposure to some of these components is reported to increase the likelihood of developing negative effects on human and animal health.

For these reasons, the United Stated Environment Protection agency (US EPA) has created regulations for the discharge of chlorinated solvents to the environment. Two examples of widespread chlorinated compounds are 1,1,1-trichloroethene (TCE) and 1,1,1-trichloroethane (TCA). The US EPA recommended the maximum contaminant level for TCA to be 0.2mg/L (US EPA, 2009).

Various treatments for TCA and TCE are available, involving different decontamination approaches. The use of microorganisms to reduce TCA and TCE to their dechlorinated counterparts has been reported widely. As a relevant example, the use of a similar reactor setup as the MCfR discussed here, a hydrogen-based membrane biofilm reactor, uses dechlorinating bacteria attached to the membranes as a biocatalyst for the reaction (Chung & Rittmann, 2007).

The MCfR presents some advantages over the biofilm reactor because it can tolerate a wider range of conditions for the liquid, can better tolerate aerobic atmosphere, and requires a lower hydraulic retention time. The data presented in this section corresponds to the batch tests performed on an MCfR presented in Luo et al., 2020. Points used as measured concentrations were obtained by extracting the data by means of the tool WebPlotDigitizer (Version 4.4, available at: https://automeris.io/WebPlotDigitizer)
3.2. Simulation Objectives

The paper by was selected since the reactor is similar to the one presented in Chapter 2. Also, since these are dechlorination reactions as well, this will allow to test the validity of the assumptions presented in the previous chapter. Furthermore, the reaction mechanism proposed by the authors will be evaluated and build upon, presenting an expanded version which will include adsorption steps.

3.3. Mass Conservation Equations

The data considered corresponded to the tests performed in total recirculation mode presented in Figure 3 from Luo et al., 2020. The general form of the batch reactor equation was presented in Eqn. (1.15) and will be applied for both reactions in this system. The differential equation governing the concentration of the contaminants and products in the reactor will be:

\[ V_R \frac{dC_i}{dt} = A_M R_i \quad \text{Eqn. (3.1)} \]

where \( i \) can be TCA, 1,1-dichloroethane (DCA), chloroethane (MCA), ethane (ET), TCE or Cl. \( V_R \) is the total volume of liquid in the system; \( C_i \) is the concentration of the component \( i \); \( A_M \) is the total area of the fibers; \( R_i \) represents the net production rate per unit area for component \( i \). For hydrogen, the mass balance will be:
\[
\frac{dC_{H_2}}{dt} = Q_{in} + \frac{A_m}{V_R} R_t = 0
\]  
Eqn. (3.2)

where \( Q_m \) is the gas influx into the system through the membrane. This mass balance is equal to zero to represent the invariance of dissolved hydrogen concentration in water as it will be constantly supplied through the membrane. Furthermore, we will consider this concentration to be the saturation concentration of hydrogen in water at 25\(^\circ\)C, as used previously. The parameters used in all the mass balances are presented in Table 3-1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor volume ((V_R))</td>
<td>mL</td>
<td>60</td>
</tr>
<tr>
<td>Total surface area ((A_M))</td>
<td>m(^2)</td>
<td>0.0362</td>
</tr>
<tr>
<td>Hydrogen concentration ([H_2])</td>
<td>(\mu)M</td>
<td>780</td>
</tr>
</tbody>
</table>

3.4. **Proposed Reaction Mechanism for TCA Dechlorination**

The reaction from TCA to ET will undergo the steps previously presented for surface reactions. The considered steps will be the adsorption of the reactant to the surface, bimolecular reactions with adsorbed hydrogen, and desorption from the surface. Adsorption and desorption reactions are assumed to be in fast equilibrium and substitution reactions will be considered irreversible. The reaction mechanism is detailed in steps (3.4.1) – (3.4.9)
\[ Cl_3C - CH_3 + * k_1 \rightleftharpoons k_{-1} Cl_3C - CH_3 * \]  
Step (3.4. 1)

\[ Cl_3C - CH_3 * + H * k_2 \rightarrow HCl_2C - CH_3 * + Cl * \]  
Step (3.4. 2)

\[ HCl_2C - CH_3 * k_3 \rightleftharpoons k_{-3} HCl_2C - CH_3 ** \]  
Step (3.4. 3)

\[ HCl_2C - CH_3 * + H * k_4 \rightarrow H_2ClC - CH_3 * + Cl * \]  
Step (3.4. 4)

\[ H_2ClC - CH_3 * k_5 \rightleftharpoons k_{-5} H_2ClC - CH_3 ** \]  
Step (3.4. 5)

\[ H_2ClC - CH_3 + H * k_6 \rightarrow H_3C - CH_3 * + Cl * \]  
Step (3.4. 6)

\[ H_3C - CH_3 * k_7 \rightleftharpoons k_{-7} H_3C - CH_3 ** \]  
Step (3.4. 7)

\[ Cl * + H * k_8 \rightleftharpoons k_{-8} Cl^- + H^+ + 2 * \]  
Step (3.4. 8)

\[ H_2 + 2 * k_9 \rightleftharpoons k_{-9} 2H * \]  
Step (3.4. 9)

Adding all the above steps leads to the overall chemical reaction for TCA dechlorination shown in Equation 3-1:

\[ 3Cl_3C - CH_3 + 6H_2 \rightarrow CH_3 - CH_3 + H_2ClC - CH_3 + HCl_2C - CH_3 + 6Cl^- + 6H^+ \]

Equation 3-1: Overall reaction for dechlorination of TCA

From the steps above and using the method described in sections 1.3 and 1.4, the concentration of the adsorbed components can be written from the equilibrium condition for reversible reactions. For this case, the expressions found for adsorbed
components are shown in Eqns. (3.3) - (3.8), where replacements have been made when possible. Adsorption equilibrium constants are written with a capital $K$.

\[
[H \ast] = [\ast] \sqrt{K_9 H_2} \quad \text{Eqn. (3.3)}
\]

\[
[Cl \ast] = \frac{[\ast][Cl][H^+]}{K_B \sqrt{K_9 H_2}} \quad \text{Eqn. (3.4)}
\]

\[
[TCA \ast] = K_1 [TCA][\ast] \quad \text{Eqn. (3.5)}
\]

\[
[DCA \ast] = \frac{[DCA][\ast]}{K_3} \quad \text{Eqn. (3.6)}
\]

\[
[MCA \ast] = \frac{[MCA][\ast]}{K_5} \quad \text{Eqn. (3.7)}
\]

\[
[ET \ast] = \frac{[ET][\ast]}{K_7} \quad \text{Eqn. (3.8)}
\]

