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Elucidating the dechlorination mechanism of hexachloroethane by Pd-doped zero-valent iron microparticles in dissolved lactic acid polymers using chromatography and indirect monitoring of iron corrosion

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Abstract

The degradation mechanism of the pollutant hexachloroethane (HCA) by a suspension of Pd-doped zero-valent iron microparticles (Pd-mZVI) in dissolved lactic acid polymers and oligomers (referred to as PLA), was investigated using gas chromatography and the indirect monitoring of iron corrosion by continuous measurements of pH, oxidation-reduction potential (ORP) and conductivity. The first experiments took place in the absence of HCA, to understand the evolution of the Pd-mZVI/PLA/H_2O system. This showed that the evolution of pH, ORP and conductivity is related to changes in solution chemistry due to iron corrosion, and that the system is initially cathodically controlled by H^+ mass transport to Pd surfaces because of the presence of an extensive PLA layer. We then investigated the effects of Pd-mZVI particles, temperature, initial HCA concentration and PLA content on the Pd-mZVI/PLA/HCA/H_2O system, to obtain a better understanding of the degradation mechanism. In all cases, HCA dechlorination first requires the production of atomic hydrogen H^*—involving the accumulation of tetrachloroethylene (PCE) as an intermediate—before its subsequent reduction to non-chlorinated C_2 and C_4 compounds. The ratio between Pd-mZVI dosage, initial HCA concentration and PLA content affects the rate of H^* generation as well as the rate-determining step of the process. A pseudo-first-order equation can be applied when Pd-mZVI dosage is much higher than the theoretical stoichiometry (600 mg for $[HCA]_0$ = 5-20 mg L^{-1}). Our results indicate that the HCA degradation mechanism includes mass transfer, sorption, surface reaction with H^*, and desorption of the product.

Keywords

Hexachloroethane; Pd/Fe microparticles; Iron corrosion; Physical and chemical monitoring; Dechlorination mechanism; Lactic acid polymers

1. Introduction

Since the first application of zero-valent iron (ZVI) as granular particles in permeable reactive barriers (PRBs) for *in situ* remediation of contaminated groundwater in the 1990s (Gillham and O'Hannesin 1994; O'Hannesin and Gillham 1998), ZVI has been the subject of widespread research to improve the reactivity, stability and transport of such particles in the subsurface environment (Zhang 2003; Crane and Scott 2012; O 'Carroll et al. 2013; Yan et al. 2013; Tosco et al. 2014; Liu et al. 2014b; Fu et al. 2014; Zhao et al. 2016; Reddy et al. 2016; Stefaniuk et al. 2016; Sun et al. 2016; Mu et al. 2017). The use of microscale ZVI (mZVI) particles appears to be a sustainable option, as they are less expensive and less bactericidal, and have a longer life in field experiments

than nanoscale ZVI (nZVI) particles (Lee et al. 2008; Comba et al. 2011; Noubactep et al. 2012; Velimirovic et al. 2012, 2013a, 2018). However, irrespective of their size, iron particles have a low electron efficiency toward contaminants and react mainly with water to produce Fe^{2+} and H_2 (Schöftner et al. 2015; Fan et al. 2016; Tang et al. 2017b). It was realized that bimetallic particles, especially Pd-ZVI ones, can be used to increase the degradation rate by taking advantage of the hydrogenation reactions that generate atomic hydrogen H^* on the second metal (Lowry and Reinhard 1999; Kim and Carraway 2003; Lien and Zhang 2007; Xie and Cwiertny 2013; Liu et al. 2014b). Finally, the use of a polymeric coating is essential for improving the stability, dispersion and transport of the particles in groundwater (He et al. 2007; Phenrat et al. 2008; Kaifas et al. 2014; Kocur et al. 2014; Reddy et al. 2014; Han et al. 2016; Kumar et al. 2017; Fang et al. 2018).

Despite these improvements, the exact mechanism of contaminant removal by iron-based particles still remains unclear. The particles have a core-shell structure, with an Fe^0-core encapsulated by a thin, defective and semiconducting shell of mixed-valence Fe_xO_y iron oxides (Martin et al. 2008; Filip et al. 2014; Liu and Zhang 2014; Ling et al. 2017; Bae et al. 2018). This shell is known to be the seat of all contaminant remediation processes through a combination of adsorption, reduction and co-precipitation processes (Noubactep 2008). For bimetallic particles, the presence of the second metal results in the formation of galvanic cells, Fe acting as an anode and preferentially oxidized and the second metal acting as the main cathodic site (Grittini et al. 1995; Lien and Zhang 1999), which implies that the reduction process occurs mainly on its surface. In both cases, the growth and structural evolution of the shell with time in the ZVI/H_2O system—also known as aging—generally results in a decrease of its porosity and electrical conductivity (Mu et al. 2017) and in the entrapment of the second metal (Yan et al. 2010; Ling and Zhang 2014), affecting the kinetics of iron oxidation and thus all degradation processes (Kumar et al. 2014; Liu et al. 2017). Understanding the evolution of ZVI particles and its impact on the solution chemistry is therefore crucial for evaluating their reactivity, fate and other effects.

Direct characterization methods, such as microscopic and spectroscopic techniques or total-iron measurements (Nurmi et al. 2005; Sun et al. 2006; Sarathy et al. 2008; Baer et al. 2008), require the recovery of solids and sample stabilization, which can be hardly feasible in the field. Such techniques are useful for characterizing the structural evolution of the iron-oxide shell, but they do not provide direct quantitative evidence of iron corrosion. Corrosion rates are commonly estimated by indirect characterization methods, especially hydrogen production measurements (Liu and Lowry 2006; Velimirovic et al. 2014), but this method is unsuitable for Pd-ZVI particles as hydrogen sorption occurs on the Pd surface (Chaplin et al. 2012). Other indirect methods focus on changes in the solution chemistry, e.g. pH and oxidation-reduction potential (ORP), due to the addition of ZVI particles and

69 the resulting reactions in the ZVI/H_2O system (Yu et al. 2014). In field applications, though the complex water
70 chemistry can alter the individual characterization ability of these methods, such indirect methods can show up
71 evidence for ZVI-impacted zones due to the transport of iron-corrosion products, with their associated changes
72 in biogeochemical conditions (Elliott and Zhang 2001; He et al. 2010; Wei et al. 2010, 2012, Shi et al. 2011,
73 2015; Kocur et al. 2014). The combined use of probes appears therefore as an effective tool for understanding
74 both the reactivity and fate of iron-based particles over short- and long-term time scales (Grieger et al. 2010; Shi
75 et al. 2015).

76 In our previous study, we showed that the use of continuous pH and ORP measurements was effective in
77 laboratory experiments for characterizing the degradation mechanism of hexachlorobutadiene (HCBD) by Pd-
78 doped ZVI microparticles (noted Pd-mZVI) suspended in dissolved lactic acid polymers and oligomers (referred
79 to as PLA) (Rodrigues et al. 2017a). PLA is a low-cost biodegradable polymer, widely used for the
80 denitrification of water (Wang and Chu 2016), which we selected as surface modifier to (i) Increase the viscosity
81 of the suspension for preventing aggregation, (ii) Provide hydrophobicity on the particle surface for improving
82 the contact with the hydrophobic pollutant, and (iii) Create acidic conditions through PLA hydrolysis and the
83 release of organic acids for obtaining optimal conditions for the reductive dechlorination of highly chlorinated
84 organic compounds. In addition, in field experiments, PLA acts as a slow-release source of carbon and hydrogen
85 that can stimulate biodegradation by organohalide-respiring bacteria, to maintain reductive conditions over the
86 long term. The efficiency of polyesters, such as polyhydroxyalkanoates (PHA), has already been proven for the
87 bioremediation of COCs (Aulenta et al. 2008; Pierro et al. 2017). The use of ZVI-based particles with a
88 biodegradable slow-release carbon and hydrogen source appears thus as a sustainable strategy for creating an *in*
89 *situ* reactive zone for pollution treatment. It combines the reactivity of a short-term chemical treatment—
90 especially for highly chlorinated and recalcitrant contaminants—with maintaining reductive conditions for long-
91 term bioremediation, in order to prevent a potential rebound effect after the aging of iron-based particles (Baric
92 et al. 2012; Bruton et al. 2015; Koenig et al. 2016; Kocur et al. 2016; Chronopoulou et al. 2016; Xu et al. 2017;
93 Herrero et al. 2019).

94 The objective of our study was to elucidate the degradation mechanism of hexachloroethane (HCA, C_2Cl_6) using
95 Pd-mZVI in PLA, through the indirect monitoring of iron corrosion and its associated changes in solution
96 chemistry by means of continuous measurements of pH, ORP and conductivity. HCA is a common highly
97 chlorinated pollutant found in soil and groundwater, with a low aqueous solubility (Rodrigues et al. 2017b). It is
98 mainly used in the production of pyrotechnic devices and metal alloys, but it can also be a by-product of

fabricating lower chlorination products (Stringer and Johnston 2001). Though HCA is known to be relatively persistent in the environment (Howard 1989), it can undergo reductive dechlorination (Butler and Hayes 1998; Patterson et al. 2001; Lien and Zhang 2005; Song and Carraway 2005; Wu et al. 2014; Zhu et al. 2018). Many chlorinated intermediates can accumulate during this transformation, especially chlorinated ethanes, ethylenes and acetylenes, some of them (TCE and vinyl chloride) being classified as human carcinogens by IARC.

Understanding the HCA degradation mechanism is therefore important for preventing any accumulation of toxic byproducts. Experiments were first done in the absence of HCA for evaluating any changes in the Pd-mZVI/PLA/H_2O system. We then investigated the effects of Pd-mZVI particles, temperature, initial HCA concentration and PLA content on the Pd-mZVI/PLA/HCA/H_2O system, to provide a better insight into the degradation mechanism.

