A three-electrode column for Pd-catalytic oxidation of TCE in groundwater with automatic pH-regulation and resistance to reduced sulfur compound fouling

Songhu Yuan\textsuperscript{a,b,∗}, Mingjie Chen\textsuperscript{c}, Xuhui Mao\textsuperscript{b}, Akram N. Alshawabkeh\textsuperscript{b,∗}

\textsuperscript{a} State Key Lab of Biogeology and Environmental Geology, China University of Geosciences, 388 Lumo Road, Wuhan 430074, PR China
\textsuperscript{b} Department of Civil and Environmental Engineering, Northeastern University, 400 Snell Engineering, 360 Huntington Avenue, Boston, MA 02115, United States
\textsuperscript{c} Atmospheric, Earth and Energy Division, Lawrence Livermore National Laboratory, P.O. Box 808, L-184, Livermore, CA 94550, United States

\date{Article history:
Received 2 June 2012
Received in revised form 13 September 2012
Accepted 4 October 2012
Available online 13 October 2012}

\date{Keywords:
Pd
Electrolytic
TCE
Groundwater remediation
Reduced sulfur compounds}

\date{A B S T R A C T

A hybrid electrolysis and Pd-catalytic oxidation process is evaluated for degradation of trichloroethylene (TCE) in groundwater. A three-electrode, one anode and two cathodes, column is employed to automatically develop a low pH condition in the Pd vicinity and a neutral effluent. Simulated groundwater containing up to 5 mM bicarbonate can be acidified to below pH 4 in the Pd vicinity using a total of 60 mA with 20 mA passing through the third electrode. By packing 2 g of Pd/Al\textsubscript{2}O\textsubscript{3} pellets in the developed acidic region, the column efficiency for TCE oxidation in simulated groundwater (5.3 mg/L TCE) increases from 44 to 59 and 68% with increasing Fe(II) concentration from 0 to 5 and 10 mg/L, respectively. Different from Pd-catalytic hydrodechlorination under reducing conditions, this hybrid electrolysis and Pd-catalytic oxidation process is advantageous in controlling the fouling caused by reduced sulfur compounds (RSCs) because the in situ generated reactive oxidizing species, i.e., O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2} and *OH, can oxidize RSCs to some extent. In particular, sulfite at concentrations less than 1 mM even greatly increases TCE oxidation by the production of SO\textsubscript{4}\textsuperscript{−}, a strong oxidizing radical, and more "OH.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Electrochemical methods have attracted great interests for water treatment, particularly for degradation of biorefractory pollutants (Brillas et al., 2009; Chen, 2004; Reddy and Cameselle, 2009). Contaminated groundwater has moderate electrical conductivity (500–1000 \textmu\textOmega/cm) and low concentrations of pollutants. These features support the applicability of electrochemical processes for groundwater remediation. Compared with wastewater treatment, in situ groundwater remediation requires high stability electrodes because the remediation could be applied for a few years and electrode replacement is costly. Direct oxidation or reduction of contaminants on the surface of the anode or the cathode requires special electrocatalytic electrode materials, that will work at high overpotential conditions to obtain vigorous redox condition (Anglada et al., 2009; Chen et al., 2003; Carter and Farrell, 2009; Mishra et al., 2008; Vlyssides et al., 2004; Yang et al., 2007; Zhao et al., 2010). These electrodes, e.g., boron doped diamond (Anglada et al., 2009; Carter and Farrell, 2009; Mishra et al., 2008) and Pd supported materials (Chen et al., 2003; Yang et al., 2007), can achieve high degradation
efficiency. However, they are costly and are difficult to implement for large-scale groundwater remediation.

The products of water electrolysis, H₂O, O₂, H⁺ and OH⁻ (1–2), using low-cost stable electrodes, such as Ti-based mixed metal oxide (Ti/MMO), provide opportunities for combining electrolysis with other processes for groundwater remediation. For example, O₂ produced at the anode can be used for aerobic degradation (Franz et al., 2002; Lohner and Tiehm, 2009; Lohner et al., 2011), H₂ produced at cathode can be delivered for anaerobic degradation (Lohner and Tiehm, 2009; Lohner et al., 2011; Weathers et al., 1997), and OH⁻ produced at cathode can be utilized for contaminant hydrogenolysis (Gent et al., 2009).

