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### Water Research



# A kinetic model for 2,4-dichlorophenol adsorption and hydrodechlorination over a palladized biofilm

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#### ABSTRACT

Adsorption and catalytic hydrodechlorination (HDC) of aqueous 2,4-DCP by palladium nanoparticles ( $Pd^{0}NPs$ ) associated with a biofilm (i.e., a  $Pd^{0}$ -biofilm) was investigated in terms of the removal efficiency of 2,4-DCP, dechlorinated product selectivity, and reduction kinetics. Experiments were executed with  $Pd^{0}$ -biofilm and with abiotic  $Pd^{0}NPs$ -film alone. The 2,4-DCP-adsorption capacity of  $Pd^{0}$ -biofilm was 2- to 5-fold greater than that of abiotic  $Pd^{0}NPs$ -film, and the adsorption accelerated dechlorination by  $Pd^{0}$ -biofilm, including selectivity to phenol instead of mono-chlorophenols. A mechanistic kinetic model was developed to represent the sequential adsorption and reduction processes. Modeling results represented well the removal of 2,4-DCP and quantified that  $Pd^{0}$ -biofilm had a strong affinity for adsorbing 2,4-DCP. The strong adsorption increased the volume-averaged concentration of 2,4-DCP concentration of 2,4-DCP led to a 2- to 4-fold increase in the reduction rate of 2,4-DCP removal and full dechlorination despite its low concentration in bulk water.

#### 1. Introduction

Because of its large-scale production and broad applicability, 2,4dichlorophenol (2,4-DCP) is one of the most common chlorophenols in aquatic environments (Gao et al. 2008, Gonzalez et al. 2012, House et al. 1997). 2,4-DCP also is an emerging disinfection by-product (DBP) in chlorinated swimming-pool water (Xiao et al. 2012) and tap water (Lin 1982, Tang and Huang 1996, Zhang et al. 2005), with concentrations reaching up to  $2.2 \pm 0.3 \text{ mg} \text{eL}^{-1}$ . Due to its cytotoxicity, carcinogenicity, and slow biodegradation, the U.S. Environmental Protection Agency (EPA) lists 2,4-DCP as a priority pollutant and has set a maximum contaminant level (MCL) of 0.1 mg $\text{eL}^{-1}$  for drinking water (U. S. EPA, 2012).

Since the C-Cl bond makes chlorinated organics stable and persistent (Ding et al. 2018, He et al. 2018, Long et al. 2021), dechlorination of 2, 4-DCP is an effective method to initiate detoxification of 2,4-DCP. Catalytic hydrodechlorination (HDC) by precious-metal catalysts is a promising approach for dechlorination, because hydrogen gas (H<sub>2</sub>) is the

sole chemical input required and HDC has fast kinetics, mild operating conditions, and no secondary waste stream (Luo et al. 2021, Zhou et al. 2021a). The mechanism of HDC is based on having atomic hydrogen (H\*), which is generated on the catalyst's surface by homolytic cleavage of adsorbed H<sub>2</sub>. H\* is activated and able to replace Cl in chlorinated organics (Fu et al. 2019). Elemental palladium (Pd<sup>0</sup>) is the most studied catalyst due to its great H<sub>2</sub>-absorption capacity and ability to form H\* (Chaplin et al. 2012).

Despite its advantages, conventional  $Pd^0$ -catalytic dechlorination has been thwarted by two challenges: The first challenge is poor efficiency of H<sub>2</sub> supply due to its low water solubility, which limits reduction kinetics and also can create safety concerns if it off-gases (Zhou et al. 2019). The second challenge is low catalyst longevity due to losses. In practical application,  $Pd^0$  nanoparticles ( $Pd^0NPs$ ) are immobilized on packed supports (Cantillo and Kappe 2014, Greco et al. 2015) or structured interfaces (Marks et al. 2019, Wang et al. 2018) having large surface areas that allows high activity. Because of the fine structure and large contact surface with liquid, these catalysts are liable to mechanical

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shedding (Wang et al. 2018) and/or chemical leaching (Cantillo and Kappe 2014, Greco et al. 2015). Moreover, preparing and stabilizing these catalysts commonly require environmental unfriendly and energy-consuming steps (Zhou et al. 2021a). Another approach to enhance HDC performance is to take advantage of catalyst's adsorption capacity, studies have confirmed that adsorption affects catalyst reactivity. For example, Pd<sup>0</sup> supported on granular activated carbon by cetyltrimethylammonium bromide functionalization (Zhou et al. 2021b) gave strong adsorption of 2,4-DCP that dramatically accelerated HDC rates. However, the effect of adsorption of reactants onto Pd-based catalysts has received rare attention, and process of sequential adsorption and reduction over Pd-based catalysts has not been clear.

