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Stable dechlorination of Trichloroacetic Acid (TCAA) to acetic acid catalyzed by palladium nanoparticles deposited on H₂-transfer membranes

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A R T I C L E   I N F O

Article history:
Received 18 November 2020
Revised 9 January 2021
Accepted 12 January 2021
Available online 15 January 2021

Keywords:
Disinfection byproducts
Trichloroacetic acid (TCAA)
Palladium nanoparticle (PdNP)
Hollow fiber membrane
Catalytic dechlorination

A B S T R A C T

Trichloroacetic acid (TCAA) is a common disinfection byproduct (DBP) produced during chlorine disinfection. With the outbreak of the Coronavirus Disease 2019 (COVID-19) pandemic, the use of chlorine disinfection has increased, raising the already substantial risks of DBP exposure. While a number of methods are able to remove TCAA, their application for continuous treatment is limited due to their complexity and expensive or hazardous inputs. We investigated a novel system that employs palladium (Pd⁰) nanoparticles (PdNPs) for catalytic reductive dechlorination of TCAA. H₂ was delivered directly to PdNPs in situ coated on the surface of bubble-free hollow-fiber gas-transfer membranes. The H₂-based membrane Pd film reactor (H₂-MPIR) achieved a high catalyst-specific TCAA reduction rate, 32 L/g-Pd/min, a value similar to the rate of using homogeneously suspended PdNP, but orders of magnitude higher than with other immobilized PdNP systems. In batch tests, over 99% removal of 1 mM TCAA was achieved in 180 min with strong product selectivity (≥ 93%) to acetic acid. During 50 days of continuous operation, over 99% of 1 mg/L influent TCAA was removed, again with acetic acid as the major product (≥ 94%). We identified the reaction pathways and their kinetics for TCAA reductive dechlorination with PdNPs using direct delivery of H₂. Sustained continuous TCAA removal, high selectivity to acetic acid, and minimal loss of PdNPs support that the H₂–MPIR is a promising catalytic reactor to remove chlorinated DBPs in practice.

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1. Introduction

Chlorination, the most widely applied method for water disinfection, forms numerous disinfection byproducts (DBPs) (Hruday, 2009). The second group of most common DBPs (after trihalomethanes) are the haloacetic acids (HAAs), including mono-, di-, and tri- chloroacetic acids (MCAA, DCAA, and TCAA) (Hong et al., 2013; Krasner et al., 2006). Exposure to HAAs in drinking water is associated with an increased risk of cancer (Boorman et al., 1999; Villanueva et al., 2004), and recent studies suggest that HAA exposure increases antibiotic resistance in bacteria (Li et al., 2016; Lv et al., 2014). The U.S. Environmental Protection Agency (EPA) posted a maximum contaminant level (MCL) of 60 μg/L for the sum of five haloacetic acids (HAA5), including three chloroacetic acids (CAAs) and two bromoacetic acids (Pontius, 1999). With the outbreak of the Coronavirus Disease 2019 (COVID-19) pandemic, the use of chlorine for disinfection has increased and is increasing the risks of DBP exposure, especially in raw water (Chang et al., 2020; Wang et al., 2020). Pulp-mill wastewaters have still higher concentrations of HAAs (Hoekstra et al., 1999). An effective method for HAA removal will minimize undesired outcomes associated HAAs in water.

Reductive methods for HAAs removal have included chemical, electrochemical, and sonochemical methods. For instance, Wang et al. (2008) reported reductive dechlorination of TCAA using membrane-immobilized palladium/iron, with acetic acid (AA) (60%), DCAA (14%), MCAA (26%) as the products. However, the TCAA-removal efficiency decreased to below 60% after 8 cycles. Using a three-dimensional graphene–copper-foam electrode with an applied cathode potential of −1.2 V, Mao et al. (2016) achieved 95% removal of 500 mg/L TCAA within 20 min at pH 6.8, with acetic acid (AA) (70%) and MCAA (25%) as the major products.
at 180 min. Esclapez et al. (2015) reported the dechlorination of TCAA via high-frequency sonoelectrochemical degradation using a Pb cathode, with MCAA (20–40%) and DCAA (10–50%) as the major products. Although these studies provide promising results for TCAA removal, toxic byproducts, including DCAA and MCAA, were produced using these methods, and they did not demonstrate continuous treatment. Furthermore, chemical inputs, such as an electrolyte (e.g., Na₂SO₄), were required for most of electrochemical methods.