Although catalytic hydrodechlorination by Pd and H₂ is very effective in transformation of chlorinated solvents in groundwater (Chaplin et al., 2012; Hildebrand et al., 2009; Lowry and Reinhard, 2000, 2001; Nutt et al., 2005; Schueth et al., 2004), transportation, storage and in situ injection of gaseous H₂ is hazardous and costly. As a solution, in situ generation of H₂ at the cathode by water electrolysis (2) is proposed for Pd-catalytic hydrodechlorination of chlorinated organics (Mcnab and Ruiz, 1998; Zheng et al., 2012). Simultaneous generation of O₂ at the anode (1) may compete for [H] and suppress contaminant hydrogenolysis (Lowry and Reinhard, 2000). Our recent work shows that anodic O₂ may combine with cathodic H₂ on Pd surface generating H₂O₂ (3) (Yuan et al., 2011), which can be decomposed to strong oxidizing OH radicals (oxidation potential: 2.8 V vs SHE) by Pd and intrinsic Fe(II) in groundwater (4) (Yuan et al., 2012). In this hybrid electrolysis and Pd catalytic process, oxidation instead of hydrodechlorination is proven as the dominant pathway for trichloroethylene (TCE) degradation (Yuan et al., 2012). Weak acidity (pH ≤ 4) is required to attain high degradation efficiency, which could be critical for actual application.

\[
\begin{align*}
2\text{H}_2\text{O} & \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \\
2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{H}_2 + \text{O}_2 & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{H}^+ \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{H}_2\text{O}
\end{align*}
\]

It is well recognized that reduced sulfur compounds (RSCs), which are produced from anaerobic bacterial respiration in aquifers, dramatically deactivate Pd during hydrodechlorination (Chaplin et al., 2012; Davie et al., 2008; Lowry and Reinhard, 2000; Schueth et al., 2004). Oxidizing reagents, such as hypochlorite (Chaplin et al., 2007; Davie et al., 2008; Lowry and Reinhard, 2000), hydrogen peroxide (Schueth et al., 2004), and permanganate (Angeles-Wedler et al., 2008), can regenerate sulfur-fouled Pd catalyst to some extent by oxidizing RSCs, and co-existence of MnO₄⁻, an oxidant, can also prevent Pd deactivation (Angeles-Wedler et al., 2008). When water electrolysis is combined with Pd catalytic oxidation in the presence of Fe(II), the in situ generated reactive oxidizing species, i.e., O₂, H₂O₂ and ·OH, are capable of oxidizing RSCs simultaneously while degrading contaminants, thereby preventing Pd deactivation. Our recent preliminary results in batch setups show that sulfite significantly enhances TCE oxidation whereas sulfide slightly inhibits the oxidation under electro-generated oxidizing conditions (Yuan et al., 2012). However, the mechanism for the distinct influence has not been elucidated. In particular, the unexpected degradation enhancement in the presence of sulfite, as well the transformation kinetics under flow conditions are interesting and requires investigation.

In this study, a Pd-containing electrolytic column using three electrodes, two cathodes and one anode, is developed to achieve automatic pH-regulation, that is, weak acidity in Pd vicinity and neutral effluent. The column performance is evaluated for transformation of TCE, a common contaminant at many sites in the United States, in simulated groundwater. The reactive transport of contaminants is simulated, and the influence of sulfite and sulfide on degradation under flow conditions is evaluated. Ultimately, the main objectives are to evaluate contaminant degradation with automatic electrochemical pH-regulation, and to reveal the mechanism for the influence of RSCs on TCE degradation by the process.