The irreversible reactions will depend on the concentration of the adsorbed intermediates, which will be solved for in the next steps. The rates for irreversible dechlorinations are shown in Eqn. (3.9) – (3.11).

\[
r_2 = k_2 [TCA \ast][H \ast] \quad \text{Eqn. (3.9)}
\]

\[
r_4 = k_4 [DCA \ast][H \ast] \quad \text{Eqn. (3.10)}
\]

\[
r_6 = k_6 [MCA \ast][H \ast] \quad \text{Eqn. (3.11)}
\]

Since the concentration of chloride was reported for this case, it will be considered in the site balance. This will allow the reevaluation of the assumption of fast desorption presented in Chapter 2. The site balance is presented in Eqn. (3.12).
The expression for the concentration of free sites was calculated by replacing Eqn. (3.3) - (3.8) in Eqn. (3.12) and solving for [*].

\[ C_t = [*] + [TCA *] + [DCA *] + [MCA *] + [Cl *] + [H *] \]  
\text{Eqn. (3.12)}

\[ [*] = \frac{C_t}{K_3[DCA] + \frac{[ET]}{K_7} + \frac{[MCA]}{K_5} + \sqrt{K_9[H_2]} + K_1[TCA] + \frac{[Cl][H^+]}{K_8\sqrt{K_9[H_2]}} + 1} \]  
\text{Eqn. (3.13)}

To obtain the rate of formation for the measured components the stoichiometric relations found in the mechanism were used and led to a usable expression for their production rate that can be used to solve the mass balance. These expressions are shown in Eqns. (3.14) - (3.17).

\[ R_{TCA} = -r_2 \]  
\text{Eqn. (3.14)}

\[ R_{DCA} = r_2 - r_4 \]  
\text{Eqn. (3.15)}

\[ R_{ET} = r_6 \]  
\text{Eqn. (3.16)}

\[ R_{CI^-} = r_2 + r_4 + r_6 \]  
\text{Eqn. (3.17)}
3.5. Results and Discussion

3.5.1. Results For Modeling Considering Chloride Adsorption in The Membrane

Solving the mass balance and optimizing for the kinetic constants and the number of active sites produces data that closely resembles the experimental observations. The fit to the original data is shown in Figure 3-1.

Figure 3-1: Experimental and Simulated results for concentration of aqueous components for batch operation of a TCA reducing MCIR, including adsorbed chloride. Simulated data is shown with straight lines.

From Figure 3-1 we can see that the model closely resembles the experimental data, however some differences are seen when 30<t<70. This could be explained by the fact that the original data did not satisfy the carbon balance specially during those
times. The model adjusted the concentration calculations accordingly and therefore predicts a slightly higher than reported ET concentration.

As an additional insight that the model produces are the calculated concentration of adsorbed components in the catalyst film, which is presented in Figure 3-2. The calculated concentrations agree on the fact that the concentration of adsorbed intermediates is low throughout the experiment, and the mechanism progresses rapidly after the first dechlorination. The calculated concentration of H* remains mostly constant which suggests high availability of this component in and near active sites to maintain a reactive surface. Adsorbed chloride concentration increases proportionately to aqueous chloride concentration, which suggests that after most of the original TCA is converted to ET, which has very little adsorption affinity, adsorbed chloride becomes the prevalent species in the surface.

![Figure 3-2: Simulated results for concentration of adsorbed components for batch operation of a TCA reducing MCfR, including adsorbed chloride](image-url)
The calculated parameters shown in Table 3-2 suggest that the first dechlorination reaction is the slowest and becomes faster for each successive dechlorination \((k_2 < k_4 < k_6)\). This might indicate that the carbon in position 1 in TCA has the most steric hindrance when bonded with 3 chlorine atoms, and as they are removed it is easier for adsorbed hydrogens to access this carbon to undergo a nucleophilic unimolecular substitution reaction.

Table 3-2: Simulation parameters obtained for the dechlorination of TCA, including chloride adsorption

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>k2</td>
<td>0.2</td>
<td>(\mu\text{mol/m}^2\text{s})</td>
</tr>
<tr>
<td>K3</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>k4</td>
<td>1.6</td>
<td>(\mu\text{mol/m}^2\text{s})</td>
</tr>
<tr>
<td>K5</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>k6</td>
<td>5.6</td>
<td>(\mu\text{mol/m}^2\text{s})</td>
</tr>
<tr>
<td>K7</td>
<td>27.0</td>
<td>-</td>
</tr>
<tr>
<td>K8</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>K9</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Ct</td>
<td>1.3</td>
<td>#sites/nm^2</td>
</tr>
</tbody>
</table>

The adsorption constants point out to TCA being a species that is favorably adsorbed into the membrane \((K_1 > 1)\). DCA is mostly equilibrated between its adsorbed and desorbed state \((K_3 \approx 1)\), MCA is more favorably desorbed, and ET has a large desorption constant \((K_7 >> 1)\). This is consistent with the observed behavior of the reactor and the distribution of products.
For chloride, the model predicts an equilibrium between the adsorbed and desorbed species, for the reasons described before. Hydrogen adsorption is calculated to be small, and the value of $C_t$ is also low, compared to the maximum of 13 Pd atoms in a nm$^2$ that could conduct this reaction.

This suggests two things about what an active site * is for this case. The model predicts that TCA will need an empty vacant site in the catalyst to adhere, and in this case, we expect the surface to be saturated with H*. This would mean that in the 13 Pd atoms in a nm of catalyst, 6 pairs of H$_2$ molecules can adsorb, leaving just one empty space for TCA to adsorb. For TCA to react a C-Pd bond seems necessary for the reaction to happen. Once TCA finds an empty space it will react quickly and desorb.

Evidence for this is shown in the paper as well, as a higher catalyst dosage in the MCfR do not correlate strongly to higher reaction rates for TCA reduction(Luo et al., 2020). A conclusion for the model could be that for this specific case, mass transfer to the reactive sites will play an important role.

3.5.2. Results For Modeling Ignoring Chloride Adsorption in The Membrane

To validate the assumption made in Chapter 2 where chloride was assumed to be quickly desorbed from the membrane, the same assumption will be implemented here. The reaction mechanism will be the same, except that Step (3.4.8) will be changed to be irreversible and fast in the direction that favors aqueous chloride, as shown in Step (3.4.10).
\[ \text{Step (3.4.10)} \]

\[ Cl^* + H^* k_8 \rightleftharpoons k_{-8} Cl^- + H^+ + 2^* \]

This change will affect the site balance statement as well, by removing adsorbed chloride from the equation, producing Eqn. (3.18) and Eqn. (3.19)

\[ C_t = [*] + [TCA *] + [DCA *] + [MCA *] + [H *] \quad \text{Eqn. (3.18)} \]

\[ [*] = \frac{C_t}{\frac{[DCA]}{K_3} + \frac{[ET]}{K_7} + \frac{[MCA]}{K_5} + \sqrt{K_9[H_2]} + K_1[TCA] + 1} \quad \text{Eqn. (3.19)} \]

The production rates will not be affected, and the ones presented in Eqns. (3.14) – (3.17) will remain valid.