Among all reductive methods, catalytic reductive dechlorination using palladium nanoparticle (PdNP) is especially promising (De Corte et al., 2011; Hennebel et al., 2009), since H₂ is as the only input needed; not needed are the external energy or chemical inputs required in most other methods, e.g., solar radiation, sonic power, hydro-peroxide or iron (Feijen-Jeurissen et al., 1999; Han et al., 2017; Jewell and Davis, 2006; Liu et al., 2001). H₂ is nontoxic and readily available, can be purchased in bulk or formed on-site by electrolysis or methane reforming, and has mature handling methods that ensure its safe use (Dincer, 2012; Lv et al., 2012; Wegner et al., 2006). H₂ can be used as reductant to convert dissolved Pd⁴⁺ ion to zero-valent PdNPs through self-catalyzed reduction. PdNPs are effective because they strongly adsorb H₂ and activate it to the reactive H⁺ atoms on the PdNP surface. The reactive H⁺ atom has been proven useful for reducing a wide range of oxidized contaminants: e.g., trichloroethene, nitrate, and chlorophenols (El-Sharnouby et al., 2018; Liu et al., 2001; Zhou et al., 2017), as well as dehalogenation of DBPs: e.g., trihalomethanes and HAAs (Mao et al., 2018; Xu et al., 2020).

Efficient H₂ delivery is mandatory because of its low solubility in water and combustibility. Delivering H₂ with nonporous gas-transfer membranes is a well-studied approach for safe and controllable H₂ delivery to biofilms, using the H₂-based membrane biofilm reactor (H₂-MBR) (Lv et al., 2020; Zhao et al., 2013; Zhou et al., 2017). In this study, we develop and demonstrate a H₂-based palladium-film reactor (H₂-MPR), a modification of the H₂-MBR that utilizes PdNPs instead of biofilm. We in situ synthesized PdNPs that self-assembled on the membrane surface. Using TCAA as a model compound, the membrane achieved safe and controllable H₂ delivery to the coated PdNPs for catalytic dechlorination of halogenated DBPs. We elaborate the reaction kinetics and pathways for TCAA catalytic reductive dechlorination.

2. Materials and methods

2.1. System configuration and setup

Fig. 1A is a schematic of the one-column bench-scale H₂-MPR, which shared the configuration of previous studies (Zhao et al., 2013; Zhou et al., 2017). It had a total working volume of 35 mL and contained one bundle of 120 identical hollow-fiber membranes in a glass tube (6-cm internal diameter and 24-cm long). The hollow-fiber membrane used in this study was made by nonporous polypropylene and had a 200–μm outer diameter, –105–μm inner diameter, and ~52–μm wall thickness (Teijin, Ltd., Japan). The 120 fibers provided 0.018 m² surface area. H₂ gas (~99.9%) was supplied to both ends of the fiber bundle at a pressure controlled by a pressure regulator. A peristaltic recycling pump (Masterflex®, USA) was set at 50 mL/min to mix the water in the reactor, and the sampling point was along the pumping tube.

All solutions were prepared using analytical-grade reagents (Millipore Sigma, USA) and Millipore ultra-pure water (specific conductivity of 18.2 MΩ). The synthetic DBP water for batch tests and continuous operation was made with 33 mg/L NaCl (imitating low Cl− level in tap and raw water), 1 mM KH₂PO₄, 1 mM Na₂HPO₄ (as buffer with initial pH~7.2), and the CAAs (concentration depended on the experiment) dissolved in ultra-pure water. The synthetic DBP water used for pH-controlled batch tests was buffered with a 10-mM KH₂PO₄ plus NaOH to fix the pH at 3, 5, 7, 9 and 11. The pH changes during all batch and continuous operation were less than 0.3 units.