The H<sub>2</sub>-delivery challenge can be overcome by adapting the H<sub>2</sub>based membrane biofilm reactor (MBfR), which efficiently delivers H<sub>2</sub> to biofilms growing in bubble-free gas-transfer membranes (Lee and Rittmann 2002). In particular relevance here, the H<sub>2</sub>-based MBfR was used for *in-situ* generation of Pd<sup>0</sup>NPs that spontaneously accumulated within the biofilm (i.e., a Pd<sup>0</sup>-biofilm) (Zhou et al. 2016a) and exhibited stable catalytic activity for long-term HDC of *para*-chlorophenol (Long et al. 2021) and 2,4-DCP (Wu et al., 2022). In addition, biomass can adsorb 2, 4-DCP (Gao and Wang 2007, Kennedy et al. 1992, Ning et al. 1996, Wu and Yu 2006), which may enhance its susceptibility to hydrodechlorination, while kinetics of coupled adsorption and catalytic HDC processes over Pd<sup>0</sup>-biofilm have not been studied. Creating a partnership among H<sub>2</sub>-delivery membranes, biofilm, and Pd<sup>0</sup>NPs in a Pd-containing MBfR offers promises for safe, cost-effective, and sustainable HDC.

We evaluated a H<sub>2</sub>-based, palladized membrane biofilm reactor (i.e., a Pd-MBfR) for continuous HDC of 2,4-DCP. Experimentally, we assessed the kinetics of adsorption and reduction, and we documented the primary transformation pathway of 2,4-DCP in the Pd-MBfR. The central feature of this work was a coupled adsorption and reduction model that we use to illuminate and quantify the mechanisms underlying HDC of 2,4-DCP in the Pd-MBfR.

#### 2. Materials and methods

#### 2.1. Reactor figuration, inoculation, and feeding

We operated in parallel two reactors of the same dual-tube configuration (illustrated in Fig. S1, Supporting Information) as in a previous work (Wu et al. 2021). Each reactor contained a main bundle of 32 nonporous polypropylene hollow-fiber membranes (200-µm outer diameter, 100-110-µm inner diameter, Teijin, Japan) in one column, and a coupon bundle of 10 identical fibers used as sampling in the other column. The reactor had a total membrane surface area of 54 cm<sup>2</sup> with a working volume of 65 mL. Pure H<sub>2</sub> gas was supplied to fiber bundles at different pressures controlled by a pressure regulator, and it diffused through the fiber walls in a bubble-free manner. A solute's concentration in reactor was well mixed by a recirculation rate of 150 mL•min<sup>-1</sup> provided by a peristaltic pump (Longer 1515X, China). The temperature was maintained at  $25 \pm 2^{\circ}$ C.

We inoculated one of the reactors with anoxic sludge from Wusong wastewater treatment plant (Baoshan, Shanghai) and fed the reactor continuously with a 0.5-mM NO<sub>3</sub><sup>-</sup> medium to accumulate biofilm on the membranes. After two months, mature biofilms formed in this MBfR. The detail of inoculation and feeding were described in our previous work (Wu et al. 2022).

#### 2.2. Synthesis of $Pd^0NPs$ supported on $H_2$ -transfer membranes

We introduced 0.8 mM Pd(II) (as Na<sub>2</sub>PdCl<sub>4</sub>) into the MBfR in batch mode with the H<sub>2</sub> pressure of 20 psig (2.3 atm) to produce biogenic Pd<sup>0</sup>NPs within the biofilm (Pd<sup>0</sup>-biofilm). The composition of the Pd(II)containing medium is provided in Wu et al. (Wu et al. 2022). The Pd<sup>0</sup>-deposition process was carried out three times (each batch lasted 2 days) until a dark  $Pd^0$ -biofilm formed on the fibers and > 99% of the soluble Pd(II) was immobilized after each addition. The biofilm retained 32.8 mg total  $Pd^0$  or 6.07 g  $Pd^0/m^2$ .

Another membrane catalyst-film reactor (Zhou et al. 2021a) (MCfR, the same configuration as in the Section 2.1) was used to prepare an abiotic  $Pd^0NPs$ -film following the same methods, but without a biofilm. Strictly auto-catalytic reduction of Pd(II) led to the deposition 35.6 mg  $Pd^0$  or 6.59 g  $Pd^0/m^2$  directly on the H<sub>2</sub>-transfer membrane.