The data fit resulting from this modification to the reaction mechanism is presented in Figure 3-3. As expected, the fit to the experimental data remains very similar which points that the model can adapt to different conditions and still provide a simulation that resembles the original data.
The main difference with the case shown in Section 3.5.1 will be the predicted concentration of adsorbed components. Since chloride is excluded from surface concentration, the now most prevalent species is ET as its final aqueous concentration is the highest. The behavior of the curves for adsorbed 2,4-DCP and the intermediates remains similar, with 2,4-DCP concentration dropping as it is depleted and the intermediates being transformed rapidly to ET and not accumulating in the membrane. The plot for the concentration of adsorbed species for this case is presented in Figure 3-4.
Figure 3-4: Simulated results for concentration of adsorbed components for batch operation of a TCA reducing MCfR, excluding adsorbed chloride

The most important conclusions can be found from the computed values for the rate constants in each case. As we change the mechanism, the rates will undoubtedly change to accommodate the new assumptions. We can see however that the relative rate of the dechlorination reactions remains the same ($k_2 < k_4 < k_6$). This further suggests that the initial reaction is indeed rate limiting, and probably is mass transfer limited as well.

Other difference that can be observed is that when chloride is excluded, the equilibrium constants are calculated as more favorable towards the desorption of intermediate species (2-CP and 4-CP, as shown by the values of $K_3$ and $K_5$), however this is balanced out by the increase in calculated reaction rate. ET also shows a significant reduction in its desorption constant, this is because we have excluded
chlorine adsorption, a larger concentration of adsorbed ET will be calculated to maintain the site balance. A summary comparing the parameters obtained in each case is presented in Table 3-2

Table 3-3: Comparison of simulation parameters obtained for the dechlorination of TCA, for the cases where chlorine is included and excluded from the site balance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cl-included</th>
<th>Cl-excluded</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>4.7</td>
<td>1.6</td>
<td>-</td>
</tr>
<tr>
<td>k2</td>
<td>0.2</td>
<td>0.4</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>K3</td>
<td>1.1</td>
<td>5.8</td>
<td>-</td>
</tr>
<tr>
<td>k4</td>
<td>1.6</td>
<td>6.0</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>K5</td>
<td>2.8</td>
<td>6.4</td>
<td>-</td>
</tr>
<tr>
<td>k6</td>
<td>5.6</td>
<td>8.0</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>K7</td>
<td>27.0</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>K8</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K9</td>
<td>0.03</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>Ct</td>
<td>1.3</td>
<td>1.0</td>
<td>#sites/nm²</td>
</tr>
</tbody>
</table>

3.6. Proposed Reaction Mechanism for TCE Dechlorination

Compared to the previous sections, proposing a reaction mechanism for TCE presents an additional challenge, because during these experiments there was no reported evidence of other alkenes or DCA detected. This implies that TCE undergoes two substitution and two addition steps to transform to MCA, which was the other product reported. The mechanism presented here is one of the possible combinations
of substitution and addition reactions that will not produce DCA as an intermediate.

This reaction mechanism is summarized in Steps (3.6.1) – (3.6.10).

\[
\begin{align*}
HClC &= CCl_2 + k_1 \Leftrightarrow k_{-1}(HClC = CCl_2) \quad \text{Step (3.6.1)} \\
(HClC = CCl_2) + H & \rightarrow HClC = CClH + Cl \quad \text{Step (3.6.2)} \\
HClC &= CClH + H \Leftrightarrow k_{-3}(HClC - CClH_2) + * \quad \text{Step (3.6.3)} \\
(HClC - CClH_2) + H & \rightarrow HClC = CCl_2 + Cl \quad \text{Step (3.6.4)} \\
(HClC - CH_3) + H & \rightarrow k_{-5}(H_2ClC - CH_3) + * \quad \text{Step (3.6.5)} \\
(H_2ClC - CH_3) & \rightarrow k_{-6}H_2ClC - CH_3 + * \quad \text{Step (3.6.6)} \\
(H_2ClC - CH_3) + H & \rightarrow H_3C - CH_3 + * \quad \text{Step (3.6.7)} \\
H_3C - CH_3 & \rightarrow k_{-8}H_3C - CH_3 + * \quad \text{Step (3.6.8)} \\
Cl + H & \rightarrow k_{-9}Cl^- + H^+ + 2 \quad \text{Step (3.6.9)} \\
H_2 + 2 & \rightarrow k_{-10}2H \quad \text{Step (3.6.10)}
\end{align*}
\]

Sum over all the reactions leads to the overall mass action statement for this reaction, as shown in Equation 3-2.

\[
2HClC = CCl_2 + 7H_2 \rightarrow CH_3 - CH_3 + H_2ClC - CH_3 + 5Cl^- + 5H^+
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{Equation 3-2: Overall reaction for dechlorination of TCE}
\end{align*}
\]
In the same manner as the preceding examples, the concentration of adsorbed species was derived from the equilibrium reactions in the mechanism. The free radical intermediaries are not shown but are considered in the mechanism. The expressions for adsorbed species in this case are shown in Eqns. (3.18) – (3.22)

\[
[H\,*] = [*] \sqrt{K_{10}H_2}
\]  
Eqn. (3.20)

\[
[Cl\,*] = \frac{[*][Cl][H^+]}{K_9\sqrt{K_{10}H_2}}
\]  
Eqn. (3.21)

\[
[TCE\,*] = K_1[TCE][*]
\]  
Eqn. (3.22)

\[
[MCA\,*] = \frac{[MCA][*]}{K_6}
\]  
Eqn. (3.23)

\[
[ET\,*] = \frac{[ET][*]}{K_8}
\]  
Eqn. (3.24)

As the irreversible reaction steps are going to be considered as the slow steps of the mechanism, then the production speed of the reactants and products will be given by Steps (3.6.2) and (3.6.7), and their reaction rate expression is given in Eqn. (3.23) and (3.24) respectively.

\[
r_2 = k_2[TCE\,*][H\,*]
\]  
Eqn. (3.25)

\[
r_7 = k_7[MCA\,*][H\,*]
\]  
Eqn. (3.26)

The site balance does consider all possible adsorbed species and is used to determine the number of available sites, shown in Eqn. (3.26).