2. Materials and methods

2.1. Chemicals

TCE (99.5%) and cis-dichloroethylene (cis-DCE, 97%) were purchased from Sigma–Aldrich. H₂O₂ (30%) and Na₂SO₃ (98.1%) were purchased from Fisher Sci. Na₂S·9H₂O (98%) and tert-butylic alcohol (TBA, 99%) were obtained from Acros. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was provided by Cayman Chemical Company (USA). Excess TCE was dissolved into 18.2 mℓ/cm high-purity water to form a TCE saturated solution (1.07 mg/mL at 20 °C), which was used as stock solution for preparing aqueous TCE solutions. Palladium on alumina powder (1% wt. Pd, Sigma–Aldrich) with average particle size of 6 μm was used as catalyst in batch experiments. Palladium on alumina pellet (0.5% wt. Pd, Sigma–Aldrich) at much larger average size of 3.2 mm (Fig. S1 in Supporting Information) was used in column experiments. Deionized water (18.0 mℓ/cm) obtained from a Millipore Milli-Q system was used in all the experiments. All chemicals used in this study were above analytical grade.

2.2. Three-electrode column experiments

A vertical acrylic column (3.175 cm inner diameter × 30 cm length) (Fig. 1) was used for flow-through experiments. Three pieces of MMO mesh were installed in sequence as Anode, Cathodes 1 and 2. Preliminary results indicate that Fe(II) was precipitated prior to Pd vicinity when Cathode 1 was placed at the bottom, so the aforementioned electrode sequence is employed. 2 g of Pd/Al₂O₃ pellets were supported by Cathode 1 reaching a monolayer of pellet bed. This dosage of catalyst is employed because moderate removals of contaminants can be achieved to facilitate comparisons. By adjusting the rheostat, small fraction of current will pass through Cathode 2 so that an automatic pH-regulation can be achieved. No fillings were packed between the Anode and Cathode 1 in order to reduce the electric resistance. All the remaining space in the column was packed with 4-mm glass bead with a porosity of 0.65. The
total and pore volume (PV) of the column are 245 and 160 mL, respectively. Simulated TCE-contaminated groundwater (5.3 mg/L) was prepared by dissolving TCE-saturated solution in 3 mM Na$_2$SO$_4$ and 0.5 mM CaSO$_4$ deoxygenated solution (~800 \$\mu$S/cm). The simulated contaminated groundwater was stored in gas-tight collapsing bad. Prior to electrolysis, the column was flushed by 2 PVs of contaminated groundwater. Adsorption of TCE on Pd/Al$_2$O$_3$ pellets and glass beads was measured to be insignificant. The flow rate was maintained at 2 mL/min (0.25 cm/min) using a peristaltic pump (Cole Parmer). A total current of 60 mA, with voltage varying from 22 to 30 V, was sustained with 40 and 20 mA passing through Cathodes 1 and 2, respectively. At regular time intervals, 1 mL of aqueous solution was sampled from 6 ports (see Fig. 1 for locations) and immediately mixed with 1 mL of methanol for analysis.

Four sets of column experiments were conducted with testing parameters as listed in Table 1. The first set (Columns C1–C4) evaluates the automatic pH-regulation at different operation conditions and different bicarbonate concentrations. The second set (Columns C5–C9) evaluates the performance of contaminant oxidation with automatic pH-regulation in the presence of different concentrations of Fe(II). The third set (Columns C10–C11) investigates the influence of sulfite and sulfite on TCE degradation. And the last set (Column C12) assesses the long-term performance of this process on resisting fouling by sulfide.

![A schematic of three-electrode column.](image)