2.2. In situ deposition of PdNPs on the H₂-transfer membranes

We deposited PdNPs on the H₂-transfer membrane using an in situ reduction method. We first filled the reactor with an Na₂PdCl₄ solution of 0.1 to 5 mM. We then turned on the H₂ supply with a pressure of 10 psig (1.69 atm absolute pressure) and started the recirculation pump. Autocatalytic reduction of Pd⁴⁺ to PdNPs occurred directly on the membranes, and complete reduction and deposition required 6 to 12 h. The initial Pd⁴⁺ concentration affected the duration of the reduction and deposition process; details of the duration for different initial Pd⁴⁺ concentration are listed in Supplementary Material Table S1. Fig. 1B shows how the
solution turned from dange to clear, while the membranes became black due to the coated PdNPs. Fig. 1C shows the membranes coated with different surface loadings of PdNPs. Aqueous-phase measurement of Pd$^{2+}$ gave negligible concentration at the end of the reduction and deposition period. We washed the reactor twice with deionized water to remove any suspended PdNPs and residual Pd$^{2+}$.

2.3. Characterization of the membrane-supported PdNPs

After depositing PdNPs on the membrane surface, we used a scalpel to cut off 2 or 3 fiber pieces, each 0.5 to 1 cm long, for solid-state characterization. We employed scanning transmission electron microscopy (STEM; JEM-ARM200F), transmission electron microscopy (TEM; Philips CM 12), and energy dispersive X-ray microanalysis (EDX) coupled with STEM to characterize the membrane coatings. The chemically flexed fibers were sectioned using a Leica Ultracut-R microtome at 70 nm thick for the TEM and STEM analysis. Details of chemical fixation are described by Zhou et al. (2014).

2.4. Batch and continuous tests

For each batch test, we purged the MPR with pure N$_2$ gas for 15 min before filling the MPR with synthetic medium containing DBP. All batch kinetic tests were conducted in triplicate using three individual H$_2$–MPRs with the same conditions. Except for batch tests using different PdNP loading and H$_2$ pressure, all the batch tests were conducted with MPR coated from a solution of 1 mM Pd$^{2+}$ and supplied with 3 psig H$_2$. In continuous operation, the same synthetic medium was fed into the MPR using a peristaltic pump with a constantly controlled flow rate. In order to evaluate any impacts of other constituents in the water, we used tap water (Tempe AZ, USA) to make synthetic medium (instead of ultrapure water) in the final stage. The tap water had Total Dissolve Solids (TDS), Hardness, and Dissolved Organic Carbon (DOC) concentrations of 560 mg/L, 250 as mg CaCO$_3$/L and 1.6 mg/L, respectively. Effluent water samples were collected and measured every day after filtration through 0.22-μm polyvinylidene difluoride syringe filter. When the effluent concentrations of all the substrate and the products were stable for three days (a variability less than 5%), we considered the MPR reached the steady state.

2.5. Analytical methods

All aqueous samples for TCAA, DCAA, MCAA, AA, and chloride were first filtered through 0.22-μm polyvinylidene difluoride syringe filter and then quantified using anionic chromatography (IC) (Metrosep 930 Compact IC). The IC had a Metrosep A supp 5 –250/4.0 column and an eluent of 1 mM sodium bicarbonate (NaHCO$_3$) and 3.2 mM sodium carbonate (Na$_2$CO$_3$) with a flow rate of 0.7 ml/min. The detection limits of TCAA, DCAA, MCAA, AA, and chloride were 15, 15, 10, 10, and 3 μg/L, respectively.

To verify the actual PdNPs loading on membrane polymer, an entire bundle of fiber membranes coated with PdNPs was dissolved through microwave-assisted total digestion (Luo et al., 2020) at the end of catalysts loading batch tests. An inductively coupled plasma mass spectrometry (ICP-MS; PerkinElmer NexION® 1000) was used to measure the Pd concentration of digested Pd solutions and effuents taken during continuous operation.