#### 2.3. Sample collection and characterization

To characterize  $Pd^0NPs$  deposited on the membranes, we collected ~5-cm-long sections from coupon fibers. After chemical fixation and ultra-microtome slicing, following the method described in a previous work (Wu et al. 2021), these fiber sections were analyzed using transmission electron microscopy (TEM, Hitachi H-7650, Japan) and high-resolution electron microscopy (HRTEM; FEI F20, The Netherlands) coupled with energy-dispersive X-ray (EDX) spectroscopy. We separated solids form fibers in the Pd-MBfR and the MCfR and then immediately freeze-dried them for subsequent X-ray diffraction (XRD) using an X' Pert PRO MPD diffractometer with Cu- K $\alpha$  radiation.

#### 2.4. Sampling and analyses

Liquid samples taken from the sampling ports of the reactors were immediately filtered through 0.22-µm polytetrafluoroethylene syringe filters. The Pd(II) concentration was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES; Agilent 720ES, USA). We measured the filtered samples for 2,4-DCP, *ortho*-chlorophenol (2-CP), *para*-chlorophenol (4-CP), phenol, and cyclohexanone using a highperformance liquid chromatography with an Agilent C18 column (HPLC, Shimadzu LC-20A, Japan). Cl<sup>-</sup> was quantified by an ion chromatograph (IC; Dionex Aquion, USA) with an AS-19 column. pH and DO was measured using a multi-Parameter Meter (HACH HQ40d, USA).

#### 2.5. Adsorption experiments

For batch adsorption experiments performed in the Pd-MBfR and the MCfR, the H<sub>2</sub> supply was replaced with N<sub>2</sub>, and the medium was replaced by 65 mL of fresh medium contained 2,4-DCP at a target concentration (10, 20, 30, 40, 50, or  $60 \mu$ M). This medium was prepared by adding a 5-mM 2,4-DCP stock solution to the basic medium that had been purged with N<sub>2</sub> (Wu et al. 2022). Between each experiment, the reactors were rinsed with the basic medium in the continuous mode for 20 h (10 HRTs) to thoroughly remove adsorbed 2,4-DCP; no CPs was detected in the liquid by 20 h. During each batch experiment, we routinely measured the 2,4-DCP concentration in the liquid and computed the mass of adsorbed 2,4-DCP by difference. All adsorption experiments were conducted in triplicate.

#### 2.6. Adsorption-kinetics modeling

In the Pd-MBfR, Pd<sup>0</sup>-biofilm's adsorption of 2,4-DCP is described by:

$$2, 4 - DCP + Pd^{0} - biofilm \xrightarrow{k_{1}} 2, 4 - DCP_{ads} \cdots Pd^{0} - biofilm$$
(1)

and the formation rate of adsorbed 2,4-DCP from 2,4-DCP and  $Pd^0$ -biofilm is given by

$$\frac{\mathrm{d}C_{\mathrm{ads},t}}{\mathrm{d}t} = k_1 \left( C_{\mathrm{ads},0} - C_{\mathrm{ads},t} \right) C_t \tag{2}$$

where  $k_1$  is the rate constant of adsorption (L•µmol<sup>-1</sup>•min<sup>-1</sup>);  $C_t$  is the 2,4-DCP concentration in the liquid (µM);  $C_{ads,0}$  is saturated adsorption concentration of 2,4-DCP inside the biofilm (µM); and  $C_{ads,t}$  is the volume-averaged concentration of 2,4-DCP inside the biofilm (µM) at time *t* (min).

To obtain the saturated adsorption concentration ( $C_{ads,0}$ ), we represented the adsorption capacities of Pd<sup>0</sup>-biofilm for 2,4-DCP using the Langmuir isotherm:

$$Q_{\rm e} = \frac{Q_0 b C_{\rm e}}{b C_{\rm e} + 1} \tag{3}$$

where  $Q_0$  is the maximum adsorption density per unit of membrane surface area (µmol•m<sup>-2</sup>),  $Q_e$  is the equilibrium adsorption density on the membrane surface (µmol•m<sup>-2</sup>), b is the Langmuir equilibrium constant related to the energy of adsorption (L•µmol<sup>-1</sup>), and  $C_e$  is the equilibrium solute concentration (µM). Since the adsorption experiments gave  $C_e$ and  $Q_e$  values, Eq. (3) could be solved for b and  $Q_0$  using non-linear fitting.