**Table 1 – Parameters and results associated with column experiments.**

<table>
<thead>
<tr>
<th>No*</th>
<th>Column description</th>
<th>Steady-state pH</th>
<th>Fitted rate constants $k$ (min$^{-1}$)</th>
<th>Removal efficiency$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pd vicinity</td>
<td>Effluent</td>
<td>At electrodes</td>
</tr>
<tr>
<td>C1</td>
<td>3 mM Na$_2$SO$_4$ + 0.5 mM CaSO$_4$</td>
<td>2.5–3.0</td>
<td>7.5–8.0</td>
<td>–</td>
</tr>
<tr>
<td>C2$^c$</td>
<td>3 mM Na$_2$SO$_4$ + 0.5 mM CaSO$_4$</td>
<td>3.5–4.0</td>
<td>6.5–7.5</td>
<td>–</td>
</tr>
<tr>
<td>C3</td>
<td>3 mM Na$_2$SO$_4$ + 2 mM NaHCO$_3$</td>
<td>3.5–4.5</td>
<td>7.5–8.5</td>
<td>–</td>
</tr>
<tr>
<td>C4</td>
<td>3 mM Na$_2$SO$_4$ + 5 mM NaHCO$_3$</td>
<td>3.5–5.0</td>
<td>8.0–8.5</td>
<td>–</td>
</tr>
<tr>
<td>C5</td>
<td>5.3 mg/L TCE, no Pd/Al$_2$O$_3$, 10 mg/L Fe(II)</td>
<td>2.5–3.5</td>
<td>6.5–7.0</td>
<td>0.090$^d$</td>
</tr>
<tr>
<td>C6</td>
<td>5.3 mg/L TCE, no Pd/Al$_2$O$_3$, 10 mg/L Fe(II)</td>
<td>2.5–3.5</td>
<td>6.5–7.0</td>
<td>0.090$^d$</td>
</tr>
<tr>
<td>C7</td>
<td>5.3 mg/L TCE, 2 g Pd/Al$_2$O$_3$, 5 mg/L Fe(II)</td>
<td>2.5–4.0</td>
<td>6.5–7.5</td>
<td>0.090$^d$</td>
</tr>
<tr>
<td>C8</td>
<td>5.3 mg/L TCE, 2 g Pd/Al$_2$O$_3$, 5 mg/L Fe(II)</td>
<td>2.7–4.0</td>
<td>6.5–7.5</td>
<td>0.090$^d$</td>
</tr>
<tr>
<td>C9</td>
<td>5.3 mg/L TCE, 2 g Pd/Al$_2$O$_3$, 10 mg/L Fe(II)</td>
<td>2.7–4.5</td>
<td>6.5–7.5</td>
<td>0.090$^d$</td>
</tr>
<tr>
<td>C10</td>
<td>5.3 mg/L TCE, 2 g Pd/Al$_2$O$_3$, 1 mM sulfite</td>
<td>2.5–4.5</td>
<td>6.5–7.5</td>
<td>0.090$^d$</td>
</tr>
<tr>
<td>C11</td>
<td>5.3 mg/L TCE, 2 g Pd/Al$_2$O$_3$, 5 mg/L Fe(II), 31.3 $\mu$M sulfide</td>
<td>2.5–4.5</td>
<td>6.5–7.5</td>
<td>0.090$^d$</td>
</tr>
<tr>
<td>C12$^f$</td>
<td>5.3 mg/L TCE, 2 g Pd/Al$_2$O$_3$, 5 mg/L Fe(II), 31.3 $\mu$M sulfide</td>
<td>2.5–4.5</td>
<td>6.5–7.5</td>
<td>0.090$^d$</td>
</tr>
</tbody>
</table>

---

*a* For C5–C11, 3 mM Na$_2$SO$_4$ and 0.5 mM CaSO$_4$ were dissolved in groundwater as background electrolytes.

*b* Removal efficiency refers to total fitted removal percentages of TCE in columns under steady state.

*c* Two electrodes were used.

*d* Reaction rate at Cathode 1.

*e* Reaction rate at Cathode 2.

*f* A much longer period of 10 d was lasted.

*g* Time-dependent rate constants in the region between Anode and Cathode 2.
2.3. Degradation in batch mode

The same experimental setup as reported previously (Yuan et al., 2012) is used for degradation of TCE in batch setup at ambient temperature (25 ± 1 °C). Experimental details are described in Section S1 in the Supporting Information.

2.4. Chemical analysis

TCE, cis-DCE, phenol and toluene were measured by a 1200 Infinity Series HPLC (Agilent) equipped with a 1260 DAD detector and a Thermo ODS C18 column (4.6 × 50 mm). The mobile phase was a mixture of acetonitrile and water (60:40, v/v) at 1 mL/min. The detection wavelength was 210 nm. Sulfite at concentration higher than 1 mM was also measured by HPLC using the same procedure as for TCE analysis. Sulfide was detected at 665 nm on a spectrometer (Caly & Whitmore Corp.) after coloration with TiSO4 (Eisenberg, 1943).