2.6. Kinetic modeling

Assuming that the reductions of TCAA, DCAA, and MCAA occurred independently, we set up three reactions (Eqs. (1), (2), and (3), respectively) to simulate the reactions occurring in the H$_2$–MPR:

$$\text{C}_2\text{H}_5\text{O}_2\text{Cl}_2 + (a + 2b + 3c)\text{H}_2 \rightarrow \text{aC}_2\text{H}_2\text{O}_2\text{Cl}_2 + \text{bC}_2\text{H}_3\text{O}_2\text{Cl} + \text{c}\text{H}_2\text{O}_2 + (a + 2b + 3c)\text{HCl}$$

(1)

$$\text{C}_2\text{H}_5\text{O}_2\text{Cl}_2 + (d + 2e)\text{H}_2 \rightarrow \text{dC}_2\text{H}_2\text{O}_2\text{Cl} + \text{eC}_2\text{H}_4\text{O}_2 + (d + 2e)\text{HCl}$$

(2)

$$\text{C}_2\text{H}_5\text{O}_2\text{Cl} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2\text{O}_2 + \text{HCl}$$

(3)

In Eq. (2), a, b and c represent the reaction selectivities of TCAA reduction to DCAA, MCAA, and AA, respectively. In Eq. (3), d and e represent the reaction selectivities of DCAA reduction to MCAA and AA, respectively. All reaction rates followed first-order kinetics, Eqs. (4)-(7), with first-order rate constants $k_1$, $k_2$ and $k_3$ obtained from the bath tests with TCAA, DCAA or MCAA as the sole reactant.

$$\frac{d[\text{TCAA}]}{dt} = - k_1[\text{TCAA}]$$

(4)

$$\frac{d[\text{DCAA}]}{dt} = ak_1[\text{TCAA}] - k_2[\text{DCAA}]$$

(5)

$$\frac{d[\text{MCAA}]}{dt} = bk_1[\text{TCAA}] + dk_2[\text{DCAA}] - k_3[\text{MCAA}]$$

(6)

$$\frac{d[\text{AA}]}{dt} = ck_1[\text{TCAA}] + ek_2[\text{DCAA}] + k_3[\text{MCAA}]$$

(7)

Then, the first-order rate constants were used as independent parameters to calculate product selectivity using the results of TCAA-dechlorination batch tests.

The model, used to calculate the first-order rate constants and product selectivities, was executed in MATLAB 7.0. The sum of squared relative residual (SSRR) (Cristóvão et al., 2009) was used to assess the goodness of fit between the model results and the experimentally measured values (Supplementary Material, Table S2):

$$\text{SSRR} = \sum_{i=1}^{n} \left( \frac{S_{\text{m},i} - S_{\text{e},i}}{S_{\text{e},i}} \right)^{2}$$

(8)

where n is the number of samples in the experiments, and $S_{\text{m},i}$ and $S_{\text{e},i}$ are component concentrations in the model and experiment, respectively.

2.7. Specific activity, selectivity, and statistical analyses

The catalyst-specific activity (L/g Pd-min) was calculated by dividing the first-order rate constant (1/min) by the Pd loading (g Pd/L: the weight of PdNPs coated on membrane divided by the reactor working volume). Catalyst-specific activity is a commonly metric of the kinetics of PdNPs-catalyzed reactions (Fritsch et al., 2003; Nutt et al., 2006). The product selectivity was calculated by dividing the product concentration (at the end of batch tests or in the effluent) with the reactant concentration (at the beginning of batch tests or in the influent). All error bars in the figures represent the standard deviation of the triplicate results from three individual reactors.