 $C_{ads,0}$  was derived from  $Q_0$ :  $C_{ads,0} = Q_0 \bullet S/V_f$ , where *S* is membrane surface area (54 cm<sup>2</sup>), and  $V_f$  is volume of the Pd<sup>0</sup>-biofilm (14.5 mL, measured at the completion of the experiments).  $C_{ads,t}$  in Eq. (2) could be eliminated as an independent variable by using the mass balance:  $C_{ads,t} \bullet V_f = (C_0 - C_t) \bullet V_w$ , where  $V_w$  is the working volume of the Pd-MBfR (50.5 mL). Then, to obtain  $k_1$ , we integrated Eq. (2) to give a relation-ship between  $C_t$  and time (min):

$$\frac{C_{ads,0} \cdot \frac{V_{t}}{V_{w}} - C_{0}}{C_{t} + C_{ads,0} \cdot \frac{V_{t}}{V_{w}} - C_{0}} = 1 - e^{-\left(C_{ads,0} \cdot \frac{V_{t}}{V_{w}} - C_{0}\right) \cdot k_{1} \cdot t} \cdot \frac{C_{0}}{C_{ads,0} \cdot \frac{V_{t}}{V_{w}}}$$
(4)

where  $C_0$  is the initial 2,4-DCP concentration ( $\mu$ M) in the liquid, and  $C_e$  is the 2,4-DCP concentration ( $\mu$ M) at equilibrium.

#### 2.7. Dechlorination experiments

A series of steady-state dechlorination experiments investigated the kinetics of 2,4-DCP reduction in the Pd<sup>0</sup>-MBfR and the MCfR. The experiments were organized into three series, summarized in Table 1. Prior to each substage, the reactor was returned to the baseline condition, which was the basic medium containing 100  $\mu$ M 2,4-DCP, 15 psig for H<sub>2</sub>, and 0.53 mL•min<sup>-1</sup> influent flow. Each substage lasted 8 HRTs, which was long enough for concentrations to reach steady state for the liquid phase. Replicate samples were collected at 6, 7, and 8 HRTs, and the results are presented as the average values  $\pm$  the standard deviation.

#### 2.8. Modeling for kinetics of a coupled adsorption and reduction process

Pd<sup>0</sup>-catalyzed hydrogenation reactions follow pseudo-first-order kinetics (Wang et al. 2013, Xu et al. 2016, Zhao et al. 2016). The reduction rate of adsorbed 2,4-DCP in a batch reaction for a Pd-MBfR is

$$-\frac{dC_{ads,t}}{dt} = k_{ap}C_{ads,t}$$
(5)

Table 1	
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System	operating	conditions	for	the	steady-state	e experiments
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Series	Substages	H <sub>2</sub> pressure (psig)	Flow rate (mL∙min <sup>-1</sup> )	HRT (h)	2,4-DCP (μM)
1	1-1	15	0.177	6	100
	1-2		0.265	4	
	1-3		0.53	2	
	1-4		1.06	1	
	1-5		1.53	0.7	
2	2-1	15	0.265	4	25
	2-2				50
	2-3				100
	2-4				135
	2-5				200
3	3-1	15	0.53	2	25
	3-2				50
	3-3				100
	3-4				135
	3-5				200

where  $k_{ap}$  denotes the apparent first-order rate constant (min<sup>-1</sup>).

In a continuous reactor at steady state, the adsorption rate of 2,4-DCP (Eq. (2)) equals its reduction rate (Eq. (5)):

$$k_1 (C_{\text{ads},0} - C_{\text{ads}}) C_{\text{eff}} = k_{\text{ap}} C_{\text{ads}}$$
(6)

where  $C_{\text{eff}}$  is the stable concentrations of 2,4-DCP in effluent ( $\mu$ M);  $C_{\text{ads},0}$  is the saturated concentration of 2,4-DCP in Pd<sup>0</sup>-biofilm ( $\mu$ M); and  $C_{\text{ads}}$  are the stable concentrations of 2,4-DCP in Pd<sup>0</sup>-biofilm ( $\mu$ M).

Rearranging Eq. (6) yields:

$$\frac{\left(C_{\text{ads},0} - C_{\text{ads}}\right)C_{\text{eff}}}{C_{\text{ads}}} = \frac{k_{\text{ap}}}{k_1} = K_{\text{m}}$$
(7)

The constant  $K_m$  ( $\mu$ M) is the ratio of reduction and adsorption rate constants. Solving Eq. (7) yields the concentration of the 2,4-DCP adsorbed in the Pd<sup>0</sup>-biofilm at steady state:

$$C_{\rm ads} = \frac{C_{\rm ads,0} \cdot C_{\rm eff}}{K_{\rm m} + C_{\rm eff}} \tag{8}$$

Then, the overall rate of 2,4-DCP removal in Pd<sup>0</sup>-biofilm is

$$=k_{\rm ap}C_{\rm ads} = \frac{k_{\rm ap}C_{\rm ads,0} \cdot C_{\rm eff}}{K_{\rm m} + C_{\rm eff}}$$
(9)

Eq. (9) describes the steady-state reaction rate once the product of  $k_{ap}$  and  $K_m$  are obtained, since  $C_{eff}$  is a readily measurable quantity.