The •OH levels were determined by DMSO trapping and HPLC according to the literature (Section S2, Tai et al., 2004). In order to identify the generation of new radicals, 100-µL sample collected from the batch degradation system without contaminants was immediately mixed with 25 µL of 0.2 M DMPO to form DMPO-radical adduct, which was then collected from the batch degradation system without contaminants was immediately mixed with 25 µL of 0.2 M DMPO to form DMPO-radical adduct, which was then trapped at 405 nm after coloration with TiSO4 (Eisenberg, 1943).

The •OH levels were determined by DMSO trapping and HPLC according to the literature (Section S2, Tai et al., 2004). In order to identify the generation of new radicals, 100-µL sample collected from the batch degradation system without contaminants was immediately mixed with 25 µL of 0.2 M DMPO to form DMPO-radical adduct, which was then measured by electron spin resonance (ESR) assay. The ESR spectra were obtained on a Bruker EMX ESR spectrum with dimethyl-p-phenylene (Environmental Protection Administration of China, 2002), and H2O2 was analyzed at 405 nm after coloration with TiSO4 (Eisenberg, 1943).

The •OH levels were determined by DMSO trapping and HPLC according to the literature (Section S2, Tai et al., 2004). In order to identify the generation of new radicals, 100-µL sample collected from the batch degradation system without contaminants was immediately mixed with 25 µL of 0.2 M DMPO to form DMPO-radical adduct, which was then measured by electron spin resonance (ESR) assay. The ESR spectra were obtained on a Bruker EMX ESR spectrum with dimethyl-p-phenylene (Environmental Protection Administration of China, 2002), and H2O2 was analyzed at 405 nm after coloration with TiSO4 (Eisenberg, 1943).

3. Results and discussion

3.1. Automatic pH-regulation in three-electrode columns

Using the three-electrode electrolytic column, groundwater pH within the Pd vicinity quickly dropped to about 2.5 in the absence of bicarbonate (Fig. 2a). As one third of the cathodic current is shared by Cathode 2, the H+ produced at Anode is theoretically one third more than the OH− produced at Cathode 1. Moreover, because no beads were filled in the space between Anode and Cathode 1, OH− produced at Cathode 1 was immediately neutralized by H+ produced at Anode under the assistance of electro-generated bubbling of O2 and H2. In contrast, the space between Cathodes 1 and 2 was fully packed with Pd/Al2O3 pellets and glass beads, OH− produced at Cathode 2 was difficult to migrate to the Pd vicinity in an opposite direction to groundwater flow. Consequently, the automatic development of low pH within the Pd vicinity was attained. As a comparison, the pH in the Pd vicinity dropped to only 3.5 in the conventional two-electrode column.

The automatic pH-regulation is further evaluated using bicarbonate buffering groundwater. Fig. 2a shows that pH within the Pd vicinity quickly declined to 3.5 in the presence of 2 mM bicarbonate, and the decrease occurred slowly when 5 mM bicarbonate was present. Theoretical calculation of bicarbonate concentrations that can be acidified by the three-electrode column indicate that 20 mA of total 60 mA shared by Cathode 2 is capable of decreasing the pH of a 6.3 mM bicarbonate solution to a value of 4.0 (Table S1). Fig. 2b shows that neutral effluent can be maintained in this three-electrode column. The local acidity developed around Pd catalyst provides the possibility of contaminant oxidation in the presence of Fe(II) (Yuan et al., 2012). This is the first study to report automatic pH-regulation of groundwater using a three-electrode column system.
3.2. TCE degradation in columns