\[
C_t = [*] + [TCE\,*] + [DCE\,*] + [DCA\,*] + [MCA\,*] + [MCA\,*] \\
+ [ET\,*] + [Cl\,*] + [H\,*]
\]  
Eqn. (3.27)
\[ [\ast] = \frac{C_t}{\sigma} \]

where:

\[
\sigma = \frac{[ET]}{K_8} + \sqrt{K_{10}[H_2]} + \frac{[MCA]}{K_6} + K_1[TCE] + \frac{[MCA]}{K_5K_6\sqrt{K_{10}[H_2]}} \quad \text{Eqn. (3.28)}
\]

\[
+ \frac{[Cl][H^+]}{K_9\sqrt{K_{10}[H_2]}} + \frac{[MCA]}{K_3K_4K_5K_6\sqrt{(K_{10}[H_2])^3}}
\]

\[
+ \frac{[MCA]}{K_4K_5K_6K_{10}[H_2]}
\]

The last required step is to write the rate of consumption and formation of the measured species in terms of the irreversible steps. The stoichiometry of the process provides the information for this, and the resulting rates for the measured components are shown in Eqn. (3.27) – (3.30).

\[ R_{TCE} = -r_2 \quad \text{Eqn. (3.29)} \]

\[ R_{MCA} = r_2 - r_7 \quad \text{Eqn. (3.30)} \]

\[ R_{ET} = r_7 \quad \text{Eqn. (3.31)} \]

\[ R_{Cl} = 2r_2 + r_7 \quad \text{Eqn. (3.32)} \]

### 3.7. Results and Discussion

The results of the algorithm applied to this data set are shown in Figure 3-5.

For this data set the same observation regarding the completeness of the mass
balance was observed, and the model compensated it with a higher calculated ET concentration. Overall, the simulated performance correlates with experimental data.

Figure 3-5: Experimental and Simulated results for concentration of aqueous components for batch operation of a TCE reducing MCfR. Simulated data is shown with straight lines.

For the concentration of the adsorbed species, which is shown in Figure 3-6, the main difference with the previous result is the high calculated H* concentration and low Cl⁻ concentration. This suggests that an atom of adsorbed hydrogen is required neighboring an active site for an alkene to molecule to adsorb. This is suggested in the proposed reaction mechanism as well. In this high H* concentration conditions, Cl is weakly bound to the surface and desorbs quickly.
Figure 3-6: Simulated results for concentration of adsorbed components for batch operation of a TCE reducing MCfR

The simulated parameters for TCE dechlorination are shown in Table 3-4. The values obtained for the reaction steps are low, which suggests that for this case the dechlorination step being rate limiting might hold true. The calculated number of active sites is also small, which might suggest that for TCE to adsorb in the catalyst two adjacent sites are required.
Table 3-4: Simulation parameters obtained for the dechlorination of TCE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>3.12</td>
<td>-</td>
</tr>
<tr>
<td>k2</td>
<td>0.07</td>
<td>µmol/m²s</td>
</tr>
<tr>
<td>K3</td>
<td>2.66</td>
<td>-</td>
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<tr>
<td>K4</td>
<td>0.23</td>
<td>-</td>
</tr>
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<td>K5</td>
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</tr>
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<td>K6</td>
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<td>-</td>
</tr>
<tr>
<td>Ct</td>
<td>2.09</td>
<td>#sites/nm²</td>
</tr>
</tbody>
</table>

3.8. Conclusions

The data shown in this Chapter proves the robustness of the algorithm, given that the reactor is operated under a different mode, with another configuration, and different reactions. The takeaway is that the algorithm can be readily adapted to changing conditions and that as more information is available, the assumptions used can be modified to reflect the actual operation of the system.

In both cases, the results point out to fast reactions at the surface, making the assumption of negligible mass transfer to the active site unlikely. This might be due to the higher volatility of the components used in these experiments. This is a conclusion that is hinted in the original data as well, since the concentration of the measured species does not always satisfy a mass balance. At some points during the reaction the sum of concentrations of all species is not equal to the initial
concentration of TCA or TCE, which further suggests that either other intermediates were present or an equilibrium between the gas and liquid phases was not reached at those points.

The results shown here further reinforce the supposition that chloride is not adsorbed significantly in the membrane and that the supposition made in Chapter 2 is reasonable. This was a result that was derived from the simulation of TCE directly but had to be double checked for TCA. This can also suggest that the adsorption step might look like a SN$_2$ substitution, where the leaving chlorine is replaced with a bond to the Pd surface. In this scenario, when the incoming molecule collides with the adsorbed hydrogen, which acts as a nucleophile, the chlorine opposite to the place where the collision occurred is expelled.
Physical Adsorption and Catalytic Defluorination of PFOA Over Monometallic PdNPs Coated On H$_2$-Delivering Membranes

4.1. PFAS Contamination

Perfluorooctanoic acid (PFOA) is one of the most well-known polyfluoroalkyl substances (PFAS), a family of synthetic organofluorine chemical compounds (Sharpless & Yiannas, 2019). These compounds have been used in the manufacturing industry due to their resistance to stains, grease, and water (United States Environmental Protection Agency, 2016b). PFAS can be found in non-stick cookware, textiles, food packaging, electronics, medical products and firefighting foams. The high stability of the C-F bond make most PFAS stable to metabolic and environmental degradation (National Institute of Environmental Health Sciences, 2020). For this reason, fluoroalkyl substances are often referred as “forever chemicals”.
PFAS contamination has become an increasing concern for public health agencies because of the many human health effects associated with these contaminants, their persistency (Environmental Protection Agency Federal Facilities Restoration & Office, 2017), bioaccumulation in humans and wildlife (Oliaei et al., 2013), numerous ways of exposure (CDC, n.d.) and growing number of PFAS being developed and tested. PFAS have been detected in blood and tissue samples from most Americans (United States Environmental Protection Agency, 2016a).

Since PFAS and PFOA are remarkably unreactive, the treatment technologies developed to remove these contaminants have relied mostly on adsorption on an appropriate substrate to later be thermally destroyed. The most common way to treat PFAS contaminated water is by adsorption with granular activated carbon, although a variety of other adsorbents have been used as well (Arias Espana et al., 2015). The principal problems with these technologies is slow adsorption kinetics (activated carbon requires over 72h to reach equilibrium) and limited adsorption capacity, requiring change or regeneration of adsorbent (chitosan has the largest reported PFOA adsorption capacity of 5.2 mmol PFOS/g (Zhang et al., 2011)). Other separation processes like membrane separations (C. Y. Tang et al., 2006), filtration and chromatography have been reported as well but their applicability for large scale operations is limited.
4.1.1. Use Of Pd-Coated MCfR for PFOA Defluorination

One of the most promising technologies to treat PFAS is chemical/advanced photochemical oxidation where the contaminants are destroyed in-situ and no further treatment is required. Some of these methods require highly reactive oxidants to drive the oxidation process (Hori et al., 2005). Another approach for PFOA decomposition is photocatalytic degradation, an emerging technology for PFAS treatment (Duan et al., 2020), where no additional reactants are needed. However, these reactions will require a source of light, which is often in the UV region. This presents additional challenges in designing an efficient reactor.