If the 2,4-DCP concentration is high enough that the adsorption of 2,4-DCP by Pd<sup>0</sup>-biofilm is saturated (i.e.,  $C_{ads} = C_{ads,0}$ ), then the maximum reduction rate ( $r_m$ ) is:

$$r_{\rm m} = k_{\rm ap} C_{\rm ads,0} \tag{10}$$

Dividing Eq. (9) by Eq. (10) yields

$$r = r_{\rm m} \frac{C_{\rm eff}}{K_{\rm m} + C_{\rm eff}} \tag{11}$$

Eq. (11) quantifies the relationship between the 2,4-DCP concentration and the reaction rate in relation to the maximum rate, and it has a form similar to the *Michaelis-Menten* and *Monod* equations (Rittmann and McCarty 2020). Thus,  $r_m$  and  $K_m$  can be determined from measured  $C_{\text{eff}}$  and r values from a set of steady-state tests.  $C_{\text{eff}}$  is measured directly, and r is calculated according to the mass balance on 2,4-DCP:

$$r = \frac{Q(C_{\rm inf} - C_{\rm eff})}{V} \tag{12}$$

where *Q* is the influent flow of the reactor (mL•min<sup>-1</sup>);  $C_{inf}$  is the influent 2,4-DCP concentration ( $\mu$ M), and *V* is the reactor's liquid volume (mL).

The mathematical model can be used for design of the operation parameters. For a given influent, the influent flow rate (or HRT) required to meet the effluent concentration below MCL can be computed by simultaneously solving Eq. (11) and Eq. (12). The volumetric loading of 2,4-DCP ( $r_L$ ) is calculated with Eq. (13):

$$r_{\rm L} = \frac{QC_{\rm inf}}{V} \tag{13}$$

#### 3. Results and discussion

#### 3.1. Characterization of Pd<sup>0</sup>-biofilm and Pd<sup>0</sup>-film

The TEM images in Fig. 1 characterize the location, morphology, and size of  $Pd^0NPs$  generated in the Pd-MBfR and the MCfR. In  $Pd^0$ -biofilm, the  $Pd^0NPs$  were highly dispersed with a statistical average  $Pd^0$  crystallite size of  $4.6 \pm 0.7$  nm (based on 270 counts, Fig. 1c). Most  $Pd^0NPs$  were distributed in the extracellular polymeric substance (EPS) matrix, and some were on the bacterial cell surfaces (Fig. 1a). In  $Pd^0$ -film, the  $Pd^0$  crystallites aggregated into larger particles and formed a continuous



**Fig. 1.** TEM images of selected areas in cross sections of  $Pd^0$ -biofilm (a) and  $Pd^0$ -film (b). The grey shapes are bacterial cells, and the dark spots are  $Pd^0$ . HRTEM images of  $Pd^0$  crystallites in  $Pd^0$ -biofilm (c) and  $Pd^0$ -film (d) with embedded EDX spectra. XRD spectra of the solid powders collected from  $Pd^0$ -biofilm and  $Pd^0$ -film (e).

multi-layer film (Figs. 1b and 1d), with average size of  $13.1 \pm 1.3$  nm (150 counts). These results indicate that the biofilm in Pd<sup>0</sup>-biofilm stabilized smaller Pd<sup>0</sup>NPs, probably due to rapid encapsulation of PdNPs in the EPS at nucleation and initial surface growth, with the sizes maintained by electrostatic stabilization through extracellular proteins (Zhou et al. 2016b).

The presence of  $Pd^0NPs$  was confirmed by the EDX spectra (embedded figures in Figs. 1c and d), and the XRD spectra (Fig. 1e) confirmed that the nanoparticles were  $Pd^0$ : The XRD patterns exhibited the four distinct diffraction peaks of  $Pd^{\circ}$  crystal structure with dominant facets of (1 1 1):  $40.1^{\circ}$  (1 1 1),  $46.7^{\circ}$  (2 0 0),  $68.1^{\circ}$  (2 2 0), and  $82.1^{\circ}$  (3 1 1). The average sizes of the  $Pd^0$  crystallites estimated from the full width at half-maximum of the (1 1 1) facet were 3.8 and 16.2 nm for  $Pd^0$ -biofilm and  $Pd^0$ -film, respectively, which are similar to the statistical results from the TEM images.