TCE degradation reached steady state after 120 min of operation (1.5 PVs) in a typical column (Fig. S3). As shown in Fig. 3a, the steady-state TCE concentrations along columns demonstrate a quick decrease when passing through Pd/Al₂O₃ fillings. Note that the decrease in TCE concentration before Pd is due to the diffusion process because no fillings were packed between Anode and Cathode 1. Without Pd/Al₂O₃ packing, TCE removals attained 31 and 36% in the absence (C5) and presence (C6) of 10 mg/L Fe(II), respectively. This suggests that the electro-Fenton process based on Ti/MMO electrode could slightly contribute to TCE oxidation. With Pd/Al₂O₃ packing, the removals of TCE increased from 44% in the absence of Fe(II) (C7) to 59% in the presence of 5 mg/L Fe(II) (C8), and further to 68% in the presence of 10 mg/L Fe(II) (C9) (Table 1). This trend is in accordance with those reported in batch experiment (Yuan et al., 2012), suggesting a dominant oxidation pathway for TCE degradation in the presence of Fe(II). Under the acidic conditions that automatically develop, more H₂O₂ was produced on Pd surface (Yuan et al., 2011, 2012), and more Fe(II) was in the form of free Fe²⁺. Thus, more oxidizing ·OH radicals were generated by the classical Fenton reaction resulting in efficient oxidation of TCE. Negligible degradation was observed after groundwater passed through Cathode 2 because negligible ·OH can be generated from Fe(II) and H₂O₂ under neutral and alkaline conditions (Yuan et al., 2012).
The reactive transport of contaminants in the column was simulated by incorporating reaction term into convection dispersion equation (smooth curves in Fig. 2). The reactions responsible for contaminant degradation in different regions are discussed in Section S3. As summarized in Table 1, with the increase in Fe(II) concentration from 0 to 5 and further to 10 mg/L, the degradation rate constants in Pd vicinity increased from 0.018 to 0.042 and further to 0.069 min⁻¹, respectively. Note that the apparent high rate constants at the electrodes are due to the small region for electrode reaction. As a result, it can be concluded that the hybrid electrolysis and Pd-catalytic process with automatic pH-regulation is capable of oxidizing TCE in groundwater with Fe(II) at concentration levels on the order of mg/L.

3.3. Effect of RSCs on TCE degradation

RSCs are recognized as Pd fouling agents in groundwater remediation (Davie et al., 2008; Lowry and Reinhard, 2000, 2001; Schueth et al., 2004). However, in the present study 1 mM sulfite greatly enhanced TCE degradation; that is, the transformation rate constants increased from 0.042 to 0.072 min⁻¹, while 31.3 μM sulfide (1 mg/L) did not result in any significant fouling effect (Fig. 3b). The mechanism for this unexpected influence of sulfite is discussed in the following section. For the influence of sulfite on TCE degradation, the results from batch experiment suggest increasing inhibition with increasing sulfide concentration (Fig. S4). However, this inhibition is much less pronounced when compared with Pd-catalytic hydrodechlorination under anaerobic condition (Lowry and Reinhard, 2000; Schueth et al., 2004). Both precipitation and oxidation may lead to the removal or transformation of sulfide. According to the solubility product constant of FeS (K_{sp} = 3.7 \times 10^{-19}) and dissociation constants of H_{2}S (pK_{a1} = 7.04, pK_{a2} = 11.96), the precipitation of sulfide was thermodynamically favorable but was calculated to be negligible at groundwater conditions of 5 mg/L Fe(II) and pH 6. Oxidation of sulfide on the MMO electrodes was addressed recently (Pikaar et al., 2011), and was also confirmed herein (Fig. S5). Furthermore, the in situ generated reactive oxidizing species, i.e., O_2, H_2O_2, and ·OH (Chen and Morris, 1972; Hoffmann, 1977), may also oxidize sulfide, thus preventing Pd deactivation.

3.4. Mechanism for sulfite-enhanced degradation

A series of batch experiments were conducted to elucidate the unexpected enhancement caused by sulfite. TCE degradation increased remarkably with the increase in sulfite concentration from 0 to 1 mM (Fig. 4a), while the production of ·OH was approximately within the same concentration range (Fig. 4b). In the presence of 3 mM sulfite, TCE degradation is slightly inhibited within initial 30 min compared with the absence of sulfite, and afterward the degradation promptly increased (Fig. 4a). At the inflexion time of 30 min, sulfite concentration decreased to less than 1 mM (Fig. S6). The production of ·OH was negligible within 40 min at 3 mM sulfite (Fig. 4b), indicating the minor contribution of ·OH oxidation to TCE degradation at this stage. It is noted that the degradation kinetics deviated from zero order in the absence of sulfite to first order in the presence of sulfite (<1 mM), whereas the generation of ·OH still followed zero order. This further suggests a new mechanism for TCE degradation in addition to ·OH oxidation in the presence of sulfite.

Since inhibition by sulfite is recognized for Pd-catalytic hydrodechlorination under anaerobic conditions (Davie et al., 2008; Lowry and Reinhard, 2000; Schueth et al., 2004), the enhancement herein must be related to the generation of oxidizing species. It is reported that SO_3^{2-} can be induced by oxidizing species to produce SO_4^{2-}, which combines with O_2 generating a strong oxidizing radical of SO_4^{1-} (2.5–3.1 V/SHE, 3.1 V/SHE, 274 W A T E R  R E S E A R C H  4 7  ( 2 0 1 3 )  2 6 9 – 2 7 8)
To identify the possible contribution of SO₄²⁻, the degradation was observed by the addition of methanol and TBA, respectively, as methanol scavenges both •OH and SO₄²⁻ while TBA scavenges only •OH (Guan et al., 2011; Liang and Su, 2009). The different inhibitory effect (Fig. 5a) implies the generation of SO₄²⁻. Note that TCE degradation with TBA addition again conformed to zero order kinetics implying a constant generation rate of SO₄²⁻ (Yuan et al., 2012). ESR assay was further employed to identify the generation of new radicals (Fig. 5b).

Characteristic spectrum of •OH with hyperfine coupling constants of \( a^H = 14.9 \text{ G} \) and \( a^H = 16.0 \text{ G} \) was evident by the addition of Fe(II) (Ranguelova et al., 2012). When 1 mM sulfite was introduced at the beginning of the experiment, several new signals appeared, which can be presumably attributed to the generation of SO₄²⁻ and unknown S-centered radicals (Guan et al., 2011; Shi et al., 1994). Because of the low concentration and weak response of SO₄²⁻, the ESR signals were not observed. However, the transformation of SO₄²⁻ to SO₃²⁻ in the presence of O₂ was proved by ESR simulation (Ranguelova et al., 2012). Note that the signals of •OH were enhanced compared with Fe(II) addition initially, which may also contribute to TCE degradation.

Then, what species are responsible for the generation of SO₄²⁻ and SO₃²⁻? Degradation of TCE in the anodic compartment with 1 g/L Pd/Al₂O₃ and 1 mM sulfite addition was negligible (Fig. S7a), and the influence of sulfite on conventional Fenton degradation is minimal (Fig. S7b). As a result, anodic oxidation, free •OH and H₂O₂ in solution can not transform SO₃²⁻ to SO₄²⁻ in this study. Based on these validation results, the combination of oxidizing species with Pd catalyst, probably the as-generated H₂O₂ and •OH chemisorbed on Pd surface, were assumed to be responsible for the transformation of SO₃²⁻. As a consequence, the following mechanism is proposed for sulfite-enhanced degradation. SO₃²⁻ donates one electron to the as-generated H₂O₂ or •OH chemisorbed on Pd surface producing SO²⁻ (7), which further combines with O₂ with the production of SO₄²⁻ (8). The one-electron reduction of SO₄²⁻ yields an oxidizing species of HSO₅⁻ (peroxymonosulfate, 1.82 V/SHE) (9), which may be transformed to •OH (10) and SO₄²⁻ (11) in the presence of Fe²⁺. Both •OH and SO₄²⁻ contribute to TCE oxidation. Because the generation of SO₄²⁻ is dependent on instantaneous SO₃²⁻ concentration, the total concentrations of •OH and SO₄²⁻ varied during degradation process, resulting in the deviation of degradation kinetics from zero to first order.

\[
\begin{align*}
\text{SO}_3^{2-} + \cdot \text{OH} & \rightarrow \text{SO}_2^- + \text{OH}^- & k_2 &= 9.5 \times 10^9 \text{M}^{-1}\text{s}^{-1} \\
\text{SO}_3^- + \text{O}_2 & \rightarrow \text{SO}_4^- & k_2 &= 1.5 \times 10^9 \text{M}^{-1}\text{s}^{-1} \\
\text{SO}_4^- + \text{H}^+ + e^- & \rightarrow \text{HSO}_5^- & k_2 &= 1.4 \times 10^8 \text{M}^{-1}\text{s}^{-1} \\
\text{HSO}_5^- + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{SO}_4^- & (10) \\
\text{HSO}_5^- + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{SO}_4^- & (11)
\end{align*}
\]
vicinity decreased from 0.041 min\(^{-1}\) in initial stage to a constant value of 0.020 min\(^{-1}\) after 4 d. The field application of Pd-catalytic hydrodechlorination of TCE in groundwater suggests that the catalytic activity of Pd can be maintained for several years (Davie et al., 2008). Therefore, a long longevity can be proposed for this hybrid electrolysis and Pd-catalytic oxidation process even in the presence of RSCs.

3.6. Implications for groundwater remediation

Using phenol and toluene as representatives of other groundwater contaminants, significant degradations are also achieved (Fig. S8). Therefore, it is technologically feasible to apply this three-electrode system for the degradation of a wide range of organic contaminants in groundwater. However, the application is dependent on groundwater conditions, i.e., buffering capacity, Fe(II) and Cl\(^{-}\) concentrations, etc. A low buffering capacity (<5 mM bicarbonate) is preferred for the automatic development of low pH in the Pd zone. The concentration of Fe(II) in groundwater at the ppm levels is required to catalyze the production of \(^{•}\)OH, while the concentration of Cl\(^{-}\) cannot be too high (<20 mM) to scavenge the \(^{•}\)OH radicals (Yuan et al., 2012). In the case of very low concentrations of Fe(II), iron-containing materials such as Fe\(_3\)O\(_4\), zerovalent iron or iron anode with small fraction of or periodical anodic current can be mixed with Pd catalysts to supply Fe(II) (Joo et al., 2005; Mao et al., 2011; Navalon et al., 2010).

As Pd catalyst is supported on the first cathode in this application, the corrosion and release of Pd (which is toxic) will be insignificant due to the cathodic protection. The leaching of Pd is measured to be minimal in our recent study using Pd and cathodic H\(_2\) for contaminant hydrodechlorination (Zheng et al., 2012). The local low pH developed in the reaction zone may also avoid or alleviate the precipitation of groundwater cations, i.e., Ca\(^{2+}\), Mg\(^{2+}\), which is found to be significant and detrimental under electrochemically developed alkaline conditions (Lohner et al., 2011). The local acidity and in situ generated oxidizing species, H\(_2\)O\(_2\) and \(^{•}\)OH have the potential to inhibit the growth of microorganism on the catalyst surface.

4. Conclusions

This study shows that a three-electrode system is capable of developing local low pH conditions for Pd-catalytic oxidation of contaminant along with neutral effluent, even in the presence of bicarbonate. In theory, any desired pH values can be developed by adjusting total current and current partition. This configuration provides an alternative approach to developing appropriate pH conditions in the subsurface wherein chemical addition is difficult. The column performance in the degradation of TCE, phenol and toluene proves the feasibility of this hybrid electrolysis and Pd-catalytic oxidation process for groundwater remediation. As oxidizing rather than reducing conditions are developed, RSCs can be oxidized by the reactive oxidizing species, i.e., \(O_2\), H\(_2\)O\(_2\) and \(^{•}\)OH. As a consequence, this process has certain potential to resist the fouling caused by RSCs. SO\(_4\)\(^{-}\), a strong oxidizing radical, and more \(^{•}\)OH can be produced in the presence of low concentration of sulfite in the process, which greatly contributes to contaminant oxidation. This mechanism is quite different from that under reducing conditions.

Acknowledgment

This work was supported by the US National Institute of Environmental Health Sciences (NIEHS, Grant No. P42ES017198), the Natural Science Foundation of China (NSFC, No. 41172220), and the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan) (No. CUGL110608). We appreciate the assistance in ESR assay by Prof. David Budil and Mr. Xianzhe Wang in Department of Chemistry & Chemical Biology, Northeastern University. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS, the National Institutes of Health or Lawrence Livermore National Security, LLC.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2012.10.009.

References

Anglada, A., Urtiaga, A., Ortiz, I., 2009. Pilot scale performance of the electro-oxidation of landfill leachate at boron-doped