The approach analyzed in this document is based on the catalytic hydrodefluorination (HDF, also known as reductive defluorination) of PFOA, where hydrogen gas (H₂) was used as an electron donor to promote the substitution of fluorine on a palladium surface. The setup used in the experiments is a hydrogen-based membrane palladium-film reactor (MCfR) as presented in previous sections. The data and information on this chapter was obtained from an unpublished manuscript by Long et al., (2021).

4.2. Simulation Objectives

In the referenced paper, both the defluorinative and non-defluorinative adsorption of PFOA was reported in the MCfR. Additionally, several partially defluorinated intermediates were detected but not quantified, which will complicate
the model. The aim is to produce a model that can account for both modes of adsorption and provide additional information on the behavior of PFOA in this reactor.

Since both reactive and unreactive adsorption are expected, we want to be able to predict what is the principal adsorption mode and calculate the amount of PFOA that adsorbs in a reactive way.

### 4.3. Proposed Reaction Mechanism

To account for the hypothesized two modes of adsorption, the adsorption is differentiated as non-reactive adsorption on an adsorbent site (⊗) and reactive adsorption on an active site (*). This hypothesis was derived from the observation that in the absence of H₂, PFOA still showed some adsorption to the membrane. Density Functional Theory (DFT) calculations made for the PFOA – Pd(111) system showed that the two possible adsorption modes correspond to an interaction of the carboxylate head group of PFOA with the membrane surface (as shown in Figure 4-1a), and parallel binding of the fluorine groups with hydrogen in the surface (shown in Figure 4-1b).
Figure 4-1: Adsorption modes for PFOA. a) shows the non-reactive adsorption on an adsorbent site (⊗), b) shows reactive adsorption due to the interaction of fluorines with an active site (*)

Since tracking individual defluorination reactions is not practical, they will be lumped by the introduction of the parameter, \( \delta \) \((0 < \delta \leq 15)\) which is the average number of fluorine atoms removed per molecule of reacted PFOA. A schematic of the process is shown in Figure 4-2 and the reaction mechanism is described in Steps (4.1) – (4.5).
Figure 4-2: Scheme of the defluorination of PFOA in the MCfR

Adsorption of PFOA on a Pd adsorption site

$$PFOA(aq) + \otimes k_1 \rightarrow PFOA^\ominus$$  \hspace{1cm} \text{Step (4.1)}

Adsorption of PFOA on an active Pd site

$$PFOA(aq) + * k_2 \leftrightarrow k_{-2} PFOA^*$$  \hspace{1cm} \text{Step (4.2)}

Averaged defluorination reactions

$$PFOA^* + \delta H^* k_3 \rightarrow P(aq) + \delta F^* + *$$  \hspace{1cm} \text{Step (4.3)}

Fluorine desorption

$$F^* + H^* k_4 \leftrightarrow_{k_{-4}} F^-(aq) + H^+(aq) + 2 *$$  \hspace{1cm} \text{Step (4.4)}
Adsorption of H\textsubscript{2} in Pd film

\[ H_2(aq) + 2 \times k_5 \leftrightarrow_{k_{-5}} 2H^* \]

Where PFOA is C\textsubscript{7}F\textsubscript{15}COO\textsuperscript{-}, * is an available active site, \( \otimes \) is an available adsorption site, PFOA*, H* and F* are adsorbed species and \( P \) is a distribution of partially defluorinated compounds which satisfies the C, F and H mass balances.

By adding the 4 equations together, we get the overall chemical reaction as follows:

\[ PFOA(aq) + \delta H_2(aq)k_{rxn} \rightarrow P(aq) + \delta F^-(aq) + \delta H^+(aq) \]

**Equation 4-1: Overall reaction for the defluorination of PFOA**

Defluorination reactions which are described by Step (4. 3) are considered the rate-limiting step while other reactions are assumed to be fast equilibriums. Using the steady-state assumption and a Langmuir-Hinshelwood type kinetics an expression for the rate of Step (4. 3) can be obtained, which depends only on the concentrations of measurable species (PFOA, H\textsubscript{2}, F\textsuperscript{-} and H\textsuperscript{+}) and has the form:

\[ r_3 = \frac{A[PFOA][H_2]^3}{\left(B[H_2]^1 + C[PFOA][H_2]^1 + D[H_2] + [F^-][H^+]\right)^2} \]

Eqn. (4. 1)

Where \( A, B, C \) and \( D \) are constants that include the equilibrium constants \( (K_1, K_2, K_4) \) the reaction rate \( (k_3) \) and the total number of active sites \( (Ct) \).
4.4. Mass Conservation Equations

A mass-balance was defined for PFOA, H₂, F⁻ and H⁺ for the system operating in recirculating mode as a semi-batch reactor as shown in Eqn. (4.2)

\[ V_R \frac{dC_i}{dt} = Q_{in}C_{i\,in} + A_M R_i \]  

Eqn. (4.2)

where \( V_R \) is the total volume of liquid in the system; \( C_i \) is the concentration of the component \( i \) (\( i \) can be PFOA, H₂, F⁻ and H⁺); \( Q_{in} \) is the flux into the system, respectively; \( A_M \) is the total area of the fibers; \( R_i \) represents the net reaction rate per unit area for component \( i \). Specifically, when \( i \) is PFOA, F⁻ and H⁺, \( Q_{in} \) equal to 0. When \( i \) is H₂, \( Q_{in} = J_{H_2}A_MC_f \), where \( J_{H_2} \) is the flux of hydrogen per unit area of membrane and \( C_f \) is a unit correction factor.

The values for \( R_i \), defined by the stoichiometry of Equation 4-1 and the definition for the reaction rate in Eqn. (4.2) will be defined as \( r_3 = -\delta R_{H_2} = \delta R_{F^-} = \delta R_{H^+} \), from which a system of 4 ordinary differential equations is obtained. Since PFOA can undergo unreactive adsorption its formation rate will include the rate of Step (4.1). Then, \( R_{PFOA} = -r_1 - r_3 \). As the production rate for H⁺ is directly proportional to the production of F⁻ the concentration of H⁺ can be modelled as an algebraic equation and the system reduces to 3 ODES.