2. Materials and methods

2.1. Chemicals

HCA (99%) and tetrachloroethylene (PCE, 99%) were purchased from Sigma-Aldrich. A mix of chlorinated hydrocarbons in methanol (200 µg mL^{-1}) containing chlorinated ethanes and ethylenes was obtained from Sigma-Aldrich for the preparation of standard solutions (EPA 502/524.2 VOC Mix). Stock solutions of HCA (5, 10 and 20 g L^{-1}) were prepared in HPLC-grade methanol, supplied by VWR. Deionized water was obtained from a Milli-Q water system (18.2 MΩ cm) and was degassed before any experiment with an ultrasonic bath at 45 kHz, followed by N_2 flushing during the preparation of batch experiments to limit the introduction of O_2.

The—partially biologically produced—Pd-doped iron microparticles (BioCAT, noted as Pd-mZVI) and the mixture of lactic acid polymers and oligomers dissolved in ethyl lactate (Dechlorem, noted as PLA) were provided by Biorem Engineering. According to the manufacturer, the particles are smaller than 10 µm with an average size of 3-5 µm, palladium representing 0.1-2 wt% of the particles. The specific surface area, measured with the BET-N_2 adsorption method (BELSORP-max, MicrotracBEL, Japan), was less than 1 m^2 g^{-1}. The suspension of Pd-mZVI in PLA was prepared before any experiments by manual mixing of the corresponding amounts of PLA and Pd-mZVI.

For the system without HCA, the experiments were also performed with nZVI particles (NANOFER STAR, obtained from Nano Iron), and the results are presented in the Supplementary data.

126 *2.2. Batch experiments*

127 Batch experiments were conducted in a 1 L cylindrical Pyrex double-walled water-jacketed reactor, equipped
128 with a mechanical-propeller stirring rod (at 300 rpm). The reactor head has hermetic ports for installing the
129 electrodes, for the introduction of the reactant and for sampling. 1 mL of the appropriate stock solution was
130 injected into the reactor filled with degassed deionized water with initial zero-headspace conditions. Reaction
131 was initiated by introducing the Pd-mZVI suspension in PLA, and 3 mL aliquots were collected at selected
132 times. The reduction was stopped by separating the particles with powerful magnets. 1 mL of the supernatant
133 aqueous phase without particles was collected and diluted (1:10) with degassed pure water into 20 mL headspace
134 vials equipped with a PTFE septum. The prepared samples were finally stocked at 4 °C and analysed within 24
135 hours.

136 *2.3. Analytical methods*

137 The bimetallic microparticles were characterized before any reaction by scanning electron microscopy coupled
138 to energy dispersive X-ray spectrometry (SEM/EDS), X-ray diffraction (XRD) and X-ray photoelectron
139 spectroscopy (XPS). SEM/EDS images were obtained with a Phenom XL microscope (Fondis Bioritech)
140 operating at 15 kV. XRD analyses were performed with a D8 Advance diffractometer (Bruker) with a CuKα
141 source (λ = 1.5406 Å) at an accelerating voltage of 40 kV and emission current of 40 mA. Samples were scans
142 from 4 to 90° 2θ at 0.03° 2θ s^{-1}. XPS analyses were performed with a K-Alpha+ spectrometer (ThermoFisher
143 Scientific) equipped with a Al anode generating Al K_α X-ray radiation. Samples were analysed at Fe 2p, Pd 3d,
144 C 1s, O 1s, N 1s and Si 2p regions after survey scans.

145 Analysis of HCA and its degradation products was performed by gas chromatography (GC/FID) using a Varian
146 CP-3800 equipped with a DB-624 column (30 m x 0.32 i.d., with a 1.80 µm film thickness). Helium was chosen
147 as carrier gas at a 1.2 mL min^{-1} flowrate. Samples were heated at 80 °C for 30 min, and 200 µL of the headspace
148 gas was withdrawn by a gas-tight syringe and introduced in the injector chamber at 250 °C (1:25 split ratio). The
149 oven was maintained at 35 °C for 5 min, and then ramped up to 245 °C at 10 °C min^{-1} with a hold for 10 min at
150 this final temperature. The FID temperature was maintained at 300 °C, and He was used as carrier gas at a
151 flowrate of 30 mL min^{-1}. Combustion in the FID was carried out with H_2 (30 mL min^{-1}) and air (300 mL min^{-1}).
152 Seven reference standards of chlorinated hydrocarbons, ranging from 50 to 5000 µg L^{-1}, were periodically
153 prepared and analysed to ensure the proper quantification of the samples. The qualitative production of non-
154 chlorinated hydrocarbons is also provided in Supplementary data.

The Pd-mZVI corrosion was monitored by measuring changes in pH, ORP and conductivity with a multi-parameter tester (Heitolab MPC 350, Heito) and recorded every 12 s using a Keithley 2700 data acquisition system controlled via KickStart software. The pH was measured with a glass electrode (Radiometer Analytical pHC3005-8, Hach), calibrated before each experiment with commercial buffer solutions (pH 7 and 4). The oxidation-reduction potential (ORP) of the solution was measured with a platinum disc electrode (Radiometer Analytical XM150, Hach) with respect to a mercury-mercurous sulphate reference electrode (MMSE, Ametek SI). ORP values were then converted and reported with respect to the standard hydrogen electrode (SHE) by adding 640 mV (saturated K_2SO_4 solution). Conductivity was measured with a 2-pole conductivity cell (Tacussel XE 150) and calibrated before each experiment with a commercial buffer solution (1413 µS cm^{-1} at 25 °C). All electrodes were placed in the aqueous solution at about one third of the reactor.

In a non-buffered system (Bae and Hanna 2015), the evolution of pH is a good indicator of iron corrosion as H^+ is directly implied in the reaction (Eq. 1).

$$Fe^0 + 2\,H^+ \rightarrow Fe^{2+} + H_2 \qquad \text{(Eq. 1)}$$

Eq. (1) is the result of iron oxidation in Fe^{2+} and H^+ reduction in H_2. The hydrogen evolution reaction (HER) occurs both on the oxide shell and on Pd. Because of the difference in the standard redox potential, Pd acts as the preferential cathodic site in the system, and the reduction of H^+ in H_2 occurs in a two-step process (Eqs. 2-3).

$$2\,H^+ + 2\,e^- \xrightarrow{Pd} 2\,H^* \qquad \text{(Eq. 2)}$$

$$2\,H^* \rightarrow H_2 \qquad \text{(Eq. 3-1)}$$

$$H^* + H^+ + e^- \rightarrow H_2 \qquad \text{(Eq. 3-2)}$$

The formation of atomic hydrogen H^* on Pd is of crucial importance as adsorbed H^* (H^*_{ads}) is the only active hydrogen species in catalytic hydrodechlorination reactions (Jiang et al. 2017; He et al. 2018; Liu et al. 2018). The cumulative H^+ consumption, or the total generated H^* yield, can be calculated considering the reduction of H^+ to H^* and the dissociation of H_2O into H^+ before its reduction to H^* (Jiang et al. 2018), as indicated in the Supplementary data (Fig. S3).

Measurements of the oxidation-reduction potential (ORP) provide information on the composition and changes in the physico-chemistry of the solution. In the presence of ZVI particles, ORP values are mainly dependent upon iron-species couples (Shi et al. 2011) and the H^+/H_2 redox couple, because of the affinity of Pt (the sensing

probe) to hydrogen adsorption (Papaderakis et al. 2017). Finally, conductivity is an indicator of the ionic content in solution. The conductivity of the solution can be calculated by the equation below (Eq. 4):

$$\sigma = \sum_i \lambda_i z_i C_i \qquad \text{(Eq. 4)}$$

where σ is the conductivity (S m^{-1}), λ_i the molar ionic conductivity of species i (S m^2 mol^{-1}), z_i the electrical charge of species i and C_i the concentration of species i (mol m^{-3}). Considering iron corrosion and HCA dechlorination, the main ionic species that can influence the conductivity are H^+ (at 25 °C, $\lambda°_{H^+}$ = 349.8 S cm^2 mol^{-1}), OH^- ($\lambda°_{OH^-}$ = 198 S cm^2 mol^{-1}), Fe^{2+} ($\lambda°_{1/2Fe^{2+}}$ = 54 S cm^2 mol^{-1}), Fe^{3+} ($\lambda°_{1/3Fe^{3+}}$ = 68 S cm^2 mol^{-1}), Cl^- ($\lambda°_{Cl^-}$ = 76 S cm^2 mol^{-1}), and the ionic species resulting from the introduction and hydrolysis of PLA. The decrease in H^+ content due to iron corrosion is responsible for a decrease in conductivity, whereas an increase in the contents of other ionic species causes an increase in conductivity.

3. Results and discussion

3.1. Characterization of Pd-mZVI particles

The characterization of the Pd-mZVI particles before reaction is shown in Fig. 1 and Fig S1. On Fig. 1a, it is shown that the smallest particles were spherical, with a diameter of 2-3 µm. Larger particles with a diameter of about 10 µm were also observed (Fig. S1a). On Fig. S1b, the largest particles show the porous structure of the external layer. In addition, EDS analysis reveals that some of the particles have a high carbon content with traces of silicium and phosphorus, which could originate from the biomass used during the bioreductive deposition of palladium nanoparticles (De Windt et al. 2005; Dien et al. 2013).

Fig. 1b shows the patterns of the Pd-mZVI particles. The peaks at 44.7°, 65.1° and 82.3°, respectively, can be indexed to the planes (110), (200) and (211) of Fe cubic crystal structure (JCPDS 06-0696), and the peaks at 40.3°, 46.9° and 68.5°, respectively, correspond to the planes (111), (200) and (220) of face centered cubic crystal structure of Pd (the peak at 82.3° can also be attributed in part to the plane (311)) (JCPDS 46-1043). However, there is no indication of crystalline phases of iron oxide, or only in very small fractions, in contrary to the pattern of nZVI particles for which the diffraction peaks corresponding to magnetite or maghemite were observed (Fig. S2a). Figs 1c, d and e show the XPS spectra of the Pd-mZVI particles. The survey scan from 0 to 1100 eV indicates the presence of Fe, Pd, C, O, N and Si on the surface of the particles (Fig. 2a). As indicated by the low signal intensities between 700 and 730 eV (Fig. 2b), the presence of Fe on the surface of the particles is very limited, in comparison to nZVI particles for which the XPS spectra indicates the presence of metallic iron

205 (Fe^0) and oxidized iron (Fe^{III}) on its surface and near-surface (Fig. S2). The particles present four peaks between
206 332 and 346 eV, named A1, B1, A2 and B2 (Fig. 2c). The two peaks A1 and A2, with binding energies of 335.4
207 and 340.7 eV respectively, match with the $3d_{5/2}$ and $3d_{3/2}$ of metallic Pd (Muftikian et al. 1996; Yan et al. 2010),
208 and the two peaks B1 and B2, with binding energies of 338.1 and 343.4 eV respectively, match with the $3d_{5/2}$ and
209 $3d_{3/2}$ of oxidized Pd (Voogt et al. 1996). The results indicate that, for Pd-mZVI particles, the core is mainly
210 composed of Fe^0, while the external surface of the particles is composed of iron oxides, carbon, silica, and
211 palladium, the latter being required for H^* generation for hydrodechlorination on the surface.

212 *3.2. Investigation of the Pd-mZVI/PLA/H_2O system*

213 Before considering HCA degradation, two experiments were performed without HCA at 25 °C in the presence of
214 600 mg of Pd-mZVI and 850 or 3400 mg of PLA. This was to investigate the influence of PLA on the corrosion
215 kinetics of Pd-mZVI and to understand how to interpret the evolution of pH, ORP and conductivity (Fig. 2).

216 With 850 mg of PLA, the introduction of PLA in solution resulted in an initial drop of pH to 2.65 (Fig. 2a, with
217 pK_a of lactic acid = 3.86 at 20 °C) and a first increase of conductivity to 350 µS cm^{-1} (Fig. 2d). Initially, the ORP
218 values were fixed by the Fe(III)/Fe(II) redox couple (Figs. 2b and c) that result from the initial partial breaking
219 of the iron oxide shell under acidic conditions (Sarathy et al. 2008; Tang et al. 2017a). This agrees with the
220 initial decrease and stabilization of pH as Fe^{3+} acts as a weak Brønsted acid (Shih et al. 2011), as indicated in Eq.
221 5.

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \quad \text{(Eq. 5)}$$

222 After 420 minutes, the pH increased from 2.65 to 6.15, and the rate of H^+ consumption is not linear but decreases
223 with time, as shown by the cumulative H^+ consumption (Fig. S3). After an initial decrease, the conductivity
224 stabilized at a minimum value of 195 µS cm^{-1} after 100 min. The decrease in H^+ content was therefore
225 compensated by an increase in other ionic-species contents, especially soluble Fe^{2+} and Fe^{3+}. After that,
226 conductivity slowly increased to 230 µS cm^{-1} at 420 min.

227 According to the Nernst equation of the Fe(III)/Fe(II) redox couple, an increase in Fe^{2+} content resulting from
228 iron corrosion (Eq. 1) causes a decrease in ORP values in the first minutes. Then, ORP drops from positive to
229 negative values (Fig. 2b), which indicates a change in the main redox couple in the system. As shown on Fig. 2c,
230 this change is well correlated with the theoretical evolution of the H^+/H_2 redox couple with pH. Hence, the
231 monitoring of ORP is a good indicator for the formation and accumulation of H_2 in the system. A similar
232 behaviour was observed for the aqueous corrosion of nZVI particles in PLA (Fig. S4), confirming that the

changes in solution chemistry are well related to the particles. However, all phenomena accelerated when using nZVI particles. The pH increased from 2.75 to 6.15 in less than 60 min, resulting in a more rapid initial decrease in both ORP and conductivity. This acceleration is probably related to the difference in specific surface area ($a_{S\ nZVI,\ BET}$ = 15.5 $m^2\ g^{-1}$) and in the cathode/anode ratio. The nZVI particles thus show a much faster corrosion rate than Pd-mZVI particles, the latter having a longer reactive lifetime.

The increase in PLA content from 850 to 3 400 mg led to a decrease in initial pH (Fig. 2a) due to PLA hydrolysis, resulting in an increase in initial conductivity (Fig. 2d). Similar changes of pH and ORP were observed, but with a time delay; the decrease and stabilization of pH values (Fig. 2a) and the fixing of ORP by the Fe(III)/Fe(II) redox couple (Figs. 2b, c) were observed during 40 min. After that, the pH sharply increased reflecting a more rapid decrease in conductivity (Fig. 2d), and the change of ORP from the Fe(III)/Fe(II) to the H^+/H_2 redox couple occurred shortly after. Compared with the experiment conducted with 850 mg of PLA, this evolution of the solution chemistry thus suggests that, despite an initial decrease in pH, iron corrosion is slow from 0 to 40 min, becoming important only after that. The polymeric coating can alter the reactivity of iron-based particles due to (i) the blocking of reactive sites and (ii) the inhibition of mass transfer to the surface due to the formation of trains and loops (Phenrat et al. 2009). Increasing the PLA content results in blocking of the reactive cathodic sites and the creation of an extensive polymer layer on the surface. Iron corrosion thus appears to be initially cathodically controlled by H^+ mass transport to the Pd surface, the effect being more pronounced when the PLA content is increased. Increasing the H^+ content at the interface causes an increase in corrosion rate, resulting in the saturation of Pd and the later recombination of H^* into H_2. A schematic illustration of the main results obtained in this section is proposed on Fig. 3.

Continuous pH, ORP and conductivity measurements allowed monitoring the consumption of H^+, mainly related to iron corrosion, and the production/accumulation of H_2 in the system according to the E-pH diagram.

3.3. Investigation of the Pd-mZVI/PLA/HCA/H_2O system

3.3.1. Effects of Pd-mZVI dosage

The effect of Pd-mZVI dosage was investigated with 150, 375 and 600 mg at 25 °C with 850 mg of PLA and 10 mg L^{-1} of HCA (Fig. 4). It is important to note that the theoretical stoichiometric requirement is 1.42 g Fe^0/g of HCA for its complete reduction to ethane. HCA completely disappears in less than 120 min with 600 mg of Pd-mZVI, while the degradation remains incomplete after 420 min with 150 and 375 mg (Fig. 4a). An increase in Pd-mZVI dosage results in more active sites for H^+ reduction and H^* generation (cathodic sites), as confirmed

by the more rapid increase in pH (Fig. 4b). As shown on Figs. 4d and e, ORP remained fixed by the Fe(III)/Fe(II) redox couple with 150 and 375 mg, while the change from Fe(III)/Fe(II) to H^+/H_2 was observed with 600 mg. This result agrees with the more rapid and greater production of H_2. With 150 and 375 mg of Pd-mZVI, the conductivity decreases during the 420 min of reaction time (Fig. 4f). This decrease is observed during the first 90 min with 600 mg of Pd-mZVI. As H^+ is the major contributor to conductivity under strong acidic conditions, this variation can be explained by a decrease in H^+ content due to iron corrosion.

HCA reduction results in the formation and accumulation of PCE (C_2Cl_4) as the only chlorinated intermediate (Fig. 4c), in agreement with the dihalo-elimination pathway observed in earlier studies with ZVI-based particles (Lien and Zhang 2005; Song and Carraway 2005; Wu et al. 2014). However, our results showed that the initial disappearance of HCA was not directly related to PCE production, as a 10-min shift was observed for PCE production irrespective of the amount of particles. This delay may indicate that HCA degradation initially involves nonreductive sorption on the Pd-mZVI/PLA/H_2O system, which is generally linked to the carbon content on the particle surfaces (Lin and Lo 2005; Velimirovic et al. 2013b). In addition, this induction period could be caused by the absence of active hydrogen species (H^*_{ads}) on the Pd surface, as He et al. (2018) suggested that the dechlorination process on Pd particles requires first their saturation by H^* (formation of palladium hydride) before any dechlorination reaction.

With 600 mg of Pd-mZVI, the change from positive to negative ORP values occurs after 100 min (Fig. 4d) whereas it occurs after only 35 min in the absence of HCA (Fig. 2b), showing that H^* is consumed during dechlorination. This change is observed only when the PCE concentration becomes low, indicating that H^* is the main reductant for both HCA and PCE degradation. However, the degradation mechanism seems different for both compounds. HCA reduction to PCE (Eq. 6) does not involve the addition of hydrogen in the molecule; atomic hydrogen acts therefore only as an electron donor. Even if this result seems to disagree with the increase in pH, it is important to note that iron particles have a very low electron efficiency toward contaminants, i.e. most parts of iron react with water (Schöftner et al. 2015; Fan et al. 2016; Tang et al. 2017b). PCE reduction results in the formation of ethane, ethylene and C_4 compounds (Fig. S6), without accumulation of chlorinated intermediates in solution. This result was confirmed by GC/MS measurements with lower quantitation limits (0.1-1 µg L^{-1} depending on the compound). The production of C_4 compounds indicates that coupling reactions occur during the reaction. Hence, PCE reduction first results in the formation of C_2 surface complexes, with the

loss of chloride ions due to the breaking of C-Cl bonds on the catalyst (Sriwatanapongse et al. 2006; Heck et al. 2008), followed by progressive hydrogenation and/or coupling reactions between C_2 fragments (Eqs. 7-10).

$$CCl_3CCl_3 + 2\,e^- \rightarrow CCl_2 = CCl_2 + 2\,Cl^- \quad \text{(Eq. 6)}$$

$$CCl_2 = CCl_2 \xrightarrow{Pd} C_2^{\ddagger} + 4\,Cl^- \quad \text{(Eq. 7)}$$

$$C_2^{\ddagger} + 6\,H^* \xrightarrow{Pd} C_2H_6 \quad \text{(Eq. 8)}$$

$$C_2^{\ddagger} + 4\,H^* \xrightarrow{Pd} C_2H_4 \quad \text{(Eq. 9)}$$

$$C_2^{\ddagger} + C_2^{\ddagger} \xrightarrow{Pd} C_4^{\ddagger} \quad \text{(Eq. 10)}$$

With 600 mg of Pd-mZVI, the small increase in ORP values (Fig. 4d)—causing a gap in the H^+/H_2 redox couple theoretical values observed after 120 min (Fig. 4e)—is caused by the loss of H_2 during sampling, as ORP remains well fixed by the H^+/H_2 redox couple without opening of the reactor (Fig. 2c). The effect is more pronounced for the penultimate sampling at 330 min because of the decrease in H^+ content and the rate of iron corrosion. The effect is even more pronounced with nZVI particles (Fig. S4), where a decrease in pH is observed after 80 min associated with a progressive increase in ORP every time the reactor is opened. These results indicate a consumption of OH^- and the formation of iron oxy-hydroxides on the surface of nZVI particles such as lepidocrocite γ-FeOOH, because of the possible introduction of dissolved O_2 (Greenlee et al. 2012; Liu et al. 2014a), as well as of ferrihydrite because of the presence of lactate ions (Sabot et al. 2007).

Zero-order, pseudo-first-order and second-order reactions were envisaged for fitting the experimental data. With 150 and 375 mg of Pd-mZVI, none of them resulted in a correct representation of HCA degradation (see Table 1 for the results of pseudo-first-order equations). In these cases, a two-compartment model based on first-order equations (Eq. 11) fits well with the experimental data obtained (Fig. S6), suggesting that two different reaction mechanisms explain the disappearance of HCA (Rodrigues et al. 2017a; Kim et al. 2018).

$$\frac{C}{C_0} = \alpha\, e^{-k_a t} + (1-\alpha)\, e^{-k_c t} \quad \text{(Eq. 11)}$$

where C_0 is the initial pollutant concentration, C is the pollutant concentration at time t (min), k_a and k_c are respectively the rate constants for adsorption and chemical degradation, α represents the weight value for sorption, and 1-α represents the weight value for chemical degradation.

With 600 mg of Pd-mZVI, the production of atomic hydrogen H^* on the Pd surface is more important due to increased H^+ consumption. The rate-determining step then moves progressively from H^* production to hydro-

311 dechlorination by increasing Pd-mZVI dosage, which can explain the validity of the pseudo-first-order model
312 (Eq. 12):

$$\frac{C}{C_0} = e^{-k_{\mathrm{obs}}t} \qquad \text{(Eq. 12)}$$

313 where C is the concentration (mg L^{-1}) at time t (min), C_0 is the initial concentration (mg L^{-1}) and k_{obs} is the rate
314 constant (min^{-1}).

315 In the following section, we focus on the use of 600 mg of Pd-mZVI in order to observe as much variation as
316 possible in the different experimental parameters for a better understanding of the HCA degradation mechanism.

317 *3.3.2. Effects of temperature*

318 The effect of temperature was investigated at 12, 25 and 35 °C with 600 mg of Pd-mZVI, 850 mg of PLA and
319 10 mg L^{-1} of HCA (Fig. 5). As already observed in our previous study (Rodrigues et al. 2017a), the increase in
320 temperature results in a decrease in the initial pH due to a change in the rate of PLA hydrolysis. Results show
321 that HCA degradation is incomplete at 12 °C after 420 min (Fig. 5a). During this period, the pH increases from
322 2.94 to 3.48 (Fig. 5b), and only a decrease in conductivity with time from 390 to 225 µS cm^{-1} is observed
323 (Fig. 5f), indicating that iron corrosion is slow. At 35 °C, the HCA has completely disappeared after about
324 60 min, more rapidly than at 25 °C (Fig. 5a), and PCE accumulates at a lower rate and disappears more rapidly at
325 35 °C (Fig. 5c). In addition to the increase in the number of high-energy collisions and in the mobility of the
326 pollutant, the rise in temperature from 12 to 35 °C increases H^+ consumption (Fig. S3). Direct comparison of the
327 evolution of conductivity is more difficult here as the molar conductivity of each species is different at each
328 temperature, but the results confirm that iron corrosion is more rapid when the temperature increases (Fig. 5f).
329 The constant increase in HCA degradation rate with temperature (Table 1) can then be explained by the more
330 rapid production of atomic hydrogen on the Pd surface (He and Zhao 2008).

331 This agrees with the evolution in ORP values over time. At 12 °C, ORP is stable for 100 min and only a small
332 decrease is observed afterwards (Fig. 5d), indicating an increase in Fe^{2+} content in the solution. The ORP does
333 not decrease to the H^+/H_2 redox couple values because of the slow production of atomic hydrogen and its
334 subsequent reaction with HCA. Conversely, the accumulation of H_2, according to ORP measurements (Fig. 5d),
335 is more rapid at 35 °C than at 25 °C, as both HCA and PCE degradation occur more rapidly. Consequently, the
336 decrease in H^+ consumption under less acidic conditions (pH >5) is observed earlier at 35 °C. After the last
337 opening of the reactor at 330 min, the ORP becomes positive, indicating that the H^+/H_2 redox couple is no longer

the main contributor to the overall ORP value (Figs. 5d and e). Also, the small decrease in pH observed could indicate an OH^- consumption related to the formation of iron oxy-hydroxides on the particle surfaces. Thus, even if the temperature increase is favourable for HCA degradation, the reactive lifetime of the particles and the electron efficiency are strongly impacted. We thus focused on the use of T = 25 °C for the subsequent experiments.

Considering the pseudo-first-order model, the Arrhenius equation was used for establishing the relation between the rate constant and the temperature (Eq. 13).

$$\ln k_{\mathrm{obs}} = \ln A - \frac{E_a}{RT} \quad \text{(Eq. 13)}$$

where k_{obs} is the constant rate (min^{-1}), A is the pre-exponential factor (min^{-1}), E_a is the activation energy (J mol^{-1}), R is the universal gas constant and T is the absolute temperature (K). An almost equivalent relationship, the Eyring equation, can be used by following the transition state theory (Eq. 14).

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{B}} T}{h} \exp\left(\frac{-\Delta^{\ddagger} G^{\circ}}{RT}\right) \quad \text{(Eq. 14)}$$

where k_B is the Boltzmann constant (1.381 10^{-23} J K^{-1}), h is the Planck constant (6.626 10^{-34} J s) and $\Delta^{\ddagger}G°$ is the Gibbs energy of activation (J mol^{-1}). The relation can be linearized as Eq. 15:

$$\ln\left(\frac{k_{\mathrm{obs}}}{T}\right) = \frac{-\Delta^{\ddagger} H^{\circ}}{R} \cdot \frac{1}{T} + \ln\left(\frac{k_{\mathrm{B}}}{h}\right) + \frac{\Delta^{\ddagger} S^{\circ}}{R} \quad \text{(Eq. 15)}$$

where $\Delta^{\ddagger}H°$ is the standard enthalpy of activation (J mol^{-1}) and $\Delta^{\ddagger}S°$ is the standard entropy of activation (J $mol^{-1}{\cdot}K^{-1}$).

Results obtained from the Arrhenius plot are Ea = 106.5 kJ mol^{-1} and A = 1.21 10^{17} min^{-1} (R^2 = 0.982, Fig. S8a). The elevated activation energy indicates that, with these experimental parameters, the overall reaction is controlled by the reaction on the particle surfaces (Pilling and Seakins 1995). Results obtained from the Eyring plot are $\Delta^{\ddagger}H°$ = 104.0 kJ mol^{-1} and $\Delta^{\ddagger}S°$ = 39.8 J mol^{-1} K^{-1} (R^2 = 0.981, Fig. S8b). The positive value for the activation entropy indicates that the reaction is favourable and that the activated complex is loosely bound on the surface of the particles, which agrees with the formation and desorption of PCE as a reaction intermediate. Based on previous studies (Butler and Hayes 1998; Patterson et al. 2001; Song and Carraway 2005; Huang et al. 2012; Pizarro et al. 2018), the activated complex is suspected to be the pentachloroethyl radical (Eqs. 16-17).

$$C_2Cl_6 + e^- \rightarrow {}^{\bullet}C_2Cl_5 + Cl^- \quad \text{(Eq. 16)}$$

$${}^{\bullet}C_2Cl_5 + e^- \rightarrow C_2Cl_4 + Cl^- \quad \text{(Eq. 17)}$$

3.3.3. Effects of HCA initial concentration

The effect of the initial concentration was investigated at three HCA initial concentrations—5, 10 and 20 mg L^{-1}—at 25 °C with 600 mg of Pd-mZVI and 850 mg of PLA (Fig. 6). A change in initial concentration of the substrate has no influence on the degradation pathways, with the production of PCE and its subsequent reduction to ethane, ethylene and C_4 compounds (Fig. S9). HCA degradation-rate constants are very similar when the initial concentration increases from 5 mg L^{-1} (k_{obs} = 0.036 min^{-1}) to 10 mg L^{-1} (k_{obs} = 0.035 min^{-1}, see Table 1). As the evolution of H^+ content is quite different at both concentrations (Figs. 6b and S2), the rate-determining step cannot be attributed to H^* production, but rather to HCA dechlorination.

An increase in HCA content to 20 mg L^{-1} results in a decrease in the degradation rate constant (k_{obs} = 0.010 min^{-1}), and PCE accumulates over a longer time, but in a similar proportion as obtained with lower initial concentrations (Fig. 6c). As indicated by the pH evolution (Fig. 6b) and cumulative H^+ consumption (Fig. S3), the production of H^* is less rapid with 20 mg L^{-1}, whereas the degradation requires twice as much atomic hydrogen. As observed in Figs. 6d and e, the ORP value remains positive and is not fixed by the H^+/H_2 redox couple during the 420 min of the experiment. As shown on Fig. S10, the drop in ORP values is observed only after the complete hydrodechlorination of PCE. So, as long as dechlorination occurs, the most important fraction of H^*_{ads} available on Pd is consumed, which prevents its recombination into H_2 and its subsequent desorption. Therefore, even if the degradation rate constant is lower, a low iron/pollutant ratio will limit the loss of active hydrogen species. This result is comparable to that obtained by decreasing the amount of Pd-mZVI, where a similar evolution of conductivity with time is observed (Fig. 6f). Hence, for higher HCA initial concentrations (>20 mg L^{-1}) with 600 mg of Pd-mZVI, the reaction may be limited by the production of H^* and not by surface-reaction kinetics.

In the following section, we thus focus on the use of 10 mg L^{-1} as the initial HCA concentration.

3.3.4. Effects of PLA content

The effect of the PLA content was investigated for three initial contents—850, 1700 and 3400 mg—at 25 °C with 600 mg Pd-mZVI and 10 mg L^{-1} HCA (Fig. 7). The increase in PLA content results in a decrease in HCA degradation rate constants, from 0.035 min^{-1} with 850 mg to 0.025 min^{-1} at 3400 mg (Table 1), in agreement with

386 the later production and accumulation of PCE (Fig. 7c). With 3400 mg, more than 40% of HCA disappears in the
387 first 10 min, which indicates a more important phase transfer from water to PLA (sorption). As no PCE
388 production is observed during this time, HCA accumulates near the surface of the particles. Compared to the
389 experiment run in the Pd-mZVI/PLA/H_2O system (Fig. 2), the evolution of pH, ORP and conductivity follows
390 the same qualitative trend (Figs. 7b, d and f), although H^+ consumption is less important in the first minutes
391 (Fig. S3) and the change from a Fe(III)/Fe(II) to a H^+/H_2 redox couple occurs much later.

392 In the Pd-mZVI/PLA/H_2O system, the reductive dechlorination process requires an intimate contact between
393 pollutant and particle surface. However, as mentioned before, the increase in polymeric coating can result in a
394 high coverage rate of the particles (site blocking) and the development of an extended layer composed of loops
395 and tails (Zhu et al. 2008; Phenrat et al. 2009; Bhattacharjee et al. 2016; Louie et al. 2016). With 1700 mg of
396 PLA, the lower HCA rate constant can be attributed to higher number of sites blocked by the polymeric coating
397 and to a low production of atomic hydrogen in the first minutes. After the initial decrease and stabilization of pH
398 (Fig. 7b), the strong acidic conditions accelerate the rate of H^+ consumption (Fig. S3), which results in a more
399 rapid production of H^*. As a consequence, PCE degradation occurs rapidly. With 3400 mg of PLA, the
400 development of loops and tails on the particle surfaces will impede HCA mass transport to the surface of the
401 particles, the accumulation of HCA in turn impeding H^+ mass transport, which explains the decrease in
402 degradation rate. In addition, the accumulation of H_2 bubbles around the particles can result in the covering of
403 reactive sites and the deactivation of the catalyst (Graham and Jovanovic 1999; Wang et al. 2009), leading to a
404 further decrease in the degradation rate (Huang et al. 2016).

405 Even if the degradation rates decrease with increasing PLA content, the reactive lifetime of the particles is
406 extended thanks to the formation of iron lactate complexes and the maintenance of acidic conditions, which
407 prevent the rapid formation of any passive layer on the surface of the particles (Rodrigues et al. 2017a) as Fe^{3+}
408 and Fe^{2+} are more soluble under acidic conditions, and thus the rapid enclosure of Pd (Yan et al. 2010; Ling and
409 Zhang 2014).

410 As shown in the previous experiments, for a given initial HCA concentration, an increase in Pd-mZVI dosage
411 causes an increase in the HCA degradation rate, but a major part of the H^* will be combined as H_2, rendering it
412 unavailable for degradation. Therefore, it appears necessary to seek a compromise between HCA degradation
413 rate and electron efficiency. A 15:85 mass ratio of Pd-mZVI in PLA appears to be an optimal condition that

allows a rapid initial disappearance of the pollutant, a more controlled reactivity and the maintenance of acidic conditions, extending the reactive lifetime of the particles and preventing the formation of passive precipitates.

3.4. HCA dechlorination mechanism

Figure 8 shows a summary of the main conclusions of the dechlorination mechanism. The introduction in water of a suspension of Pd-mZVI in PLA results in the partial breaking up of the initial shell (Sarathy et al. 2008; Tang et al. 2017a); Fe^0 oxidizes to Fe^{2+}, and the resulting electrons flow from the iron core to Pd that acts as the main cathodic site ($E^0_{Pd} > E^0_{FeOx} > E^0_{Fe}$). On the Pd surface, which is a good catalyst for hydrogenation, H^+ is reduced to atomic hydrogen H^* (Volmer step), accumulating as palladium hydride (Pd-H) and as H^*_{ads}. Finally, the reaction of H^+ with H^*_{ads} (Heyrovsky step), or the combination of two H^*_{ads} (Tafel step), will result in the desorption of H_2 to the bulk solution (Fig. 3).

In the presence of HCA, the first step is mass transfer of HCA from bulk to suspension of the Pd-mZVI/PLA system. As both HCA and PLA are hydrophobic, the initial HCA disappearance is attributed to nonreductive sorption, in agreement with the absence of PCE production and the increase in initial disappearance when increasing the PLA content. The second step is the surface reaction of HCA with H^*, which results in the production and accumulation of PCE as a chlorinated by-product. The absence of other chlorinated intermediates and the production of C_4 compounds suggest that PCE undergoes rapid dechlorination, because of the breaking of C-Cl bonds on the Pd surface (Sriwatanapongse et al. 2006; Heck et al. 2008) and the formation of $C_2^{\ddagger}$ surface complexes. The third step is the progressive hydrogenation of $C_2^{\ddagger}$ into C_2 compounds, or a coupling reaction between two surface complexes into $C_4^{\ddagger}$ and its progressive hydrogenation to C_4 compounds. The last steps are the desorption of the products from the surface of the particles, and their transfer to the bulk solution (Fig. 8).

3.5. Implications for environmental application

In addition to proposing a degradation mechanism, our study allows defining some perspectives for practical applications. The laboratory results suggest that small (≈600 mg for $[HCA]_0$ = 5-20 mg L^{-1}) amounts of Pd-mZVI in PLA are sufficient for a rapid and complete pollution degradation. The use of low doses of iron particles will limit the loss of ZVI due to its spontaneous corrosion in water, as well as reducing its inhibition effects on the microbial community for *in situ* remediation (Velimirovic et al. 2015). Even if an increase in PLA content results in more acidic conditions, the effect may be less pronounced under field conditions depending on the natural buffering capacity of the aquifer. In addition, as indicated above, iron corrosion progressively results in an increase of pH to near-neutral conditions, more favourable to the growth and activity of organohalide-

443 respiring bacteria, e.g. *Dehalococcoides* strains, for biological reductive dechlorination, even if a pH decrease
444 will affect the ability of the culture to dechlorinate (Yang et al. 2017a, b). The monitoring of pH thus is a great
445 tool for evaluating the operating conditions for both abiotic and biotic reductive processes.

446 Interpretation of the ORP evolution should be more difficult in the field than in laboratory experiments, because
447 of the many redox couples and bacteria in groundwater that contribute to the overall (mixed potential) ORP
448 value (Hunting and Kampfraath 2013; Shi et al. 2015). Measuring ORP will nevertheless provide insight into the
449 creation of reductive conditions due to H_2 production. In addition, the impact on ORP values of opening the
450 reactor could mirror the influence of sampling from observation wells in the field, as ORP values are known to
451 have a harmful effect on iron reactivity, and on the presence and activity of organohalide-respiring bacteria
452 (Adrian and Löffler 2016). Finally, conductivity measurements should give indications on the ionic strength of
453 groundwater. The overall data acquired during this study have shown the interest of implementing a complete
454 multi-parametric device for the monitoring of reductive dechlorination processes in the field.

455 **4. Conclusion**

456 We investigated the mechanism of HCA degradation by a suspension of Pd-mZVI particles in PLA, using
457 indirect continuous monitoring of iron corrosion by means of measuring pH, ORP and conductivity. HCA
458 dechlorination involves the formation and accumulation of PCE as an intermediate compound, before its
459 subsequent reduction to non-chlorinated C_2 and C_4 compounds. The increase in Pd-mZVI dosage results in an
460 increased HCA degradation rate due to a greater production of atomic hydrogen H^*. With 600 mg of Pd-mZVI
461 particles, a temperature increase is favourable to HCA degradation as the production of H^* is accelerated, but at
462 the expense of the reactive lifetime of the particles. Increasing the initial HCA concentration to 20 mg L^{-1} leads
463 to a decrease in the degradation rate constant. Finally, an increase in PLA content decreases the global
464 degradation rate due to an enhanced contact between HCA and the particle surfaces that decreases the production
465 of H^*, but the maintaining of acidic conditions can prevent the rapid formation of any passive precipitates. Our
466 results indicate that the HCA degradation mechanism includes mass transfer, nonreductive sorption, surface
467 reaction with H^* and desorption of the product. Combined with gas chromatography, the continuous monitoring
468 of physical and chemical parameters of the bulk solution was proven to be a powerful tool in laboratory
469 experiments for the indirect investigation of dechlorination mechanisms in the Pd-mZVI/PLA/H_2O system.

Appendix A. Supplementary data

Supplementary data are associated with this article.

Declaration of interest

None

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797 **List of tables**

798 **Table 1** Pseudo-first order rate constants for HCA degradation under the different experimental conditions
799 (effects of Pd-mZVI dosage, temperature, HCA initial concentration and PLA content)

Figure number	$m_{Pd\text{-}mZVI}$ (mg)	T (°C)	$[HCA]_0$ (mg L^{-1})	m_{PLA} (mg)	k_{obs} (Eq. 12) (min^{-1})
4	150	25	10	850	0.002 (R^2 = 0.474)
	375	25	10	850	0.004 (R^2 = 0.860)
4, 5, 6, 7	600	25	10	850	0.035 (R^2 = 0.975)
5	600	12	10	850	0.004 (R^2 = 0.970)
	600	35	10	850	0.093 (R^2 = 0.939)
6	600	25	5	850	0.036 (R^2 = 0.940)
	600	25	20	850	0.010 (R^2 = 0.972)
7	600	25	10	1 700	0.030 (R^2 = 0.938)
	600	25	10	3 400	0.025 (R^2 = 0.951)

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List of figures

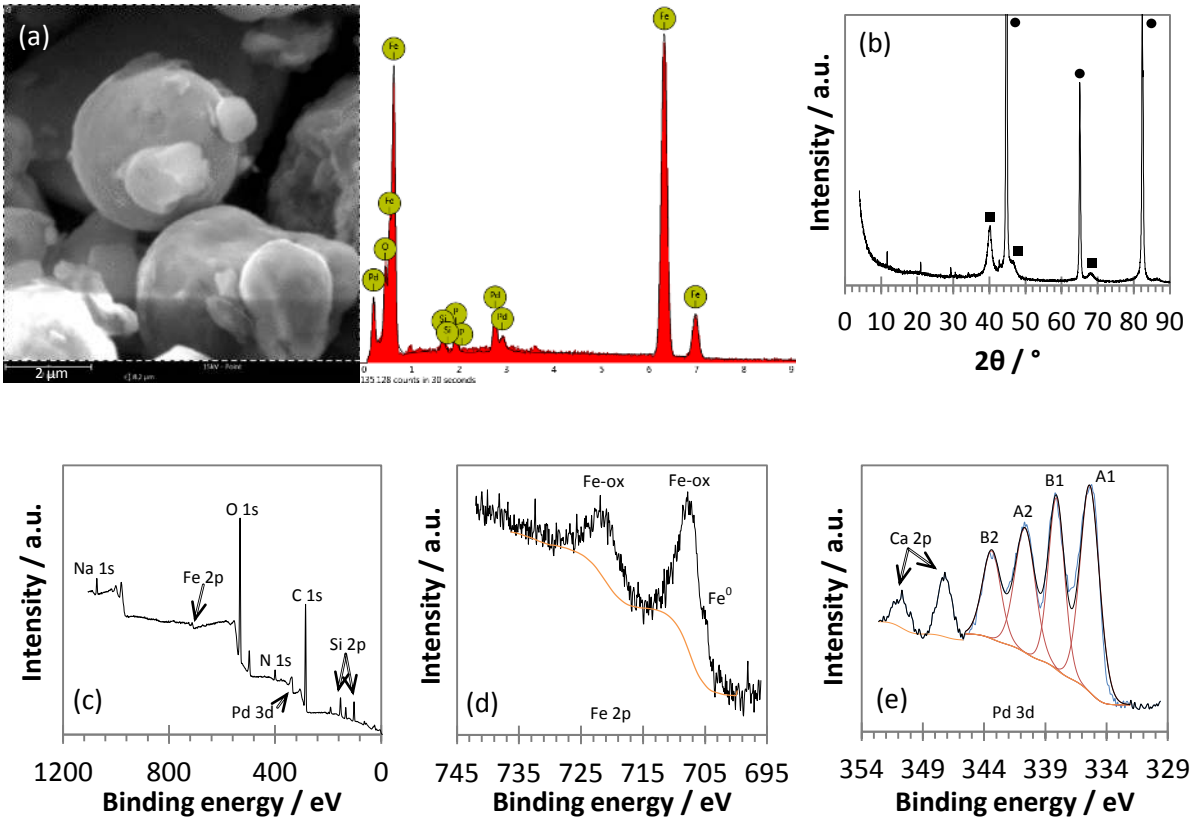

Fig. 1 Characterization of Pd-mZVI particles before reaction. (a) SEM image with EDS spectrum. The atomic concentration in the entire area is: Fe = 77.4%, O = 16.3%, Pd = 3.3%, P = 1.8%, Si = 1.2%; (b) X-ray diffraction pattern, where solid circles and squares represent Fe^0 and Pd^0, respectively; X-ray photoelectron spectra: (c) Survey scan, (d) Fe 2p, (e) Pd 3d

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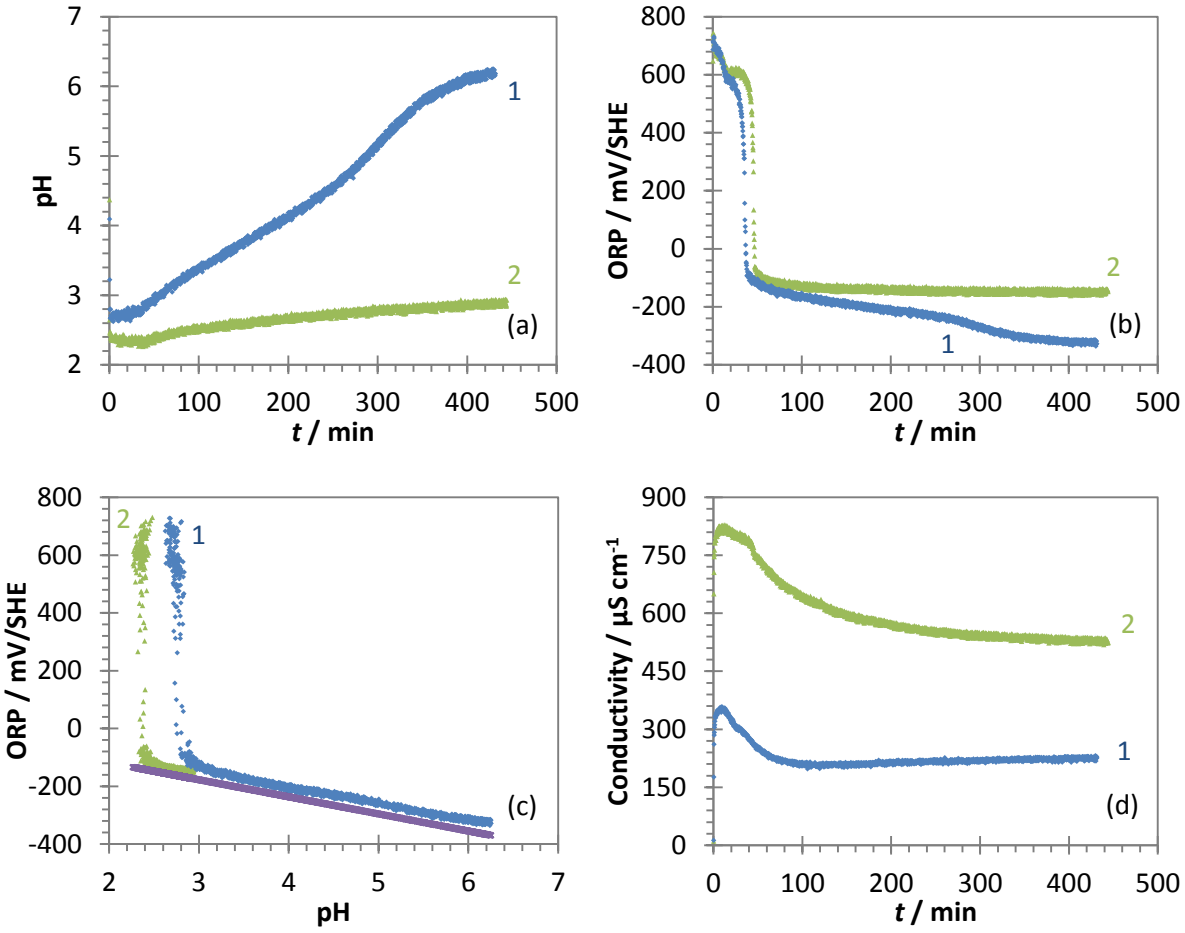

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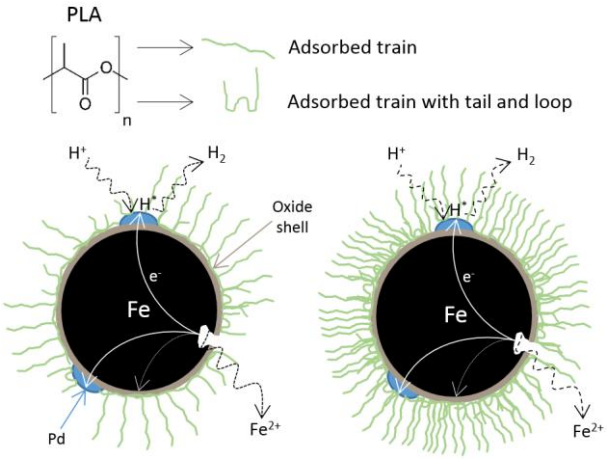
810 ◆ (1) = 850 mg PLA, ▲ (2) = 3400 mg PLA, × = H^+/H_2 redox couple

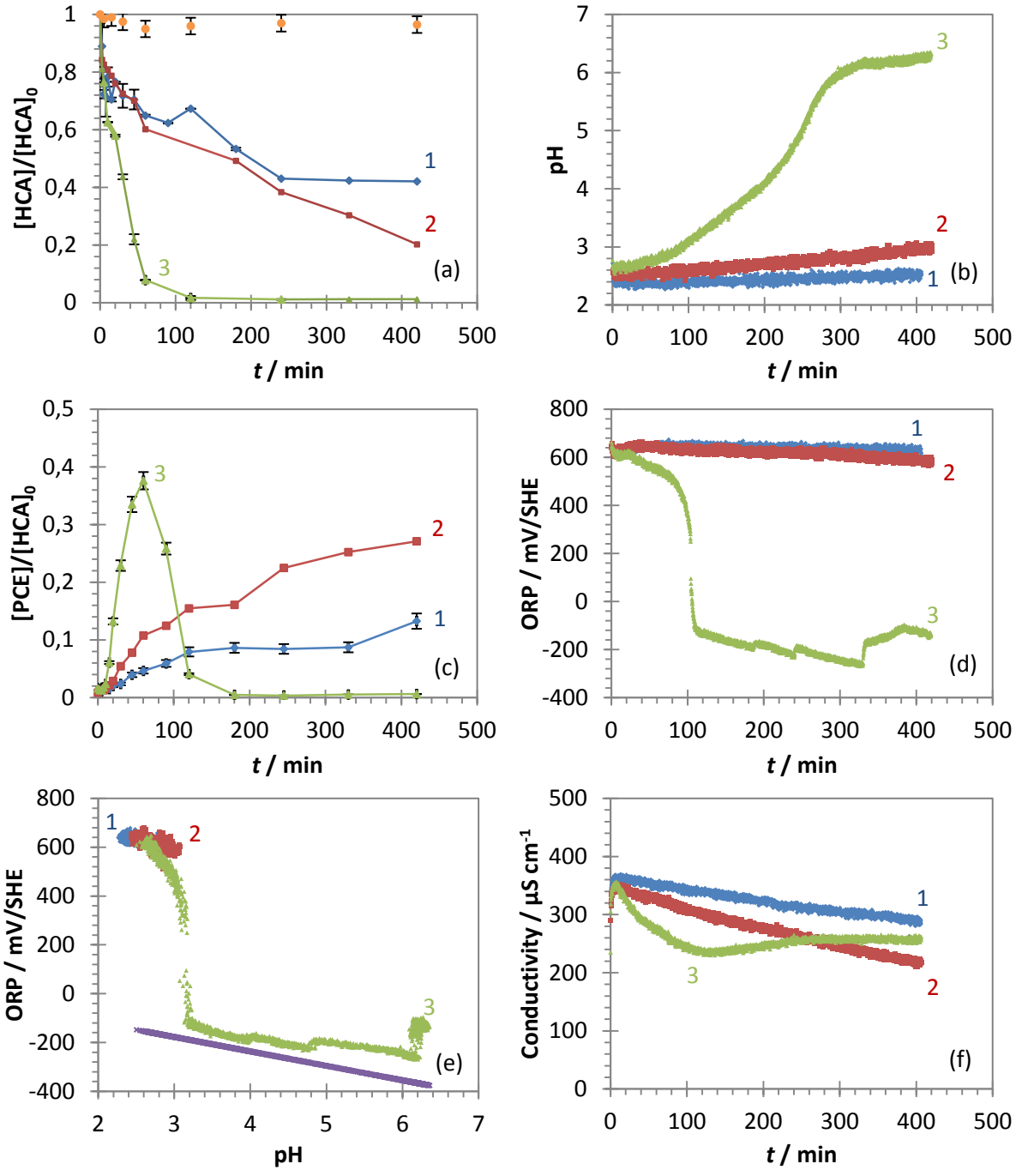
811 **Fig. 2** Monitoring of the aqueous corrosion in the Pd-mZVI/PLA/H_2O system without opening of the reactor.

812 (a) Evolution of pH with time, (b) Evolution of ORP with time, (c) Evolution of ORP with pH, (d) Evolution of

813 conductivity with time. Experimental conditions: $m_{Pd\text{-}mZVI}$ = 600 mg, T = 25 °C

814 

815 **Fig. 3** Schematic illustration of the Pd-mZVI/PLA/H_2O system, with 850 mg (left) and 3400 mg (right) of PLA.
816 Depending on the adsorbed PLA on the surface, it is represented mainly as adsorbed train or as an extended layer
817 of adsorbed train with tails and loops.



◆ (1) = 150 mg Pd-mZVI, ■ (2) = 375 mg Pd-mZVI, ▲ (3) = 600 mg Pd-mZVI, ● = blank, × = H^+/H_2 redox couple

Fig. 4 Effects of Pd-mZVI dosage on HCA dechlorination in the Pd-mZVI/PLA/HCA/H_2O system. (a) Evolution of HCA concentration with time, (b) Evolution of pH with time, (c) Evolution of PCE concentration with time, (d) Evolution of ORP with time, (e) Evolution of ORP with pH, (f) Evolution of conductivity with time. Experimental conditions: $[HCA]_0$ = 10 mg L^{-1}, m_{PLA} = 850 mg, T = 25 °C. Error bars in parts a and c represent standard deviation for n = 2

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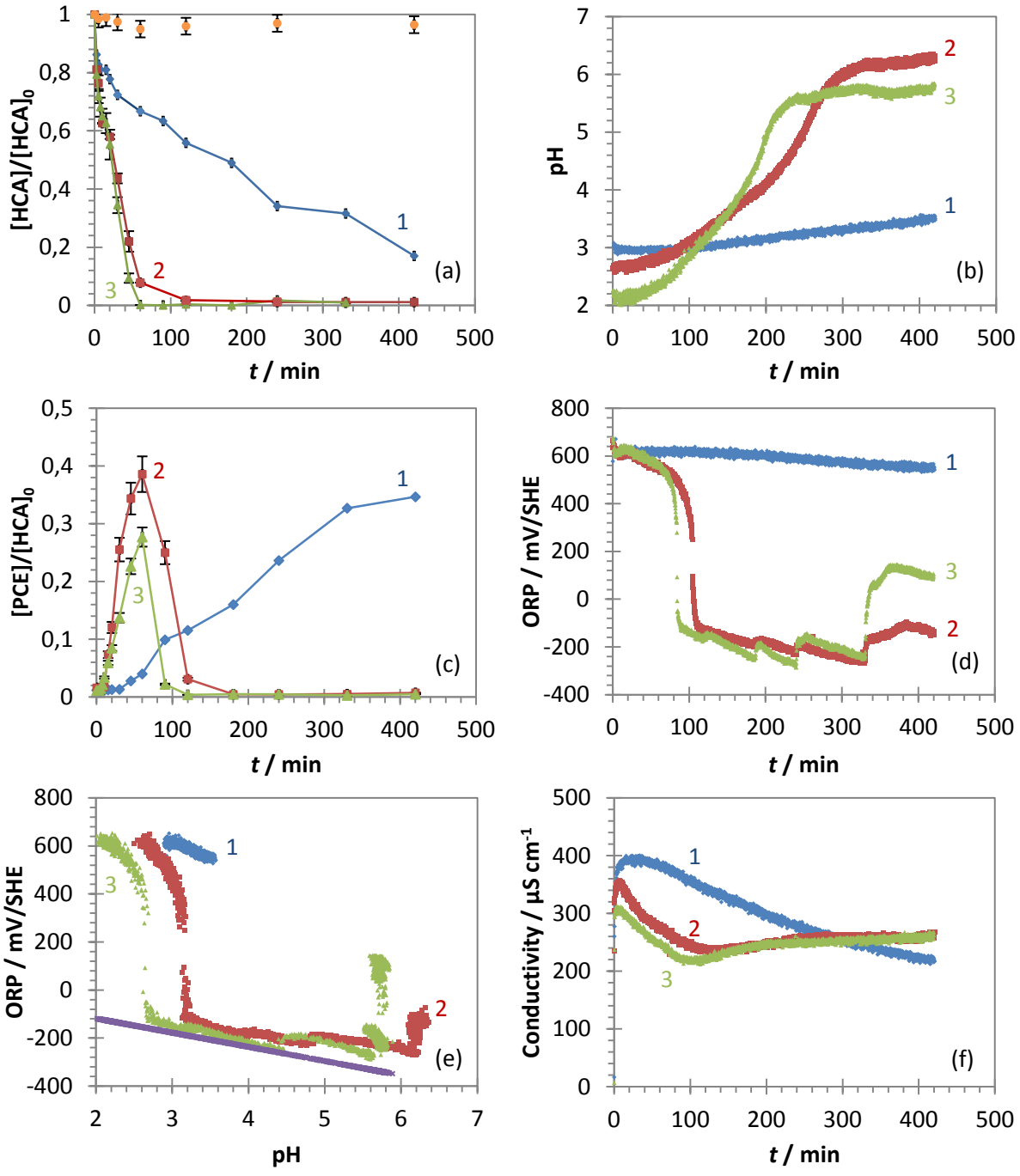

830 ◆ (1) = 12 °C, ■ (2) = 25 °C, ▲ (3) = 35 °C, ● = blank, × = H^+/H_2 redox couple

831 **Fig. 5** Effects of temperature on HCA dechlorination in the Pd-mZVI/PLA/HCA/H_2O system. (a) Evolution of
832 HCA concentration with time, (b) Evolution of pH with time, (c) Evolution of PCE concentration with time, (d)
833 Evolution of ORP with time, (e) Evolution of ORP with pH, (f) Evolution of conductivity with time.
834 Experimental conditions: $[HCA]_0$ = 10 mg L^{-1}, $m_{Pd\text{-}mZVI}$ = 600 mg, m_{PLA} = 850 mg. Error bars in parts a and c
835 represent standard deviation for n = 2

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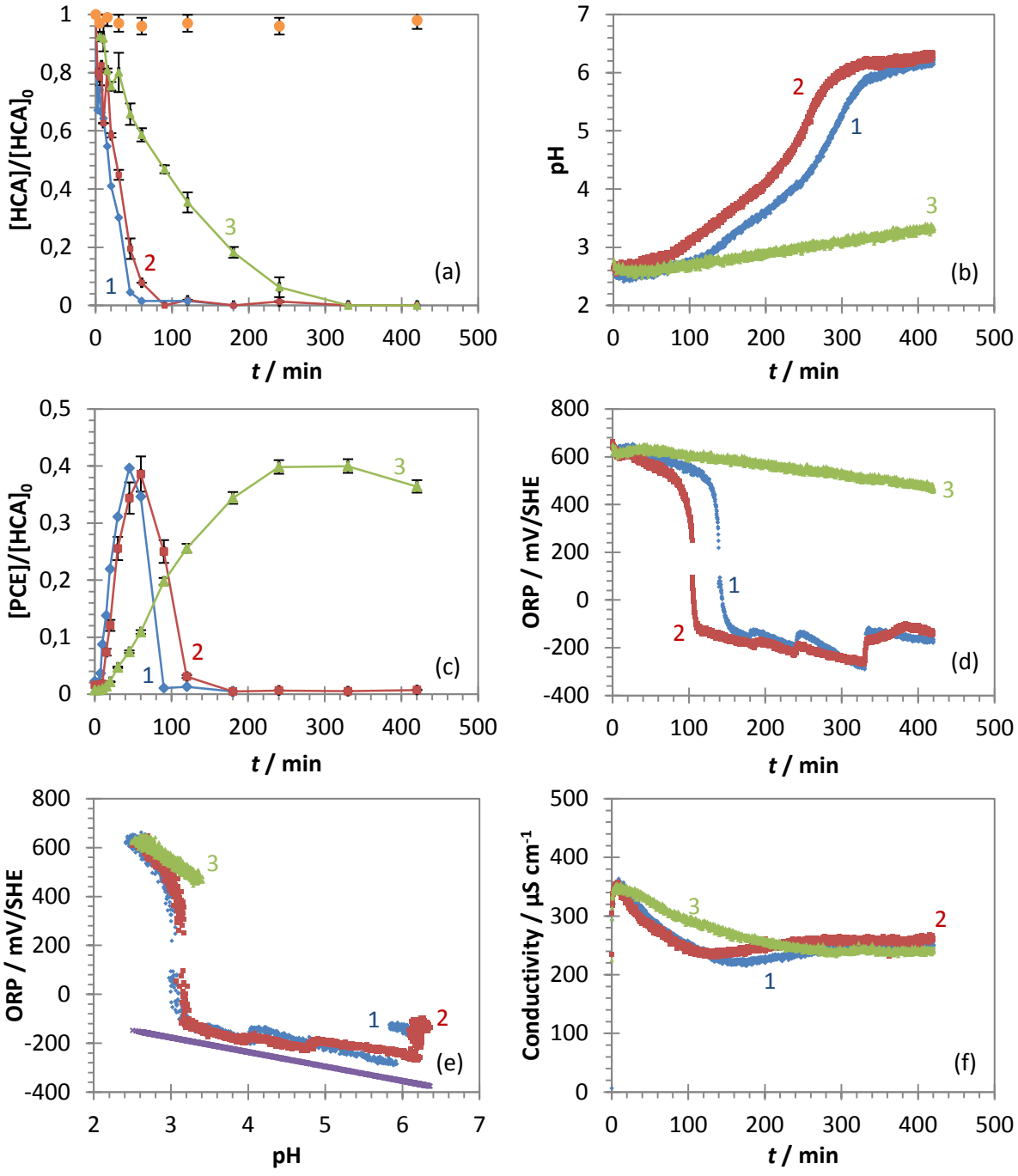
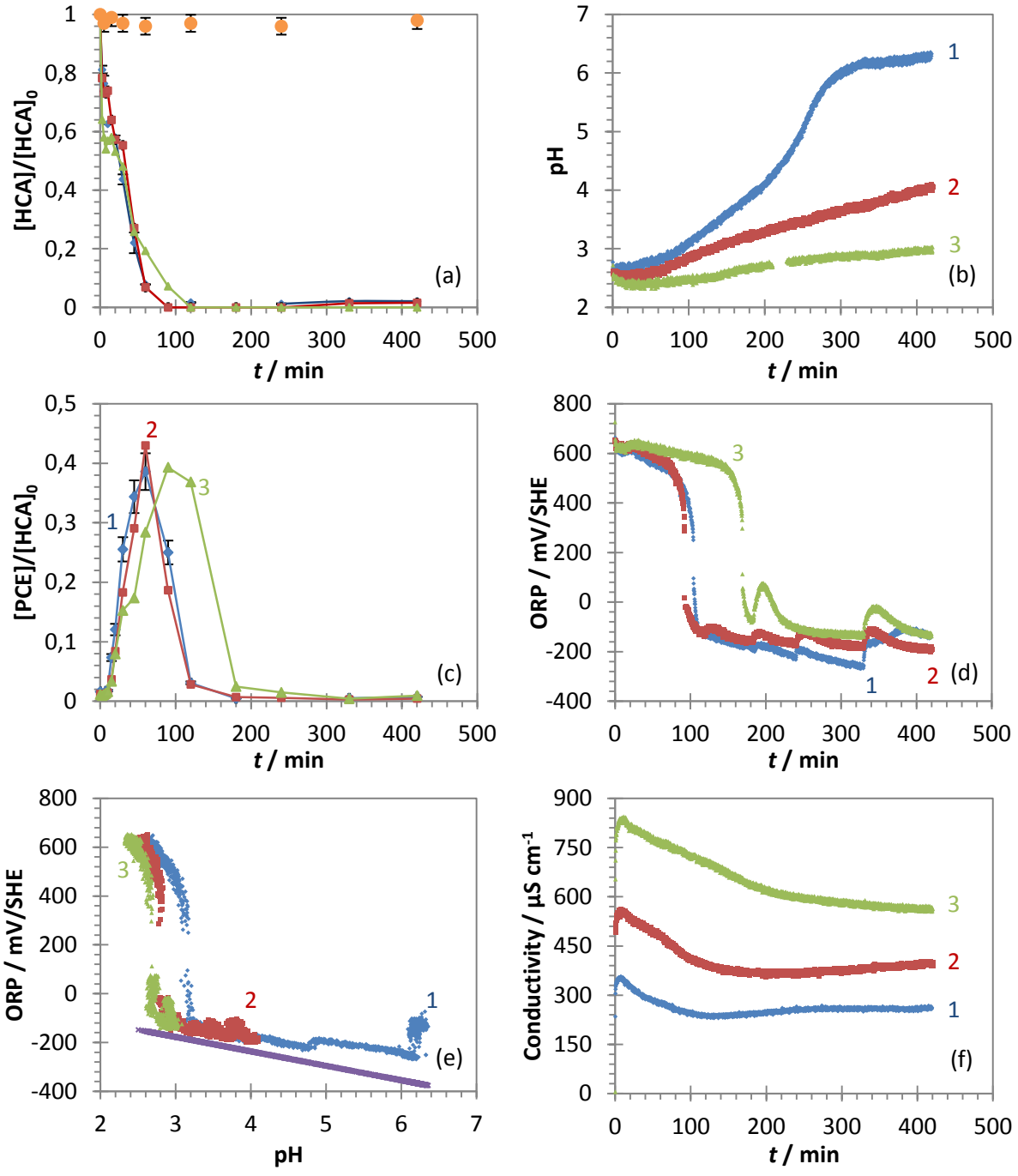


839 ◆ (1) = 5 mg L^{-1}, ■ (2) = 10 mg L^{-1}, ▲ (3) = 20 mg L^{-1}, ● = blank, × = H^+/H_2 redox couple

840 **Fig. 6** Effects of initial HCA concentration on its dechlorination in the Pd-mZVI/PLA/HCA/H_2O system. (a)
841 Evolution of HCA concentration with time, (b) Evolution of pH with time, (c) Evolution of PCE concentration
842 with time, (d) Evolution of ORP with time, (e) Evolution of ORP with pH, (f) Evolution of conductivity with
843 time. Experimental conditions: $m_{Pd\text{-}mZVI}$ = 600 mg, m_{PLA} = 850 mg, T = 25 °C. Error bars in parts a and c
844 represent standard deviation for n = 2



◆ (1) = 850 mg PLA, ■ (2) = 1 700 mg PLA, ▲ (3) = 3 400 mg PLA, ● = blank, × = H^+/H_2 redox couple

Fig. 7 Influence of PLA content on HCA dechlorination in the Pd-mZVI/PLA/HCA/H_2O system. (a) Evolution of HCA concentration with time, (b) Evolution of pH with time, (c) Evolution of PCE concentration with time, (d) Evolution of ORP with time, (e) Evolution of ORP with pH, (f) Evolution of conductivity with time. Experimental conditions: $[HCA]_0$ = 10 mg L^{-1}, $m_{Pd\text{-}mZVI}$ = 600 mg, T = 25 °C. Error bars in parts a and c represent standard deviation for n = 2

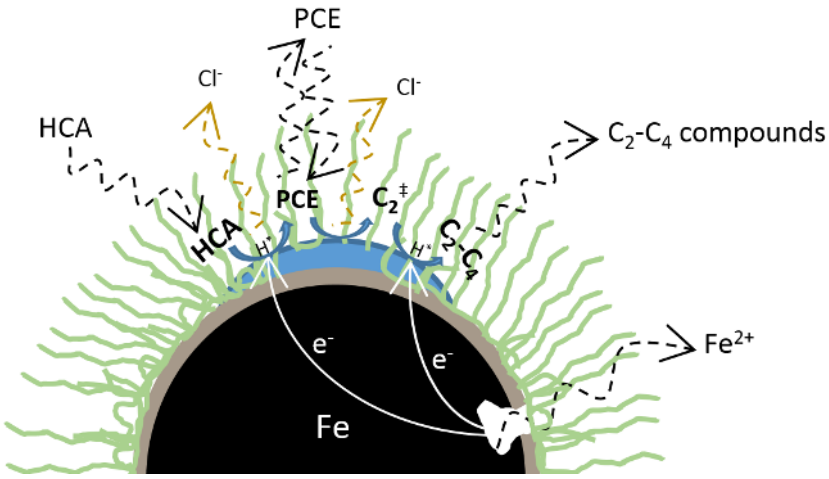


Fig. 8 Schematic illustration of reductive HCA dechlorination in the Pd-mZVI/PLA/HCA/H_2O system. Reactions proposed in Fig. 3 (production of atomic hydrogen H^*) and in this figure (HCA dechlorination) may occur simultaneously