#### 3.2. Adsorption kinetics and isotherms of 2,4-DCP

To describe the adsorption of 2,4-DCP to  $Pd^0$ -biofilm and  $Pd^0NPs$ , we conducted separate batch tests in which the initial 2,4-DCP concentration was 10, 20, 30, 40, 50, or 60  $\mu$ M. The patterns of 2,4-DCP concentrations, shown in Fig. S2, document that the adsorption capacity of  $Pd^0$ -biofilm was 2- to 5-fold larger than that of  $Pd^0$ -film, likely due to adsorption to the biofilm's cells and EPS caused by hydrophobic

interactions between 2,4-DCP and the biofilm's negatively charged components, which could be the protonation of carboxyl, phosphate, and hydroxyl functional groups (Benoit et al. 1998, Calace et al. 2002, Wang et al. 2002). It also is possible that the smaller Pd<sup>0</sup>NPs in the biofilm had greater adsorption capacity for 2,4-DCP.

A Langmuir isotherm using the  $Q_0$  and *b* values reported in Fig. 2 represented equilibrium adsorption well ( $\mathbb{R}^2$  value  $\geq 0.99$ ). Fig. 2 clearly shows that the adsorbed concentration in  $\mathbb{Pd}^0$ -biofilm reached saturation as the equilibrium concentration increased above about 15  $\mu$ M, and the saturation adsorption capacity was 174  $\mu$ mol•m<sup>-2</sup>, which indicates  $C_{ads,0}$  was 63.7  $\mu$ M.

The fitted lines in Fig. 3 show that the adsorption model for Pd<sup>0</sup>biofilm (Eq. (3)) represented the experimental results well (R<sup>2</sup> value  $\geq$  0.97 and no systematic errors). The best-fit value of  $k_1$  ranged from 0.0037 to 0.0043 L•µmol<sup>-1</sup>•min<sup>-1</sup>, with an average of 0.0039 L•µmol<sup>-1</sup>•min<sup>-1</sup>. Since the  $k_1$  range was small, using  $k_1$  for all experiments yielded almost equally good fits (not shown).

#### 3.3. Reductive dechlorination of 2,4-DCP

In continuous reduction experiments, we altered the 2,4-DCP loading by changing the influent flow rate or influent 2,4-DCP concentration. Fig. 4 presents the effluent concentration of CPs ( $C_{\text{eff}}$ ) and released Cl<sup>-</sup>. In general, increasing the 2,4-DCP loading rate decreased the 2,4-DCP



Fig. 2. Fitting of experimental adsorption capacity of 2,4-DCP on the  $Pd^0$ -biofilm using the Langmuir isotherms.



Fig. 3. Model-stimulated results for adsorption kinetics in the Pd-MBfR.

percentage removal in both reactors, but the influent flow rate had a stronger impact. Pd-MBfR always had greater 2,4-DCP removal. Fig. 4 also shows that Pd-MBfR had almost no monochlorphenols (MCPs, i.e., 2-CP and 4-CP), despite greater removal of 2.4-DCP, and effluent phenol concentrations also were lower that with the MCfR. Mass balance calculations showed 86-103% recovery of Cl input in 2,4-DCP, with most of the effluent Cl being in released Cl<sup>-</sup>. This confirms that 2,4-DCP was removed via catalytic dechlorination.

With the influent 2,4-DCP concentration of 25  $\mu$ M, an upper value of practical raw water contamination, the sum of effluent concentrations of CPs were 0.51 and 2.5  $\mu$ M for Pd-MBfR and MCfR, respectively (Fig. 4b). These results confirm that the Pd-MBfR can reduce 2,4-DCP in raw water to below the U.S. EPA MCL of 0.61  $\mu$ M with a high influent concentration of 25  $\mu$ M.

Fig. 5 summarizes the 2,4-DCP removals and product selectivities towards MCPs for different volumetric loading rates of 2,4-DCP. For the

Pd-MBfR, when the 2,4-DCP loadings increased from 0.1 to 0.5  $\mu mol \bullet L^{-1} \bullet min^{-1},$  the reduction rates proportionally increased, bringing about stable removals of > 95% and with no MCPs. In general, the accumulation of MCPs were relatively small in the both reactors because the first dechlorination was rate-limiting (Wu et al. 2021). However, the higher product selectivities to MCPs in the MCfR probably were caused by a relatively high desorption rate for the MCPs. Our previous study documented that 2,4-DCP processed a lager adsorption capacity and affinity for the Pd<sup>0</sup>NP surface, compared to that of 2-CP or 4-CP (Wu et al. 2022, Wu et al. 2021). A higher 2,4-DCP concentration intensified competitive adsorption of 2,4-DCP onto Pd<sup>0</sup>NP surface, which accelerated the desorption of MCPs without further dechlorination. Because the biofilm in Pd<sup>0</sup>-biofilm dispersed the Pd<sup>0</sup>NPs and maintained them with smaller sizes (discussed in Section 3.1), the contact surface for 2,4-DCP was larger, which minimized competitive adsorption. Moreover, MCPs released from the Pd<sup>0</sup>NP surface could be trapped in the biofilm and further dechlorinated.

## 3.4. Kinetics and mechanisms for multistep removal of 2,4-DCP in $Pd^{0}$ -biofilm

Distinct kinetic patterns, illustrated in Fig. 6, reveal that the removal of 2,4-DCP in the Pd-MBfR followed saturation kinetics. At 2,4-DCP concentrations below  $\sim$  5  $\mu$ M, the reduction rate increased almost linearly with 2,4-DCP concentration. As the 2,4-DCP concentrations increased, however, removal kinetics began to saturate and almost reached a plateau. Saturation kinetics of 2,4-DCP removal can be represented by Eq. (11). Fig. 6 shows the best-fit values of  $K_{\rm m}$  and  $r_{\rm m}$  ( $K_{\rm m}$  = 7.31 µM and  $r_m = 1.47$  µmol•L<sup>-1</sup>•min<sup>-1</sup>), which gave R<sup>2</sup> = 0.98 and no systematic errors. In contrast, the reduction rate of 2,4-DCP in the MCfR followed first-order kinetics ( $R^2 = 0.97$ ) up to about 36  $\mu$ M, at which point the kinetics rapidly saturated.  $K_{\rm m}$  reflects the affinity of the Pd<sup>0</sup>biofilm for 2,4-DCP, and the low value of  $K_{\rm m}$  (7.31  $\mu$ M) supports strong affinity for 2,4-DCP, which allows a rapid reduction rate for relatively low 2,4-DCP concentrations (< 20  $\mu$ M); the rate is 2- to 4-fold greater than in the MCfR for  $C_{eff} \leq 10 \, \mu\text{M}.$  This feature makes the Pd-MBfR wellsuited to treat waters with relatively low 2,4-DCP concentrations.

The 2,4-DCP reduction rates were proportional to the concentration of 2,4-DCP. An apparent first-order reduction-rate constant in the Pd-MBfR,  $k_{\rm ap} = 0.028 \ {\rm min}^{-1}$ , listed in Table 2 and calculated according to Eq. (7), was slightly smaller than  $k_1$  in the MCfR (0.033 min<sup>-1</sup>). The values of  $k_{\rm ap}$  and  $r_{\rm m}$  were then used to compute concentrations of adsorbed 2,4-DCP ( $C_{\rm ads}$ ) inside Pd<sup>0</sup>-biofilm by using Eq. (5). The calculated  $C_{\rm ads,0}$  (55.6  $\mu$ M) was not much lower than the fitted value of  $C_{\rm ads,0}$  from adsorption experiments (63.7  $\mu$ M), which also indicates the adsorption was a strong determinant of the reduction rate. Fig. 7a displays the quantitative relationship between  $C_{\rm ads}$  and  $C_{\rm eff}$ . The calculated  $C_{\rm ads}$  values were significantly higher than that the bulk-phase concentration of 2,4-DCP ( $C_{\rm eff}$ ) < 40  $\mu$ M. Therefore, adsorption of 2,4-DCP accelerated the kinetics of 2,4-DCP reduction by concentrating 2,4-DCP in Pd<sup>0</sup>-biofilm.

The reason for 2,4-DCP enrichment inside  $Pd^0$ -biofilm can be explained by relative kinetics. We calculated initial adsorption rates (Eq. (2)) and initial reduction rates (Eq. (5)) by letting  $C_{ads} = C_{eff}$ , and the calculated results for different 2,4-DCP concentrations are displayed in Fig. 7b. When  $C_{eff} < 47 \mu$ M, the adsorption rates exceeded the reduction rate, which resulted in the enrichment of 2,4-DCP in the Pd<sup>0</sup>-biofilm. The reduction rate matched the adsorption rate ( $C_{eff} \ge 47 \mu$ M) only when the adsorption rate saturated. This indicates that the overall kinetics were controlled by adsorption for most concentrations of 2,4-DCP. The calculated maximum reduction rate, 1.26  $\mu$ mol•L<sup>-1</sup>•min<sup>-1</sup>, almost equals the measured one (1.24  $\mu$ mol•L<sup>-1</sup>•min<sup>-1</sup>, shown in Fig. 6), supporting that the model well reflects the simultaneous of adsorption and reduction of 2,4-DCP in Pd<sup>0</sup>-biofilm.

Based on the distribution of Pd<sup>0</sup>NPs in Pd<sup>0</sup>-biofilm, the kinetics results, and modeling, we propose the multistep transformation pathway



Fig. 4. The effluent concentrations of CPs and released  $Cl^-$  for (a) different influent flow rates with influent 2,4-DCP of 100  $\mu$ M and (b and c) different influent concentrations with a flow rate of 0.265 and 0.53•mL min<sup>-1</sup>, respectively. The right-hand axis for  $Cl^-$  release has concentration values that are twice the concentrations on the left side for the CPs; this reflects that 1 mol 2,4-DCP has two  $Cl^-$  equivalents and allows for direct comparison of 2,4-DCP loss (difference between green points and green bars) with  $Cl^-$  release (blue circles). The error bar is the standard deviation of the triplicate samples.



**Fig. 5.** Comparison of average percentage removals and product selectivities for continuous 2,4-DCP reduction in the Pd-MBfR and the MCfR for different influent loadings of 2,4-DCP.

of 2,4-DCP shown in Fig. 8. Adsorption of 2,4-DCP inside the biofilm is the first step; then 2,4-DCP is absorbed by  $Pd^0$  with activation of the C-Cl bond and the formation of Cl•••Pd bond (Wu et al. 2021); and the C-Cl bond is broken through coupled electron-transfer from activated H\* also adsorbed to the  $Pd^0$  surface. The faster adsorption kinetic leads to the enrichment of 2,4-DCP in  $Pd^0$ -biofilm, and the concentrated 2,4-DCP



Fig. 6. Comparisons of measured and the best-fit kinetics for 2,4-DCP reduction in the Pd-MBfR and the MCfR.

accelerates the HDC rate.

#### Conclusion

In the H<sub>2</sub>-based Pd-MBfR, *in-situ* generated  $Pd^0NPs$  associated with the biofilm to form a stable  $Pd^0$ -biofilm that provided greater removal of 2,4-DCP than  $Pd^0NPs$ -film alone. The  $Pd^0$ -biofilm was an efficient

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#### Table 2

Results of the adsorption + reduction model fitting to reduction rates of 2,4-DCP for various 2,4-DCP concentrations in the Pd-MBfR.

$r_{\rm m}(\mu { m mol} \bullet { m L}^{-1} \bullet { m min}^{-1})$	$K_{\rm m}(\mu { m M})$	$k_1(L \bullet \mu mol^{-1} \bullet min^{-1})$	$k_{\rm ap}({\rm min}^{-1})$	$C_{\mathrm{ads},0}(\mu\mathrm{M})$	R <sup>2</sup>
1.47	7.31	0.00389	0.0281	55.6	0.982



Fig. 7. Calculated 2,4-DCP concentrations inside the Pd<sup>0</sup>-biofilm for different effluent 2,4-DCP concentrations (a). Comparison of initial adsorption rates and initial reduction rates for different effluent 2,4-DCP concentrations in the Pd-MBfR, which were calculated by letting  $C_{ads}$  equal to  $C_{eff}$  (b).



Fig. 8. Proposed pathways of catalyzed by  $Pd^0NPs$  in the Pd-MBfR and the MCfR. 2,4-DCP is first adsorbed by  $Pd^0$ -biofilm, and then it is dechlorinated on the  $Pd^0NPs$ . Dechlorination results in a small amount of released MCPs (Wu et al. 2021). MCPs that desorbs can be further reduced to phenol.

adsorbent for 2,4-DCP, and this increased the catalytic contact of 2,4-DCP with activated H\* on Pd<sup>0</sup> surface. Operated in the continuous-flow mode, the Pd-MBfR achieved up to 99% reduction of 2,4-DCP to phenol and could reduce 2,4-DCP to below 0.1 mg•L<sup>-1</sup>.

Kinetic modeling simulated well the adsorption and reduction of 2,4-DCP in continuous-flow conditions. It showed that the Pd-MBfR gave a greater reduction rate than that did the MCfR, particularly for lower 2,4-DCP loadings, because adsorption of 2,4-DCP by the biofilm enhanced the availability of 2,4-DCP to the catalyst. Thus, experimental results and mechanistic modeling describe how coupling Pd<sup>0</sup>NPs and biofilm promoted 2,4-DCP removal and enhanced the product selectivity towards phenol.

#### **Declaration of Competing Interest**

The authors declare no competing financial interest.

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#### Supplementary materials

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