4.4.1. Experimental Setup

The reactor features a 40 mL working volume with one bundle of nonporous polypropylene hollow-fiber membranes. Hydrogen gas was supplied to both ends of
fiber bundles at 20psi. The MCfR was well mixed using a recirculation rate of 150 
ml/min achieved with a peristaltic pump, which backs the assumption of a well-
mixed fluid. The reactor was operated under total recirculation,

Additional parameters used in the simulation are shown in Table 4-1.

**Table 4-1: Parameters of reactor setup for PFOA defluorination**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor volume ($V_R$)</td>
<td>mL</td>
<td>40</td>
</tr>
<tr>
<td>Total surface area ($A_M$)</td>
<td>cm$^2$</td>
<td>181</td>
</tr>
<tr>
<td>Hydrogen concentration ([H$_2$])</td>
<td>μM</td>
<td>780</td>
</tr>
</tbody>
</table>

4.5. Results and Discussion

The results obtained for the MCfR working in full recirculation mode are 
presented in Figure 4-3. The simulated data strongly correlates with the presented 
data.
Figure 4-3: Comparison between experimental and simulated results for PFOA defluorination. Simulated data is shown with straight lines.

Of more interest is the simulation of adsorbed species, shown in which show a decline of PFOA concentration with time. The initial PFOA concentration is high because the reactor is considered to be in rapid adsorption equilibrium. The amount of adsorbed fluorine does not reach very high levels although the concentration of aqueous fluorine rapidly increases, which suggests a low adsorption affinity for fluorine which is further confirmed by the high value for the desorption constant $K_4$. 
Figure 4-4: Simulated results for concentration of adsorbed components for batch operation PFOA dechlorination in a MCfR

The calculated kinetic parameters for this reaction are presented in Table 4-2. The main takeaway from the results is that the non-reactive adsorption mode, which is dependent on $k_1$ and $\otimes$ is not favorable when $H_2$ is supplied. The low values obtained for these two parameters are in accordance with the DFT calculations result presented by the authors. The result of that simulation points out that the non-dechlorinated adsorption mode is thermodynamically less favorable than the reactive mode of adsorption, which presents a much larger rate constant ($k_3$). This is also evidenced in the fact that the concentration of active sites $C_i$ is much higher than the number of unreactive sites $\otimes$. 
This could also suggest that when the reactor is operating with H\textsubscript{2}, most sites will be occupied with $H^*$, which will reduce the number of available adsorptions only sites. In this sense, a viable adsorption only site $\bigotimes$ might require a place with low $H^*$ density around it for the PFOA molecule to be able to orient itself with the carboxylate head pointing towards the surface. On the other hand, an active site $*$ will require neighboring $H^*$ to be able to interact with the fluorine atoms in the and produce a reaction.

**Table 4-2: Simulation parameters obtained for the defluorination of PFOA**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>0.06</td>
<td>L/µmol h</td>
</tr>
<tr>
<td>$K_2$</td>
<td>6.96</td>
<td>-</td>
</tr>
<tr>
<td>$k_3$</td>
<td>1.63</td>
<td>m\textsuperscript{2}/µmol h</td>
</tr>
<tr>
<td>$K_4$</td>
<td>46.64</td>
<td>-</td>
</tr>
<tr>
<td>$K_5$</td>
<td>2.45</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$</td>
<td>8.14</td>
<td>-</td>
</tr>
<tr>
<td>$C_t$</td>
<td>3.62</td>
<td>#/nm\textsuperscript{2}</td>
</tr>
<tr>
<td>$\bigotimes$</td>
<td>0.04</td>
<td>#/nm\textsuperscript{2}</td>
</tr>
</tbody>
</table>

Furthermore, the calculated number of active sites $C_t$ suggests that PFOA interacts strongly with the catalyst surface, probably due to interactions between fluorine and $H^*$, as depicted in Figure 4-1. Another insight of the model is that the calculated number of fluorine atoms released from a PFOA molecule suggests that partially defluorinated products will occur. This was confirmed by HPLC-QTOF-MS
analysis from the samples which found evidence of a range of partially fluorinated molecules of octanoic acid.

4.6. Conclusions

The model presented here shows the flexibility of the model in the sense that it can be used for mechanisms that might include several lumped reactions, or different modes of adsorption. The algorithm is capable of incorporating these changes as long as the mass balance and rate of formations are derived from the same first principles as in the examples presented in previous chapters.

The two modes of adsorption assumed here were observed experimentally and confirmed by DFT calculations. The experimental observations pointed out that when no H₂ is present the unreactive mode of adsorption increasingly saturates the catalyst until no further adsorption is observed. However, the importance of this process when H₂ is present was yet to be determined, but the model predicts that the presence of hydrogen will hinder the inactivation of catalyst due to non-reactive adsorption.

Continuous cycles of reactions were studied for this case and the observed behavior does suggest that a part of the incoming PFOA is being adsorbed on an unreactive way and blocking some sites for further reaction. Currently, the model cannot account for this accumulation and the simulations after the first cycle are not
very accurate. This is explained with more detail on Chapter 6, where suggestions for future work are included.
Proof Of Concept for A 3D Printed Palladium Catalytic Support

5.1. Introduction

Additive manufacturing processes, or more commonly known as 3D printing, is the process of constructing 3 dimensional objects from a digital model. The term additive emerges from the fact that this technology builds the printed object from the ground up by continually depositing new material in an ordered manner. This type of process has become increasingly popular over the years as the technology required to build a printer becomes available to a larger part of consumers.

3D printing can span a large array of applications and used in several industries, ranging from the simplest, as being able to print several toys and decorations, to much more complex such as product prototyping, animal and human prosthetics, even entire houses. The ease that this process provides allows for the construction of virtually any shape with ease has been considered as a possible
technology to be brought to space, so in the case that ‘something’ is needed, it can be built in situ (Leach, 2014).

Fused deposition modelling (FDM) is the most widespread technology for 3D printing and consists of the continuous deposition of a thermoplastic material. The most common materials used for this technique are polymers, such as polylactic acid (PLA), polypropylene (PP), polyethylene terephthalate (PET), polyethylene (PE) and acrylonitrile butadiene styrene (ABS). These materials have melting points that are above 100°C which mean that they are not prone to deforming at normal room temperatures. However, other materials can be used as long as they are able to be extruded and can hold the shape afterwards. Examples of non-polymeric materials used in FDM are clay, wax, concrete and chocolate.

In the field of catalysis, this technology has been used in the fabrication of active catalyst supports, by the use of several different methods, such as electroless deposition (Jones et al., 2017), selective laser sintering (Bulatov et al., 2020), and thermal sintering (Tubío et al., 2016). There is a vast literature on several applications of this technology to diverse components, supports and reactions, however the present work tries to focus on a simple way of applying computer assisted modelling to catalytic supports.