3. Results and discussion

3.1. Characterization by electron microscopy

PdNPs coated on the membrane (with initial Na$_2$PdCl$_4$ concentration of 1 mM) were characterized using TEM and STEM coupled
with EDX. Fig. 2A is TEM micrograph of a nonporous polypropylene membrane coated with PdNPs (in the ellipse). We analyzed 94 nanoparticles, from the selected region shown in Fig. 2B, to obtain the particle-size distribution (Fig. 2C) and the EDX spectrum (Fig. 2D). Coated PdNPs displayed an average size of 2.6 nm, with the average particle-size ranging from 1.2 nm to 4.2 nm when the initial Na₂PdCl₄ concentration used for coating increased from 0.1 mM to 5.0 mM. Our previous work (Luo et al., 2020; Zhou et al., 2017) analyzed the particle size of PdNPs and confirmed that the particle size was uniformly distributed on the same coated membrane. Although several clusters of PdNPs can be observed in Fig. 2B, none of them were aggregated together; the coated PdNPs were well dispersed, suggesting that the coating process did not directly lead to particle aggregation. The EDX spectrum in Fig. 2C indicates a high purity of elemental Pd, since EDX signals corresponding to palladium oxides or other oxidized-palladium species were absent (EDX detection limit = 2%). The particle-size distribution (Fig. 2C) and EDX spectrum (Fig. 2D) confirm that small-size PdNPs well successfully coated on the membranes of the H₂–MfPR.

### 3.2. Kinetics of CAAs catalytic dechlorination

#### 3.2.1. Experimental results

To investigate the reaction pathways and product selectivity, we conducted batch tests with TCAA, DCAA, or MCAA as the individual reactant. Fig. 3A shows that 98% of 0.95 mM TCAA was removed in 45 min, while DCAA, MCAA, and AA were produced simultaneously. The concentration of produced DCAA decreased to below the detection limit (15 μg/L) within 150 min. At the end of the batch test, 0.90 mM AA was produced as the main product, along with 0.05 mM MCAA as a minor byproduct. The mass balances of acetic acid and chlorine closed at the end of the batch test (Supplementary Material, Figure S1).

When 1.06 mM DCAA was added to the reactor as the sole reactant (Fig. 3B), 99% removal of DCAA was achieved within 90 min. At the end of the batch test, 0.24 mM MCAA and 0.75 mM AA were produced as final products. In the batch tests for MCAA (Fig. 3C), only 13% of MCAA was reduced to AA in 180 min. When no H₂ was supplied to the membrane, neither reaction nor adsorption of
TCAA, DCAA, or MCAA occurred (Supplementary Material, Figure S2).

The reductive dechlorinations of TCAA, DCAA, and MCAA were well-represented by first-order reaction kinetics, and their rate constants were 0.08, 0.06, and 0.0015 min\(^{-1}\). These values convert to PdNP-specific catalytic activities of 7.5, 5.6, and 0.1 L/g Pd-min, respectively.

The batch-test results with different CAAs reveal that parallel and stepwise reactions happened during TCAA reductive dechlorination. Clear examples of parallel reactions are that TCAA reduction yielded DCAA and AA from the beginning, while DCAA reduction yielded MCAA and AA from the beginning. Stepwise reaction is illustrated by the lag in MCAA production from TCAA due to the need to accumulate DCAA first.

3.2.2. Modeling based on first-order reactions

The reaction selectivity values \(a, b, c, d,\) and \(e\) were estimated using the experimental data from the batch tests of TCAA reductive dechlorination and the first-order rate coefficient reported in the preceding section. The best-fits values were 0.25, 0.01, 0.74, 0.28
and 0.72, respectively, and the model lines in Fig. 3 show that they represented the results well, although DCAA had systematic error for part of the TCAA experiment. The calculated reaction selectivity reveals that only 1% of TCAA was converted to MCAA during parallel reactions of TCAA reduction, while 25% of TCAA was converted to DCAA and subsequently reduced to 28% MCAA and 72% AA; this reinforces the stepwise reaction of TCAA to AA.

The relatively poor fit for DCAA in the TCAA experiment probably was a result of an over-estimation of the first-order rate constants of DCAA reductive dechlorination \((k_2)\). This may have been caused by competition between TCAA and DCAA for the adsorption site on PdNP surface available to catalytic reduction; thus, the DCAA-reduction rate may have been lower than \(k_2\) during the TCAA batch tests. Our model does not account for competition for the adsorption sites on PdNPs. Competition would be a fruitful topic for future experimental and modeling study.

### 3.3. Pathways of TCAA dechlorination

Based on the kinetic results and modeling, we propose the TCAA-transformation pathways in Fig. 4. Pd-catalyzed reductive dechlorination of TCAA follows the Langmuir-Hinshelwood (LH) mechanism, in which adsorption of the reactants to Pd is the first step (Wu et al., 2018). In the \(H_2/\)MPR, \(H_2\) diffusing from the hollow fiber membranes adsorbs to the coated PdNPs, without any bubble formation. The adsorbed \(H_2\) molecules dissociate to become active \(H^*_{ads}\) atoms (Eq. (9)), which are very powerful reductive agents for replacing the chlorines of the CAAs (Jewell and Davis, 2006; Lien and Zhang, 2007). Dissolved TCAA also adsorbs onto the Pd\(^0\) surface and dissociates to form Pd-C bonds (Eq. (10)). The direct interaction of the Pd-C bonds with an active \(H^*_{ads}\) atom leads to stepwise Cl\(^-\) release and reduction of the C all the way to AA (Eqs. (11)-(13)) (Zhou et al., 2010).

\[
Pd + H_2 \rightarrow (H_2)_{ads} + \text{Pd} \rightarrow 2(H^*_{ads}) - \text{Pd}
\] (9)

\[
Pd + C_2O_2Cl_2 \rightarrow (C_2O_2Cl_2)_{ads} - \text{Pd}
\] (10)

\[
(C_2O_2Cl_2)_{ads} - \text{Pd} + 2(H^*_{ads}) - \text{Pd} \rightarrow (C_2H_2O_2Cl)_{ads} - \text{Pd} + Cl^- + H^+
\] (11)

\[
(C_2H_2O_2Cl)_{ads} - \text{Pd} + 2(H^*_{ads}) - \text{Pd} \rightarrow (C_2H_2O_2)_{ads} - \text{Pd} + Cl^- + H^+
\] (12)

\[
(C_2H_2O_2)_{ads} - \text{Pd} + 2(H^*_{ads}) - \text{Pd} \rightarrow (C_2H_2O)_{ads} - \text{Pd} + Cl^- + H^+
\] (13)

The direct delivery of \(H_2\) through the membrane maintains a high surface site density of active \(H^*_{ads}\) atoms, and this reduces the possibility of DCAA and MCAA desorption before they are dechlorinated, which maximizes product selectivity to the desired AA.

### 3.4. Effective conditions for TCAA dechlorination rate and product selectivity

#### 3.4.1. Effect of catalysts loading

The solution concentration of Na\(_2\)PdCl\(_4\) during PdNP coating controlled the catalyst loading on the membrane surface. In situ reduction and deposition indicated nearly 100% transfer of Pd\(^2+\) to deposited Pd\(^0\). Subsequent washing led to a loss of about 10% of the Pd\(^0\), determined by measurement of Pd after digestion of the membrane bundles. Therefore, we used 90% of loss of Pd\(^2+\) from solution to compute the Pd\(^0\) loading on the membrane surfaces; the PdNP surface loadings were 2.1, 10.4, 20.6, 40.8, and 100.2 mg Pd/m\(^2\). We used those Pd\(^0\) loadings to investigate the impact of catalyst loading on the reaction rate, catalyst-specific activity, and product selectivity in batch experiments. The results are in Fig. 5.

For kinetics, the first-order reaction rate constant for TCAA reduction (Fig. 5A) increased from 0.03 min\(^{-1}\) to 0.08 min\(^{-1}\) when the surface loading increased from 2 to ≥ 20 mg Pd/m\(^2\), but the catalyst-specific activity steadily decreased with higher Pd loading up to 100 mg Pd/m\(^2\). However, product selectivity to AA increased with higher surface PdNP loading. Among the different
catalyst surface loadings, 20 mg Pd/m² had the best balance of efficient TCAA removal, selectivity to AA, and the lowest catalyst loading. With lower loading, the coverage of catalysts was insufficient to support fast removal, while higher loading of PdNPs led to aggregation that led to lower PdNP-specific catalytic activity. The PdNPs in the H₂-MPR displayed catalytic-specific activity for dechlorination similar to suspended PdNPs, but 2 to 3 orders of magnitude higher compared with other immobilized PdNPs (El-Sharnouby et al., 2018; Lien and Zhang, 2007; Šrebowata et al., 2016; Zhou et al., 2010).

### 3.4.2. Effects of H₂ pressure and initial TCAA concentration

The H₂ pressure in the hollow-fiber membrane controls H₂ delivery capacity to the catalysts (Tang et al., 2012). Increasing the H₂ pressure from 3 to 12 psig (Fig. 5B) did not affect the catalyst-specific activity or the product selectivity. This reveals that H₂ pressure as low as 3 psig (or 1.2 atm absolute pressure) was sufficient to deliver enough H₂ to support TCAA reductive dechlorination. The lowest H₂ gas pressure we used was limited by the range of our pressure regulator. Future work could achieve lower H₂ pressure by mixing H₂ with N₂.

Decreasing the initial TCAA concentration from 1 mM to 0.01 mM (Fig. 5C) led to a small decrease in the catalyst-specific activity, from 7.7 to 6.6 L/g Pd-min, but the product selectivity to MCAA decreased from 6.7% to 1.6%. The results in Figs. 5B and 5C suggest that a higher H₂-to-TCAA ratio enhanced product selectivity to AA. Also, the efficient direct delivery of H₂ to the PdNPs enabled the relatively lower product selectivity to MCAA, compared with other reductive methods (Aslani et al., 2017; Liu et al., 2017; Mao et al., 2018).

### 3.4.3. Effects of pH on CAAs dechlorination

Batch tests were conducted to investigate the effect of pH on the dechlorination of TCAA (Fig. 5D). With TCAA as the only reactant, increasing the pH from 3 to 11 greatly raised the catalyst-specific activity from 2.4 to 12.9 L/g Pd-min, but product selectivity to MCAA increased from 5.1% to 22.7%. DCAA also remained for pH 3 and 5 because of the low reaction rate. Similar pH effects also occurred when DCAA or MCAA was the only substrate (Supplementary Material, Figure S3 A&B).

Based on the proposed dechlorination pathway, we hypothesize that the simultaneous increase of catalyst-specific activity and product selectivity to MCAA was caused by a higher desorption rate of partially dechlorinated products at high pH. A higher pH promotes the ionization of adsorbed CAAs (e.g. (C₂H₄O₂Cl⁻)ads – Pd), which increases electrostatic repulsion that accelerates the
desorption of products without further dechlorination. In addition, the higher desorption rate opens up more active catalytic sites, which leads to a faster turnover rate. Since the concentration of reactants (CAAs in the liquid and H2 from the membrane) was much higher than the active catalytic site density on the surface of coated PdNPs, the faster turnover rate should have accelerated the catalytic reduction of TCAA at higher pH.

3.4.4. Effects of initial chloride concentration on CAAs dechlorination

Increasing the initial chloride concentration from 20 to 300 mg/L (Fig. 5E) did not affect the catalyst-specific activity of TCAA reduction. However, the product selectivity to MCAA increased from 6.7% to 11.3% with higher initial chloride concentration. In contrast to TCAA, higher chloride concentration inhibited the reductive dechlorination of DCAA and MCAA (Figure S3 C&D) and led to decreases of the catalyst-specific activity from 5.6 and 0.2 L/g Pd-min to 4.8 and 0.02 L/g Pd-min, respectively. Chloride ion in aqueous phase may compete with DCAA and MCAA for adsorption onto the surface of coated PdNPs, which would lead to a higher selectivity to MCAA and to inhibition of the DCAA reductive dechlorination.

3.5. Long-term continuous dechlorination

Fig. 6A presents the effluent concentrations of TCAA, DCAA, MCAA, and AA during the 50-day continuous test of TCAA reductive dechlorination in the H2−MPFR. Table 1 summarizes the performance results at steady-state for each stage. The effluent concentration of TCAA was always below the detection limit (15 μg/L), with the product selectivity to AA always greater than 90% during continuous operation. From stage I to III, when the influent concentration of TCAA was decreased from 15 mg/L to 1 mg/L, the steady-state average effluent concentration of DCAA and MCAA decreased from 200 μg/L and 309 μg/L to 39 μg/L and <5 μg/L, respectively. With the TCAA concentration of 1 mg/L, a value close to practical raw water contamination (Pressman et al., 2010; Yeh et al., 2014), the sum of effluent concentrations of CAAs was 40 μg/L below the U.S. EPA MCL of 60 μg/L for the sum of five haloacetic acids (Calafat et al., 2003; Krasner et al., 2006). When the hydraulic retention time (HRT) was reduced to 6 and 4 h in stages IV and V, the sums of CAAs were 58 μg/L and 82 μg/L. In stage VI, when the medium was made in tap water instead of ultrapure water, TCAA removal and CAAs in the effluents were similar compared to stage IV, which indicates that other constituents in tap water had no impact on TCAA reductive dechlorination. The results reveal that, for practical applications, the HRT of the bench-scale H2−MPFR can be as low as 6 h to achieve the MCL requirement, and this corresponds to a surface loading of 4.1 mg TCAA/m²/d.

Fig. 6B, which presents the effluent concentrations of Pd, reveals that the average total palladium (Pd²⁺ + Pd⁰) concentration in the effluent was about 2.4 μg/L. This corresponds to a cumulative loss of Pd less than 4% of coated PdNPs on membrane over the 50-day continuous test, and it documents minimal loss of PdNPs during long-term continuous operation of the H2−MPFR.

Finally, we compare reactor performance of the H2−MPFR with other catalytic and electrochemical reactors in Table S3, which shows that the H2−MBFR offers competitive reaction kinetics for TCAA dechlorination and better product selectivity towards acetic acid.

![Fig. 6](image-url)
4. Conclusion

The H₂–MPR, featuring in-situ-coated PdNPs, reductively dechlorinated TCAA with high catalyst-specific rates and high selectivity to AA. Controlling the H₂-delivery capacity by the H₂ pressure in the fiber membrane lumen enabled efficient and safe H₂ supply to the PdNPs at rates required for reductive dechlorination. Over 50-days of continuous operation, an H₂–MPR coated with 20 mg Pd/m² and supplied with 3 psig H₂ achieved greater than 99% removal of 1 mg/L TCAA, with minimal formation of DCAA and MCAA (below U.S. EPA MCL for the five halocarbons). Sustained continuous TCAA removal and high selectivity to AA support that the H₂–MPR is promising as a reliable catalytic reactor for removing chlorinated DBPs in practice. Compared to other processes for TCAA removal, the H₂-based MPR offers these benefits: simple design and operation based on the in-situ PdNP coating and membrane-based H₂ supply; H₂ gas as the only reactant; sustainable continuous operation; and AA as the major product.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the generous donations from the Swettle Family Endowment, the National Science Foundation (EEC-1449500) Nanosystems Engineering Research Center on Nanotechnology-Enabled Water Treatment, the Nanotechnology Collaborative Infrastructure Southwest (NNCI-ECCS-1542160), and ASU’s Fulton Chair of Environmental Engineering. We gratefully acknowledge the use of electron microscopic facilities supervised by Mr. David Lowry in the School of Life Science, and by Mr. Karl Weiss and Dr. Manuel Roldan Gutierrez in the LeRoy Eyring Center for Solid State Science, both at Arizona State University. Yuhang Cai also gratefully acknowledges the financial support from China Scholarship Council (No. 201906680800).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.watres.2021.116841.

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