The motivation underlying these experiments is to present a way to explore a way to modify the macroscale geometry of a catalytic surface to attune the performance of a reaction. To do this, a method to attach active Pd nanoparticles to
readily available ABS filament was tested. This proof of concept shows that attaching a catalytically active metal to a 3D printed substrate is feasible.

Commercially available catalyst supports are porous materials manufactured in such a way to create submicron or nano scale pores which allow a high specific surface area. The most common supports are alumina, silica and ceramics, which are mainly used in fixed or slurry bed reactors which were presented in section 1.1.2. However, some reactions require strict control of fluid flow, species distribution and temperature. This is especially important in exothermic reactions, where a packed catalyst bed can produce hot spots that can damage the catalyst or the reactor (Danaci et al., 2018).

Another shortcoming of traditional packed and fixed catalyst beds is the channeling of liquids and gas throughout the catalyst bed. This is an inefficient way of distributing the reactants and can reduce the overall efficiency of the system. To overcome this mass and heat transfer limitations, structured catalysts and reactors can be used. Metallic structures are widely used in exothermic reactions to facilitate heat transfer, although other materials such as foils (Görke et al., 2005), foams (Frey et al., 2015) and 3D printed (Lämmermann et al., 2018) supports have been used as well.

Since FDM is a readily available technology, it is desirable to test the use of this technology as a fist approach to tailored structured catalyst supports. The material used to print was ABS since it has strong chemical resistance and is inexpensive. It
also has a high rigidity and a wide range of working temperatures (-20 to 80 °C). The goal is to produce a mobile support that can help increase turbulence in the aqueous phase to improve mass transfer to the active sites.

5.2. Experimental Work

5.2.1. Design and Printing Of 3D supports

The structures used as supports were designed in SOLIDWORKS 2020, and their shape was impellers with holed blades to create more surface defects and a larger surface area. The 3D printer used was a commercially available model (Creality Ender 3 3D Printer). The filament was white ABS (HATCHBOX ABS 3D Filament).

The shape selected had a hole to fit a 3.5cm PFTE stir bar. This assembly allowed the piece to remain submerged in water and also to rotate in a magnetic stir plate. The total calculated volume of the printed support was 10.32 cm³ with a total surface area of 89.32 cm².
5.2.2. Impregnation Of PD NPs to Printed Structure

The synthesis method was similar to the coating method for the Pd film used in the MCfR discussed in previous chapters. A precursor solution of sodium tetrachloropalladate (Na$_2$PdCl$_4$) (5,10,20 µM) in DI water was prepared and the ABS support was soaked in this solution for 24h. Afterwards the piece was dried and introduced in a solution of a 0.1 M Sodium Borohydride (NaBH$_4$) solution that acted as a reducing agent to promote the reduction of adhered Pd.

5.2.3. Determination of Catalytic Activity

The finished supports were tested for their ability to catalyze the reaction of 4-nitrophenol (4-NP) to 4-aminophenol in the presence of NaBH$_4$ as shown in Figure 5-1.
The reaction was conducted on a 10 mM 4-nitrophenol stock solution, mixed with alkaline 0.1 M NaBH$_4$ solution, as described in (Pretzer et al., 2016).

$$4\text{-nitrophenol} + NaBH_4 \rightarrow 4\text{-aminophenol} + H_2 + NaBO_2$$

**Figure 5-2: Reaction scheme for the catalytic reduction of 4-nitrophenol**

The concentration of 4-NP was measured by UV-vis spectroscopy, by measuring the absorbance of the nitro group at 400nm.

**5.2.4. Microscopy and X-ray Spectroscopy**

Morphological characterization was performed using the cross-section (for length) and top surface for pore morphology. The instrument is equipped to perform Energy-dispersive X-ray spectroscopy (EDS) analysis of the emission produced by the sample after the electron beam of the microscope has been applied. This allows to map the emissions in a spectrum, where each element produces a
distinctive signal that allows qualitative analysis of elemental composition of the sample.

5.3. Description of Results and Analysis

The color of the printed support changed from their original white color to orange, indicating adsorption of Na$_2$PdCl$_4$ salt from solution. Upon being introduced in the NaBH$_4$ solution, they instantly showed a change of color to a dark grey, indicative of an adsorbed metal. The adhesion phenomena could be explained by physical deposition of PdCl$_4^{2-}$ ions in the surface defects of the 3D printed material. These defects are seen in more detail in Figure 5-6 to Figure 5-8.

The structure of ABS shown in Figure 5-3 could also give some insight on the affinity of the negatively charged PdCl$_4^{2-}$ ion on the polymer structure. The phenyl group that is found on the styrene group has an electron-withdrawing effect, which can produce a partial positive charge on the alkyl chain. This might encourage electrostatic interactions with anions such as palladium tetrachloride. Furthermore, the deposition of metallic nanoparticles on polymers has also been reported for materials which are considered inert. The research published by Pentsak et al., 2019 shows that the polytetrafluoroethylene coating of magnetic stir bars can be contaminated with metal nanoparticles trapped in surface defects. If this holds true for a mostly neutral and unreactive material as PTFE, then assuming that similar mechanics produce adsorption in ABS is reasonable.
To test for catalytic activity, 3 levels of Na$_2$PdCl$_4$ concentration were tested (5, 10 and 20mM). The resulting supports did exhibit grey coloration but the difference between each treatment was not noticeable. Figure 5-4 shows pictures comparing before and after treatment.

Figure 5-3: Structure of Acrylonitrile butadiene styrene (ABS)
Figure 5-4: Comparison of the 3D impeller supports before and after adhesion experiments. The beakers in image a) show the initial coloration of the Na$_2$PdCl$_4$ solution in increasing concentration of 5, 10 and 20mM. Figure b) shows the final appearance of the supports after reduction.

However, when the supports were tested for catalytic activity, they all presented similar reactivity. In the three cases the reaction of 4-NP was observed, as demonstrated by the decrease in the absorbance of the nitro group at the 400nm wavelength presented in Figure 5-5a, b and c. A control with a non-treated support was also tested, and no reaction was observed in this experiment. A first order reaction constant was calculated using these spectra for each experiment and the results are summarized in Table 5-1.
Figure 5-5: UV–vis absorbance spectra for the 5mM (a), 10mM (b), 20mM (c) treated impeller. First order rate calculation for the three treatments (d)

Table 5-1: Calculated first-order reaction constant for each treatment

<table>
<thead>
<tr>
<th>Treatment Level</th>
<th>$k_{rxn} \ [mM/min]$</th>
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<tbody>
<tr>
<td>5mM Na$_2$PdCl$_4$</td>
<td>0.0142</td>
</tr>
<tr>
<td>10mM Na$_2$PdCl$_4$</td>
<td>0.0138</td>
</tr>
<tr>
<td>20mM Na$_2$PdCl$_4$</td>
<td>0.0107</td>
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The results for the rate constant are inconclusive on the effect of varying the concentration of the precursor salt on the catalytic activity of the finished product. However, the important takeaway is that the procedure used to impregnate the nanoparticles produces a reactive coating that can promote the reaction, and this is due to the metal deposited on the surface of the support.

To further confirm that the cause of the observed reaction was adhered PdNP in the support surface, scanning electron microscopy was performed on the samples. The pictures were taken of representative sections of the impellers where most of the gray color was found. Additionally, energy-dispersive X-ray spectroscopy was taken from this samples to probe for the presence of metals in the samples. The observed photographs and spectra are shown in Figures 5.5, 5.6 and 5.7.
Figure 5-6: SEM pictures of 5mM treated impeller. a) 20µm and b) 500µm. A larger version is shown in Appendix B.
Figure 5-7: SEM pictures a) 5µm and b)500µm and EDS Spectra of 10mM treated impeller. A larger version is shown in Appendix B
Figure 5-8: SEM pictures a) 5µm and b) 500µm and EDS Spectra of 20mM treated impeller. A larger version is shown in Appendix B
Figure 5-9: Detail of the section analyzed in the SEM. From left to right, a section of an impeller blade from experiment treated with 5mM, 10mM and 20mM Na$_2$PdCl$_4$ solution

At the resolution level from where the images were taken it is difficult to confirm the shape or size of the PdNP in the surface. Furthermore, it looks like the metal is not clustered in definite spots but rather dispersed throughout the surface. However, the EDS spectra confirm that Pd was detected, which corroborate the hypothesis that adsorbed Pd was responsible for the observed reaction.

5.4. Conclusions

Currently these experiments can only confirm that the proposed method for Pd impregnation does in fact deposit Pd on the surface of the 3D printed material. However, this opens the opportunity for further experimentation on how this method
can be improved and used in other applications. The main advantages that this 3D printed supports could bring is the improvement of mass transfer towards catalytic sites while minimizing catalyst leaching and providing a stable and reusable structure.

This technology could be used towards the design of catalytic monoliths, packed beds and structured supports that can be modeled to provide specific fluid behaviors inside of the pores or reduce pressure drop throughout the packing.
Recommendations for Future Work

The models developed in this research can help predict reaction mechanisms and evaluate their viability based on the supposition that invalid or less likely mechanisms will not have good correlation with experimental data. However, this hypothesis has not yet been proven true. Further experimental work on a MCfR aimed on validating the model would be necessary to provide evidence of the degree on which the assumptions assumed in this work are valid for each system.

The main area of improvement to the model would be to study the relation between the adsorption capacity of the catalyst film and number of active sites. We expect $C_t$ to be a constant value, or at least to not vary too much while operating the reactor (if no substantial catalyst leeching occurs). If this would be a fixed parameter or function, then the model will have less degrees of freedom and the model would only need to estimate the reaction constants.
Additionally, the model would benefit from improvements that can be introduced by using replicate results for each experiment. This would allow the study of the ability of the model to predict new results when the reaction conditions are the same. The analysis shown here was constrained to use data from other sources and some error is expected when translating the figures to raw data.

As discussed on the conclusions for Chapter 4, the model was applied to the PFOA reaction carried on in several cycles. However, the results differ to the data shown for the single use, as shown in Chapter 4. Moreover, as the reactor is used in successive cycles the effect of non-reactively adsorbed PFOA becomes of increasing concern, producing inconsistencies on the results. As a proof, Figure 6-1, Figure 6-2, and Figure 6-3 show how the results for these cycles.

Figure 6-1: Comparison between experimental and simulated results for PFOA defluorination in cycle 1 of successive experiments
Figure 6-2: Comparison between experimental and simulated results for PFOA defluorination in cycle 2 of successive experiments

Figure 6-3: Comparison between experimental and simulated results for PFOA defluorination in cycle 3 of successive experiments
As seen in the above figures, the model is not able to correctly simulate the PFOA concentration for Cycle 1, where more unreactive defluorination seems likely. As some non-reactive adsorption occurred in Cycle 1, this effect is seen in Cycle 2 where at later times the production of fluorine is reduced, which prevents the algorithm to continue using a smooth curve and it encounters undetermined values. Cycle 3 data looks like a good fit; however, this is only because there are less data points, and, in this case, there is neither significant production of fluorine nor PFOA defluorination.

This suggests that as the reactor is operated for longer, the accumulated effects of unreactive adsorption become increasingly significant. The model presented here, together with further analysis of the catalytic surface could provide more information on the amount of PFOA adsorbed in this way and could help identify operational variables that favor reactive adsorption over unreactive adsorption to improve reactor performance.

Regarding the experimental results shown in Chapter 5, this very preliminary set of results hints at the possibility to use polymeric matrices as supports for metallic nanoparticles. The most surprising result shown here was the facility on which the surface can be coated with Pd. However, studies on surface coverage, morphology of the nanoparticles, or catalyst leaching would be necessary to assert the possibility of considering this as an appropriate medium for further developments.
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Appendix A

Calculation of the surface atom density for FCC Pd Crystals

To calculate the maximum amount of possible Pd sites in a surface, the assumption of a face centered cubic (FCC) crystal structure for Pd is used. In this geometry, in a unit area of side $a$ has a diagonal of size $4r$ as shown in Figure A-1.

![Figure A-1: Atomic surface distribution for a FCC crystal. Where $r$ is the atomic radii, $a$ is the length of the unit cube.](image)

As seen above, the hypotenuse of the triangle of sides $a$: $a: \sqrt{2}a$ must be equal to $4r$, therefore the side $a$ can be expressed as:

$$\sqrt{2}a = 4r$$
\[ a = 2\sqrt{2}r \]

Then, dividing the total number of atom faces exposed in the unit area by the area of the unit area (which we will define to be 1nm\(^2\)) will give the total amount of atoms per unit area \( (C_{t\ max}) \):

\[
C_{t\ max} = \frac{4\text{atom} \left(\frac{1\text{atom}}{4\text{corner}}\right) + 1\text{atom}}{a^2} = \frac{2}{8r^2}
\]

For a Pd atom, the atomic radius is 0.137nm, which on replacement gives:

\[
C_{t\ max} = \frac{2\text{atom}}{8(0.137\text{nm})} = 13.32 \approx 13 \frac{\text{atoms}}{\text{nm}^2}
\]
Appendix B

Detail of Figure 5-7:

[Image of a) detail of Figure 5-7]
Detail of Figure 5-8:
Detail of Figure 5-8: