Published in final edited form as:

Chemosphere. 2019 February ; 216: 556–563. doi:10.1016/j.chemosphere.2018.10.143.

Immobilized palladium-catalyzed electro-Fenton's degradation of chlorobenzene in groundwater

Roya Nazari¹, Ljiljana Raji², Ali Ciblak¹, Sebastián Hernández³, Ibrahim E. Mousa⁴, Wei Zhou^{1,5}, Dibakar Bhattacharyya³, and Akram N. Alshawabkeh^{1,*}

¹Department of Civil and Environmental Engineering, Northeastern University, 400 Snell Engineering, 360 Huntington Avenue, Boston, MA 02115, USA

²Pioneer Valley Coral and Natural Science Institute 1 Mill Valley Road, Hadley, Ma 01035

³Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA

⁴Department of environmental biotechnology, Genetic Engineering and Biotechnology Research Institute, University of Sadat city, Menoufia, 22857Egypt

⁵Department of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, P.R. China

Abstract

This study investigates the effect of palladium (Pd) form on the electrochemical degradation of chlorobenzene in groundwater by palladium-catalyzed electro-Fenton (EF) reaction. In batch and flow-through column reactors, EF was initiated via in-situ electrochemical formation of hydrogen peroxide (H₂O₂) supported by palladium on alumina powder or by palladized polyacrylic acid (PAA) in a polyvinylidene fluoride (PVDF) membrane (Pd-PVDF/PAA). In a mixed batch reactor containing 10 mg L⁻¹ Fe²⁺, 2 g L⁻¹ of catalyst in powder form (1% Pd, 20 mg L⁻¹ of Pd) and an initial pH of 3, chlorobenzene was degraded under 120 mA current following a first-order decay rate showing 96% removal within 60 min. Under the same conditions, a rotating Pd-PVDF/PAA disk produced 88% of chlorobenzene degradation. In the column experiment with automatic pH adjustment, 71% of chlorobenzene was removed within 120 min with 10 mg L⁻¹ Fe²⁺, and 2 g L⁻¹ catalyst in pellet form (0.5% Pd, 10 mg L⁻¹ of Pd) under 60 mA. The EF reaction can be achieved under flow, without external pH adjustment and H₂O₂ addition, and can be applied for in-situ groundwater treatment. Furthermore, the rotating PVDF-PAA membrane with immobilized Pd-catalyst showed an effective and low maintenance option for employing Pd catalyst for water treatment.

Graphical Abstract

*corresponding author: aalsha@coe.neu.edu; Tel: +1 617 373 3994.

Competing interest: None

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Keywords

Electro-Fenton's reaction; Pd catalyst; chlorobenzene; groundwater remediation; three-electrode flow system

1. Introduction

Extensive use of chlorobenzene by industry has caused significant contamination in soil and groundwater (Wang et al., 2008; Moreira et al., 2012). Chlorobenzene bio-accumulates through the food chain and may cause cancer, mutagenesis, and damage to the nervous system (Zhang et al., 2011) and has been identified as a priority pollutant by the US Environmental Protection Agency (EPA) with a maximum contaminant level (MCL) of 100 $\mu\text{g L}^{-1}$ (US EPA).

Different methods have been developed to transform chlorobenzene into less toxic byproducts, including catalytic hydrodechlorination (Lee et al., 2009; Lee et al., 2010; Pagano et al., 2011), incineration (Veriansyah and Jae-Duck, 2007; Liu et al., 2011), biodegradation (Ma et al., 2005; Ziagova and Liakopoulou-Kyriakides, 2007), and adsorption (Liu et al., 2011). Advanced oxidation processes such as ultrasonic oxidation (Stavarache et al., 2003; Liu et al., 2009), ozone oxidation (Babuponnusami and Muthukumar, 2012), sonolysis (Jiang et al., 2009; Liu et al., 2011), H_2O_2 oxidation (Liu et al., 2009), photo-catalytic oxidation (Tahiri et al., 1998; Liu et al., 2009; Liu et al., 2011), and Fenton's reaction (Wang et al., 2008) were also investigated for chlorobenzene degradation. Chlorobenzene degradation intermediates induced by Electro-Fenton process are mostly aromatic and aliphatic (short-chain carboxylic acids) (Liu et al., 2009; Zazou et al., 2016).

Electrochemical methods offer the advantage of in-situ formation and control of oxidizing and reducing conditions. However, in-situ groundwater remediation requires high stability electrodes because it could be applied in-situ for a few years (Doering et al., 2001; Chen, 2004; Brillas et al., 2009; Yuan et al., 2013a; Rajic et al., 2015). Electrochemically-induced transformation can occur via direct or indirect oxidation and/or reduction mechanisms (Liang et al., 2007; Yuan et al., 2007; Rajic et al., 2015; Rajic et al., 2016a; Nazari et al., 2018). Indirect oxidation and reduction processes use electrolysis products for contaminant transformation. This allows the use of low-cost stable and reusable electrodes (e.g. Ti-based

mixed metal oxide or Ti/MMO). Examples of indirect electrochemical transformations of contaminants include reduction of chlorinated solvents through hydrodechlorination, which is supported by Pd catalyst and H₂ produced at the cathode (Rajic et al., 2015; Rajic et al., 2016b) and electrochemically-induced oxidation via Fenton's reaction (Kavitha and Palanivelu, 2004; Liang et al., 2007; Yuan et al., 2012; Yuan et al., 2013a; Wood et al., 2017; Nazari et al., 2018).

In the EF reaction, H₂O₂ is electro-generated via direct O₂ reduction at the cathode (Eq. (1)). Pd-catalyzed EF system supports H₂O₂ generation through a reaction between O₂ and H₂ produced at the anode and cathode, respectively (Eq. (2)) (Yuan et al., 2011; Yuan et al., 2013a; Nazari et al., 2018). H₂O₂ then, in the presence of a Fe²⁺ ion, generates hydroxyl radicals (•OH) (Eq. (3)). Following the reaction described in (Eq. (3)), Fe³⁺ is reduced at the cathode (Eq. (4), Eq. (5)). Electro-Fenton's reaction has been an effective method for transformation of chlorinated solvents in groundwater due to its intrinsic Fe²⁺ content (Gui et al., 2013).

Pd catalysts have been studied for the reduction of contaminants in drinking water (Young, 1999) while studies of Pd catalysts use for H₂O₂ production are limited (Xie et al., 2013; Yuan et al., 2013a). Pd catalyst increases H₂O₂ production rate by a catalytic combination of electro-generated H₂ and O₂ on Pd surface has been tested for degradation of contaminants (Yuan et al., 2011, Yuan et al., 2013a).

Membranes containing reactive nanoparticles (Fe/Pd) immobilized in a polymer film (polyacrylic acid, PAA-coated polyvinylidene fluoride, PVDF membrane) have shown high efficiency for hydrodechlorination of various chlorinated contaminants (King and Farlow, 2000; De Laat and Le, 2005). Studies reported the use of PVDF microfiltration membranes

with nominal pore sizes ranging from 200 to 650 nm and once they are functionalized with PAA, these PVDF/PAA membranes can hold nanoparticles with sizes from 50 to 200 nm (Gui et al., 2015; Hernández et al., 2015; Islam et al., 2018). The main benefits of these PVDF/PAA membranes include an open structure and a high internal surface area which ensure a high nanoparticle loading and easy active site accessibility, which further provides high active area for the catalytic activity (Smuleac et al., 2010; Hernández et al., 2014; Hernández et al., 2015). These characteristics make these membranes promising materials for supporting H₂O₂ generation and EF reaction, which has not been investigated in previous works, especially to support H₂O₂ generation.

In this study, we evaluate the effect of palladium form, as in a powder and as in a membrane, in the application of EF for chlorobenzene. Chlorobenzene is chosen due to its high toxicity, low biodegradability and because it is considered a model molecule of dioxins-like chemicals (Liu et al., 2001; Ma et al., 2005; Wang et al., 2008). The electrochemical degradation of chlorobenzene in groundwater was tested by Pd-catalyzed electro-Fenton's reaction in a two-electrode batch reactor. The treatment efficiency was investigated under different Fe²⁺ concentrations, initial pH values and current as well as Pd catalyst loading and forms, among which we tested the performance of a functionalized polyacrylic acid (PAA)/polyvinylidene fluoride (PVDF) membrane with Pd⁰ nanoparticles (no iron). The chlorobenzene degradation in a three-electrode column with automatic pH regulation was also evaluated and optimized relative to same conditions including flow rate.

2. Materials and Methods

2.1. Materials

A summary of chemicals used in this study is provided in Supporting information (SI). For membrane functionalization: acrylic acid (AA, 99%), palladium (II) nitrate hydrate (Pd(NO₃)₂), sodium borohydride (NaBH₄, 99.99%) (Sigma-Aldrich, St. Louis, MO, USA); ammonium persulfate (APS, (NH₄)₂S₂O₈) (EM Science for Merck KGaA, Darmstadt, Germany); sodium hydroxide (NaOH) solution, sodium chloride (NaCl), (Fisher Scientific, Fair Lawn, NJ, USA); isopropyl alcohol (IPA, 99.9%) and N,N'-methylenebis(acrylamide) (MBA > 99%) (Acros, New Jersey, NJ, USA); commercial scale hydrophilized PVDF microfiltration membranes (average pore size: 500 nm, thickness: 125 µm, diameter: 4.7 cm) (Nanostone, Oceanside, CA, USA). The surface area for calculations was based on the top surface area of the membrane (17.35 cm²).

Chlorobenzene-contaminated groundwater was prepared by mixing chlorobenzene saturated stock solution in background electrolyte in presence of different concentrations of Fe²⁺ ions. In all tests, initial chlorobenzene concentration was set to 5 mg L⁻¹ and its concentration in stock solution was 500 mg L⁻¹. 10 mM Na₂SO₄ solution was used as background electrolyte for all experiments. Preliminary tests using sulfate and carbonate as buffer showed that lower pH (Fig. SM-3,(SI)) values can be reached using sulfate comparing to carbonate and thus sulfate was chosen as the buffer here to optimize electro Fenton process. H₂SO₄ was used to adjust the initial pH of the solution. All tests were performed at room temperature. The analysis of this study can be found in Section 2.2 (SI).

2.3. Experimental Setup

2.3.1. Batch Tests—A one-liter acrylic cell (Fig. SM-1a-b in SI) was used as a batch electrochemical cell. Two titanium based mixed metal oxide (Ti/MMO, IrO₂/Ta₂O₅ coating on titanium mesh type, 3N international, USA) meshes with dimensions of 85 mm × 15 mm × 1.8 mm (length × width × thickness) and a surface area of 11.8 cm² were used as anode and cathode with a cathode-anode spacing of 4 cm.

Specific mass (0–2 g) of palladium on alumina was added to the solution with a stirring rate of 180 rpm. Experiments were also performed in a system shown in Fig. SM-1b, where Pd immobilized on polyacrylic acid (PAA) polyvinylidene fluoride (PVDF) membrane was used as a static disk (Pd-PVDF/PAA) mounted in Teflon holder as well as connected to the rotor (set at 180 rpm). The PVDF membrane was functionalized with PAA by in situ polymerizations of acrylic acid (Hernández et al., 2015). This functionalization is a free radical polymerization in a solution of AA in the PVDF matrix. The monomer solution, AA (20 wt. % aqueous solution) with MBA as cross-linker (1.0 mol % of AA) and APS (1.0 mol % of AA), is passed through the membrane several times and then is put at 70 °C for 0.25 to 1 hr in a N₂ atmosphere. A double ion exchange of NaCl/ Pd(NO₃)₂ on the carboxylic groups of the PAA is then performed on the PVDF/PAA membranes using NaCl (1 g/L of Na; pH ≈ 10.5; T = 21 °C) and subsequently Pd(NO₃)₂ (200 mg L⁻¹ of Pd; pH = 4.6; T = 21 °C). The Pd-PVDF/PAA membrane was prepared by reducing the Pd (II) from the ion exchange using NaBH₄, creating Pd NPs. Based on the ICPMS analysis, the amount of Pd in Pd-PVDF/PAA is 1.6 mg cm⁻² (27.8 mg) and there was no detectable leaching of Pd from both Pd/Al₂O₃ and Pd-PVDF/PAA catalysts. Adsorption of chlorobenzene on Pd/Al₂O₃ powder and Pd-PVDF/PAA was found to be negligible. All tested parameters are summarized in Table SM-1.

The experiments were conducted under constant current (Agilent E3612A). The current efficiency (Ø) was calculated using Faraday's law Eq. (6):

$$\varnothing = \frac{V * C * z_e * F * 100}{I_{applied} * t} \quad (6)$$

where *V* is reactor volume (L), *C* is chlorobenzene removed in the reactor (M), *z_e* is number of electrons involved in the reaction of one mole of chlorobenzene, *F* is Faraday's constant with a value of 96485 C mol⁻¹, *I_{applied}* is the current applied to the reactor (A), and *t* is experiment duration (s). Full mineralization of chlorobenzene to CO₂ was assumed and thus *z_e* value was assumed to be 28 electrons per mole. This value, however, will be different if other organic species are present.

2.3.2. Column Tests—Column tests were performed in a vertical acrylic tube (Fig. SM-2) with a 3.175 cm inner diameter and 30 cm in length. Three MMO mesh electrodes were installed in a sequence as Anode, Cathode 1 and Cathode 2. The anode was placed below both cathodes to generate acidic conditions and minimize Fe³⁺ precipitation. The current was split into two-thirds passing through Cathode 1 and one third passing through

Cathode 2 to maintain acidic conditions in the catalyst vicinity. The solution becomes acidic after the anode, then Cathode 1 decreases acidic conditions (Fig. SM-3) but does not completely neutralize the pH (which can be found in supporting information) since it receives only two third of the current. pH is then neutralized after Cathode 2. A summary of the parameters tested for the column experiments is listed in Table SM-2.

Pd/Al₂O₃ pellets and Pd-PVDF/PAA (1.6 mg Pd cm⁻²) were placed on Cathode 1. Adsorption of chlorobenzene on Pd/Al₂O₃ pellets and glass beads was insignificant. Based on the ICP-MS analysis there was no detectable leaching of Pd from either Pd/Al₂O₃ or Pd-PVDF/PAA. The column was packed with 4-mm glass beads with a total porosity of 0.65, excluding the space between the electrodes. The total and pore volumes of the column were 245 mL and 160 mL, respectively. To make sure the column is operating in steady-state conditions, measurements were performed after 160 min of operation. The flow rate of 2 mL min⁻¹ was maintained by a peristaltic pump (Cole Parmer, Masterflex C L⁻¹).

3. Results and Discussion

3.1.1. Membrane characterization

The membrane after functionalization with PAA and subsequent Pd nanoparticle synthesis shows an almost complete covering of the porous surface (Fig. 1b) compared with the bare PVDF membrane (Fig. 1a), which confirms an average pore size of 500 nm. In Fig. 1b is evident that the membrane is functionalized with PAA polymer (smooth surface) but in addition, it has a very large distribution of Pd NPs. These membranes reduce their permeability almost in two orders of magnitude (from about 1000 to 15 L (m hr bar)⁻¹) after PAA functionalization. The cross-section of the membrane shows that the Pd NPs are distributed in depth with a very dense distribution, see Fig. 1c. The depth of the Pd NPs distribution goes up to 10 µm (not shown). From the EDS spectra of the top surface of the Pd-PVDF/PAA membrane, the amount of Pd is even higher than the characteristic peak of fluorine of the PVDF, implying that the PAA layer with Pd NPs is covering most of the membrane surface. The atomic ratio Pd/Na from the reduction with NaBH₄ is 2/3 which is greater than the theoretical value of 1 Pd per 2 Na in each carboxylic group of the PAA. The ratio being higher than the theoretical is possibly due to the reduction of Pd²⁺ remaining in solution at the time of reduction and, that the ion exchange method used could have exchanged Pd²⁺ for Na⁺ in a 1/1 ratio leaving the membrane in solution partially charged before reduction.

Due to the smaller sizes of the Pd NPs, TEM was required to analyze the size and the nature of Pd NPs. Aggregated Pd NPs exhibit asymmetrical shapes, but the base particles of Pd (crystal phase) are shown with particle sizes between 2 and 5 nm (Fig. 2a). The Pd NPs size distribution was determined by image analysis (2D metrics) (Hernández et al., 2015). The characteristic particle size of 2.21±0.06 nm is based on the median of the gamma distribution (Fig. 2c) (Vaz and Fortes, 1988; Olson, 2011), which was fitted with *P*-values larger than the statistics Kolmogorov-Smirnov (*D*= 0.029, *P*> 0.250) and the Cramer-von Mises (*W-Sq*= 0.056, *P*> 0.250). Pd NPs could be identified by EDS and a selected area electron diffraction (SAED) (Fig. 2b-d). The SAED ring pattern coincided to Miller index of

Pd⁰ with face-centered cubic structure (111, d -spacing = 0.224 nm) (Mejías et al., 2009; Navaladian et al., 2009). The EDS spectra also confirm the presence of Pd (Fig. 2d).

Another important characteristic that influences on chlorobenzene removal is the effect of different pH (Fig. SM-4) which can be found on Section 3.1.2 (SI).

3.1.3. Influence of Fe²⁺ concentrations on chlorobenzene removal—The presence of Fe also influences the chlorobenzene degradation and follows a first-order reaction (Fig. 3a). In the absence of Fe²⁺, chlorobenzene removal was limited due to electro-induced reduction via hydrodechlorination mechanism at the cathode. The chlorobenzene decay rate increased from 0.002 min⁻¹ in the presence of 2 mg L⁻¹ Fe²⁺ to 0.032 min⁻¹ in the presence of 10 mg L⁻¹ Fe²⁺. The relationship between Fe concentration and chlorobenzene removal percentage is shown in Fig. 3b. Higher Fe²⁺ concentrations increase [•]OH concentration leading to improved chlorobenzene removal, which is in accordance with previous studies (Liang et al., 2007). All further tests were conducted with 10 mg L⁻¹ of Fe²⁺.

The similar results for pH (Fig. SM-4) and Fe (Fig. 3a) imply a direct relationship between the first-order rate constants and the change in pH and/or Fe concentrations: [H⁺] and [Fe²⁺] are related to the free radical production (Eq. (3)).

3.1.4. Influence of Pd catalyst concentration and form on chlorobenzene removal—Under identical conditions, an increase in Pd/Al₂O₃ concentration from 0 g L⁻¹ to 2.0 g L⁻¹ (0 mg L⁻¹ to 20 mg L⁻¹ total Pd), increased chlorobenzene removal from 48% to 84% (Fig. 4a). The first-order rate constant for chlorobenzene removal increased from 0.012 min⁻¹ in the absence of Pd/Al₂O₃ to 0.032 min⁻¹ in the presence of 2 g L⁻¹ Pd/Al₂O₃ (20 mg L⁻¹ Pd) (Table SM-3). In the absence of Pd, 48% of chlorobenzene was removed due to (a) reaction with H₂O₂ produced via two-electron reduction of anodic oxygen at the cathode, and/or (b) hydrodechlorination at the cathode (Yuan et al., 2013b). In Pd/Al₂O₃ tests, chlorobenzene removal increases from 48% in absence of a catalyst to 68% with 0.5 g L⁻¹ of Pd/Al₂O₃ (5 mg L⁻¹ Pd), with less improvement in removal with higher Pd/Al₂O₃ concentration. Addition of Pd/Al₂O₃ enhances the formation of H₂O₂, due to the high ability of Pd to capture hydrogen within its lattice as well as the high surface area available for the reaction. The relationship between Pd concentration and chlorobenzene removal percentage is shown in Fig. 4b.

Chlorobenzene removal after 60 min of treatment increases from 84% in the presence of Pd/Al₂O₃ to 88% when Pd-PVDF/PAA was used in the rotation mode (Fig. 4c). The reaction follows the first-order kinetics, with $k = 0.037 \text{ min}^{-1}$, which was the same order as the reactions supported by Pd (Table SM-3). The surface area-normalized reaction rate constant ($k_{SA} = 0.0059 \text{ L m}^{-2} \text{ min}^{-1}$) is calculated from the specific surface area of the Pd NPs ($a_S = 225.8 \pm 8.7 \text{ m}^2 \text{ g}^{-1}$), obtained from the characteristic particle size, and the Pd loading into the membrane ($\rho_M = 27.8 \text{ mg L}^{-1}$), see Eq. (7).

$$k = k_{SA} \cdot a_{S\bullet} \cdot \rho_M \quad (7)$$

The performance of the static Pd-PVDF/PAA membrane was limited although the solution was stirred under the same speed due to the limited mass transfer to Pd sites within the membrane. Rotating Pd membrane was based on the concept similar to the cage paddle for the solid phase extraction. The rotation of the membrane disk enhances mass transfer and improves the availability of reactive species. A similar concept has been also applied for a rotating disk, ringdisk or cylinder electrode used in the pre-concentration step which has been shown to greatly enhance the mass-transfer efficiency and ensures more reproducible mass-transfer conditions than stirring of the solution (Lee et al., 2008). Functionalized membrane systems prevent loss and aggregation of the catalysts, which cannot be controlled in the pellet form. Membranes have large surface-areas that increase reactivity, allowing catalyst reuse that makes them environmentally friendly. Additionally, PVDF and PAA are robust materials that may not interfere with the desired process (Hernández et al., 2015).

Although the steady-state removal increase is insignificant, the removal rate in the first 30 min of treatment increased by 44% in the Pd membrane presence. The results presented in Fig. 4d indicates that the Pd membrane supports H_2O_2 formation. In the electrochemical system, H_2O_2 concentration is determined by the generation and consumption. In the Pd-catalyzed system, H_2O_2 was electrogenerated by Pd catalyst. However, it can also be decomposed under several pathways (even without Fe^{2+}), such as disproportion, anodic oxidation on Ti/MMO (Brillas et al., 2009; Sirés et al., 2014). The decrease of H_2O_2 concentration after 20 min is because the rate of H_2O_2 decomposition exceeds its generation. For Pd membrane, it continuously increases, which indicates that the H_2O_2 generation rate is higher than H_2O_2 decomposition rate in this process. Palladium nanoparticles with a high number of Pd atoms with a low degree of coordination have been reported to be active and selective to catalyze H_2O_2 production (Campos Martin et al., 2006). This can be confirmed by the high a_S value of the Pd NPs. The removal efficiency with Pd/ Al_2O_3 and Pd-PVDF/PAA are similar but the main advantage of the Pd-PVDF/PAA use is easy application and manipulation in contrast with the Pd/ Al_2O_3 powder, which requires filtration and removal as an additional step after water treatment.

Influence of different current (Fig. SM-5a) on chlorobenzene removal and its correlation between chlorobenzene removal efficiency and applied current (Fig. SM-5b) can be found in Section 3.1.5. (SI).

3.2. Column Tests

3.2.1. Influence of Pd catalyst and Fe^{2+} on chlorobenzene removal—In the absence and presence of 1 g and 2 g of Pd/ Al_2O_3 pellets (5 mg L^{-1} and 10 mg L^{-1} Pd), the chlorobenzene removal was 29%, 60%, and 71%, respectively (Fig. 5 and Table SM-4). This is consistent with Yuan et al. 2013 where 36% of TCE removed in the absence of Pd catalyst increased to 68% in the presence of 2 g Pd/ Al_2O_3 (Liang et al., 2007). Without Pd catalysts, chlorobenzene removal was 10% after anode, 17% after Cathode 1 and 29% in the effluent.

The overall removal mechanism under these conditions is impacted by direct electrooxidation at the anode, Fenton reaction supported by H_2O_2 generated via two-electron reduction of anodic oxygen, and/or hydrodechlorination of chlorobenzene at the cathode surface.

The highest rate of chlorobenzene degradation occurs in the cathode zone, which promotes in-situ H_2O_2 generation. The presence of Pd catalyst caused a significant increase in the chlorobenzene degradation in both anode and cathode zones. The degradation in anode zone is supported by direct electro-oxidation at the anode but also by the H_2O_2 and $\cdot\text{OH}$ diffusion from the cathode zone that occurs under the applied flow rate (2 mL min^{-1}). In support to the proposed mechanism, chlorobenzene decay in anodic zone reached 15%, 18% and 20% in the absence and presence of 5 mg L^{-1} and 10 mg L^{-1} of Fe^{2+} (Fig. SM-6). The impact of Fe^{2+} concentration on chlorobenzene removal in the anodic region indicates that H_2O_2 diffusion contributes to the removal and that the degradation mechanism in this zone relies on Fenton reaction. Further, in the absence and presence of 5 mg L^{-1} and 10 mg L^{-1} of Fe^{2+} , chlorobenzene removal efficiency in the effluent was 35%, 55%, and 71%, respectively (Fig. SM-6a) and Table SM-5). Fig. SM-6b shows the correlation between removal efficiency and the Fe^{2+} concentration. These results are in accordance with batch tests, where higher Fe^{2+} concentration led to higher removal efficiencies. The more significant increase in the removal is observed in the cathode zone than anodic compartment, which is in accordance with H_2O_2 generation in Cathode 1 vicinity. The performance of Pd-PVDF/PAA membrane was insufficient due to the limited mass flux of dissolved gases towards the membrane surface. This is caused by the small pore size of the membrane material that prevented gas bubbles passage thus limited the active surface area of the Pd-PVDF/PAA.

pH value in the Pd vicinity remains <4 while maintaining a neutral effluent pH even in the presence of a buffer. This is due to current splitting between two-cathodes (Liang et al., 2007).

3.2.2. Influence of current and flow rate on chlorobenzene removal—

Increasing the current from 0 (control) mA to 60 mA increased removal in the effluent from 2.15% to 71% while 120 mA caused a decrease in the degradation (Fig. 6a and Table SM-4). Increasing the current to 60 mA enhanced the production of H_2 and O_2 and consequently H_2O_2 generation. Higher current leads to the excess formation of H_2 and O_2 bubbles that are entrapped within electrodes vicinity and cause a decrease in EF reaction efficiency as well as electric conductivity. Fig. 6b shows that the current of 60 (40–20) mA yields the highest removal rate. The current efficiency was estimated to be 13.8%, 8.8% and 3.9% for 30 mA, 60 mA, and 120 mA respectively. This can explain that the mass transfer is the limiting factor for chlorobenzene removal in a flow-through system. Furthermore, the bubbles form at the surface of the electrodes and lower the active surface area under the higher current. Therefore, the bubbles coverage of the cathode surface adversely affects hydrodechlorination and can cause the decrease in overall chlorobenzene (Rajic et al., 2016b).

The performance of the column setup was tested under flow rates of 2, 5 and 10 mL min^{-1} . The removal rates under a flow of 2, 5 and 10 mL min^{-1} were 71%, 46%, and 33%,

respectively. As presented in Fig. SM-7a and Table SM-4, lower flow rates promote chlorobenzene degradation due to an increase in a contact time of reactive species and support chlorobenzene oxidation mechanism. Fig. SM-7a shows that the degradation in both reactive zones is significantly affected by the flow. As flow rate increases, the chlorobenzene mass fluxes range from $16 \mu\text{g min}^{-1}$ to $40 \mu\text{g min}^{-1}$ and $80 \mu\text{g min}^{-1}$. However, increased flow rate decreases the retention times in the following the order: 80 min, 32 min, and 16 min, which adversely affects the oxidation of chlorobenzene but also H_2O_2 generation and $\cdot\text{OH}$ production. The correlation between the removal efficiency and the applied flow rate is linear at each sampling port (Fig. SM-7b). Overall, lower flow rate improves chlorobenzene removal.

4. Conclusions

The Pd catalyzed-EF process removed up to 96% of chlorobenzene within 60 min in batch conditions and up to 71% under flow. Up to 88% of chlorobenzene was removed when a rotating Pd-PVDF/PAA membrane disk was used. This study shows that Pd-catalytic electro-Fenton's reaction can be a sustainable method in chlorobenzene degradation and that a more stable membrane form of Pd can be effective in groundwater treatment. Future studies can gear toward applications of this method in real conditions and remediation sides. Presence of radical scavengers like carbonate in real groundwater can potentially decrease of method efficiency and needs further investigation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Institute of Environmental Health Sciences (NIEHS, Grants No P42ES017198, Northeastern University, and P42ES007380, University of Kentucky). We appreciate the assistance in the different assays by Department of Civil & Environmental Engineering, Northeastern University; and the Chemical and Materials Engineering Department, University of Kentucky. Content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS or the National Institutes of Health.

References

- Babuponnusami A, Muthukumar K, 2012 Advanced oxidation of phenol: a comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes. *Chem. Eng. J.*, 183, 1–9.
- Brillas E, Sirés I, Oturan MA, 2009 Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. *Chem. Rev* 109, 6570–6631. [PubMed: 19839579]
- Campos-Martin JM, Blanco-Brieva G, Fierro JL, 2006 Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process. *Angew. Chem. Int. Ed*, 45, 6962–6984.
- Chen G, 2004 Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol*, 38, 11–41.
- De Laat J, Le TG, 2005 Kinetics and modeling of the Fe (III)/ H_2O_2 system in the presence of sulfate in acidic aqueous solutions. *Environ. Sci. Technol*, 39, 1811–1818. [PubMed: 15819241]
- Doering F, Doering N, Iovenitti JL, Hill DG, McIlvride WA, 2001 Electrochemical remediation technologies for soil, sediment and ground water. Retrieved.
- Gui M, Ormsbee LE, Bhattacharyya D, 2013 Reactive functionalized membranes for polychlorinated biphenyl degradation. *Ind. Eng. Chem. Res*, 52, 10430–10440. [PubMed: 24954974]

- Gui M, Papp JK, Colburn AS, Meeks ND, Weaver B, Wilf I, Bhattacharyya D, 2015 Engineered iron/iron oxide functionalized membranes for selenium and other toxic metal removal from power plant scrubber water. *J. Memb. Sci.*, 488, 79–91. [PubMed: 26327740]
- Hernández S, Lei S, Rong W, Ormsbee L, Bhattacharyya D, 2015 Functionalization of flat sheet and hollow fiber microfiltration membranes for water applications. *ACS Sustain. Chem. Eng.*, 4, 907–918. [PubMed: 29392097]
- Hernández S, Papp J, Bhattacharyya D, 2014 Metal Catalyzed Hydrogel Synthesis in PVDF Membranes for Degradation of Toxic Organic Contaminants. 2014 AIChE Annual Meeting..
- Islam MS, Hernández S, Wan H, Ormsbee L, Bhattacharyya D, 2018 Role of membrane pore polymerization conditions for pH responsive behavior, catalytic metal nanoparticle synthesis, and PCB degradation. *J. Memb. Sci.*, 555, 348–361.
- Jiang M-M, Yan X-M, Zou H, 2009 Coupled Methods for Effective Degradation of Harmful Chlorobenzene. *Int. Conf. Bioinform. Biomed. Eng...* IEEE, pp. 1–6.
- Kavitha V, Palanivelu K, 2004 The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere* 55, 1235–1243. [PubMed: 15081764]
- King D, Farlow R, 2000 Role of carbonate speciation on the oxidation of Fe (II) by H₂O₂. *Mar. Chem.*, 70, 201–209.
- Lee C-L, Jou C-JG, Huang H, 2009 Degradation of chlorobenzene in water using nanoscale Cu coupled with microwave irradiation. *J. Environ. Eng.*, 136, 412–416.
- Lee C-L, Jou C-JG, Wang HP, 2010 Enhanced degradation of chlorobenzene in aqueous solution using microwave-induced zero-valent iron and copper particles. *Water Environ. Res.*, 82, 642–647. [PubMed: 20669726]
- Lee SJ, Pyun SI, Lee SK, Kang SJL, 2008 Fundamentals of rotating disc and ring–disc electrode techniques and their applications to study of the oxygen reduction mechanism at Pt/C electrode for fuel cells. *Isr. J. Chem.*, 48, 215–228.
- Liang J, Komarov S, Hayashi N, Kasai E, 2007 Improvement in sonochemical degradation of 4-chlorophenol by combined use of Fenton-like reagents. *Ultrason. Sonochem.*, 14, 201–207. [PubMed: 16837232]
- Liu L, Zhao G, Wu M, Lei Y, Geng R, 2009 Electrochemical degradation of chlorobenzene on boron-doped diamond and platinum electrodes. *J. Hazard. Mater.*, 168, 179–186. [PubMed: 19264395]
- Liu Q, Chen Y, Wang J, Yu J, Chen J, Zhou G, 2011 Electrochemical oxidation of 1, 4-dichlorobenzene on platinum electrodes in acetonitrile-water solution: evidence for direct and indirect electrochemical oxidation pathways. *Int. J. Electrochem. Sci.*, 6, 2366–2384.
- Liu Y, Luo M, Wei Z, Xin Q, Ying P, Li C, 2001 Catalytic oxidation of chlorobenzene on supported manganese oxide catalysts. *Appl. Catal. B.*, 29, 61–67.
- Ma X, Zheng M, Liu W, Qian Y, Zhang B, Liu W, 2005 Dechlorination of hexachlorobenzene using ultrafine Ca–Fe composite oxides. *J. Hazard. Mater.*, 127, 156–162. [PubMed: 16081204]
- Mejías N, Serra-Muns A, Pleixats R, Shafir A, Tristany M, 2009 Water-soluble metal nanoparticles with PEG-tagged 15-membered azamacrocycles as stabilizers. *Dalton Trans.*, 7748–7755. [PubMed: 19759949]
- Moreira IS, Amorim CL, Carvalho MF, Castro PM, 2012 Co-metabolic degradation of chlorobenzene by the fluorobenzene degrading wild strain *Labrys portucalensis*. *Int. Biodeterior. Biodegradation*, 72, 76–81.
- Navaladian S, Viswanathan B, Varadarajan T, Viswanath R, 2009 A rapid synthesis of oriented palladium nanoparticles by UV irradiation. *Nanoscale Res. Lett.*, 4, 181.
- Nazari R, Raji L, Xue Y, Zhou W, Alshawabkeh AN, 2018 Degradation of 4-Chlorophenol in Aqueous Solution by Sono-Electro-Fenton Process. *Int. J. Electrochem. Sci.*, 13, 9214–9230.
- Olson E, 2011 Particle shape factors and their use in image analysis part 1: theory. *Journal of GXP Compliance* 15, 85.
- Pagano M, Volpe A, Lopez A, Mascolo G, Ciannarella R, 2011 Degradation of chlorobenzene by Fenton-like processes using zero-valent iron in the presence of Fe³⁺ and Cu²⁺. *Environ. Technol.*, 32, 155–165. [PubMed: 21473278]

- Rajic L, Fallahpour N, Nazari R, Alshawabkeh AN, 2015 Influence of humic substances on electrochemical degradation of trichloroethylene in limestone aquifers. *Electrochim. Acta*, 181, 123–129. [PubMed: 26549889]
- Rajic L, Fallahpour N, Podlaha E, Alshawabkeh A, 2016a The influence of cathode material on electrochemical degradation of trichloroethylene in aqueous solution. *Chemosphere*, 147, 98–104. [PubMed: 26761603]
- Rajic L, Nazari R, Fallahpour N, Alshawabkeh AN, 2016b Electrochemical degradation of trichloroethylene in aqueous solution by bipolar graphite electrodes. *J. Environ. Chem. Eng.*, 4, 197–202. [PubMed: 26955517]
- Sirés I, Brillas E, Oturan MA, Rodrigo MA, Panizza M, 2014 Electrochemical advanced oxidation processes: today and tomorrow. A review. *Environ. Sci. Pollut. Res.*, 21, 8336–8367.
- Smuleac V, Bachas L, Bhattacharyya D, 2010 Aqueous-phase synthesis of PAA in PVDF membrane pores for nanoparticle synthesis and dichlorobiphenyl degradation. *J. Memb. Sci.*, 346, 310–317. [PubMed: 20161475]
- Stavarache C, Nishimura R, Maeda Y, Vinatoru M, 2003 Sonolysis of chlorobenzene in the presence of transition metal salts. *Open Chem*, 1, 339–355.
- Tahiri H, Ichou YA, Herrmann J-M, 1998 Photocatalytic degradation of chlorobenzoic isomers in aqueous suspensions of neat and modified titania. *J. Photochem. Photobiol. A Chem*, 114, 219–226.
- US EPA, Priority Pollutants. CWA Methods.: p.. <http://water.epa.gov/scitech/methods/cwa/pollutants.cfm>.
- Vaz MF, Fortes M, 1988 Grain size distribution: The lognormal and the gamma distribution functions. *Scr. Mater*, 22, 35–40.
- Veriansyah B, Jae-Duck K, 2007 Supercritical water oxidation for the destruction of toxic organic wastewaters: A review. *J. Environ. Sci.*, 19, 513–522.
- Wang J, Mei Y, Liu C, Chen J, 2008 Chlorobenzene degradation by electro-heterogeneous catalysis in aqueous solution: intermediates and reaction mechanism. *J. Environ. Sci.*, 20, 1306–1311.
- Wood RJ, Lee J, Bussemaker MJ, 2017 A parametric review of sonochemistry: control and augmentation of sonochemical activity in aqueous solutions. *Ultrason. Sonochem*, 38, 351–370. [PubMed: 28633836]
- Xie W, Yuan S, Mao X, Hu W, Liao P, Tong M, Alshawabkeh AN, 2013 Electrocatalytic activity of Pd-loaded Ti/TiO₂ nanotubes cathode for TCE reduction in groundwater. *Water Res.* 47, 3573–3582. [PubMed: 23726693]
- Young FR, 1999 Cavitation. *World Sci.*
- Yuan S. h., Wan J. z., Lu X. h., 2007 Electrokinetic movement of multiple chlorobenzenes in contaminated soils in the presence of β -cyclodextrin. *J. Environ. Sci.*, 19, 968–976.
- Yuan S, Chen M, Mao X, Alshawabkeh AN, 2013a A three-electrode column for Pd-catalytic oxidation of TCE in groundwater with automatic pH-regulation and resistance to reduced sulfur compound foiling. *Water Res.* 47, 269–278. [PubMed: 23121896]
- Yuan S, Fan Y, Zhang Y, Tong M, Liao P, 2011 Pd-catalytic in situ generation of H₂O₂ from H₂ and O₂ produced by water electrolysis for the efficient electro-Fenton degradation of rhodamine B. *Environ. Sci. Technol* 45, 8514–8520. [PubMed: 21866953]
- Yuan S, Gou N, Alshawabkeh AN, Gu AZ, 2013b Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with Ti/MMO cathode. *Chemosphere* 93, 2796–2804. [PubMed: 24125716]
- Yuan S, Mao X, Alshawabkeh AN, 2012 Efficient degradation of TCE in groundwater using Pd and electro-generated H₂ and O₂: A shift in pathway from hydrodechlorination to oxidation in the presence of ferrous ions. *Environ. Sci. Technol*, 46, 3398–3405. [PubMed: 22315993]
- Zazou H, Oturan N, Sönmez-Çelebi M, Hamdani M, Oturan MA, 2016 Mineralization of chlorobenzene in aqueous medium by anodic oxidation and electro-Fenton processes using Pt or BDD anode and carbon felt cathode. *J. Electroanal. Chem* 774, 22–30.
- Zhang LL, Leng SQ, Zhu RY, Chen JM, 2011 Degradation of chlorobenzene by strain *Ralstonia pickettii* L2 isolated from a biotrickling filter treating a chlorobenzene-contaminated gas stream. *Appl. Microbiol. Biotechnol*, 91, 407–415. [PubMed: 21499764]

Ziagova M, Liakopoulou-Kyriakides M, 2007 Comparison of cometabolic degradation of 1, 2dichlorobenzene by *Pseudomonas* sp. and *Staphylococcus xylosus*. *Enzyme Microb. Technol*, 40, 1244-1250.

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Highlights:

1. 96% of chlorobenzene was removed via electro-Fenton reaction in a batch reactor.
2. Column reactor was optimized to remove 71% of chlorobenzene without pH adjustment.
3. Both Pd/Al₂O₃ and Pd membrane were effective for H₂O₂ production.
4. Chlorobenzene degradation followed a first-order decay rate.
5. Three-electrode column supports electro-Fenton reaction.

Fig. 1.
a) Top surface bare PVDF membrane, b) top surface Pd-PVDF/PAA membrane, c) FIB cross-section cut of Pd-PVDF/PAA membrane. The Pd nanoparticles are the brightest points within the structure, d) EDX mapping of the top surface of Pd-PVDF/PAA

Fig. 2.

a) TEM of Pd nanoparticles in FIB cross-section lamella b) SAED pattern corresponds approximately to (111) of Pd⁰, c) Pd nanoparticle size distribution, d) EDS of Pd nanoparticles (presence of Cu from sample tip)

>Fig. 3.

a) Effect of Fe^{2+} concentration on CB concentration decay, and b) Fe concentration versus CB removal efficiency (Conditions: different Fe^{2+} concentrations, current: 60 mA, Pd: 20 mg L⁻¹, Na₂SO₄: 10 mM, pH= 3)

Fig. 4.

a) Degradation profiles of CB using different Pd/Al₂O₃ concentrations, and b) correlation between Pd concentration and CB removal efficiency (Conditions: Fe²⁺: 10 mg L⁻¹, current: 60 mA, Na₂SO₄: 10 mM, pH=3)

c) Comparison of Pd/Al₂O₃ performance with Pd membrane, and d) H₂O₂ production during treatment (Conditions: Fe²⁺: 10 mg L⁻¹ (no Fe²⁺ added for H₂O₂ production measurement), current: 60 mA, Na₂SO₄:10 mM, pH=3)

Fig. 5.

a) Effect of Pd catalysts presence on the degradation of chlorobenzene b) correlation between chlorobenzene removal efficiency and Pd concentration (Conditions: Fe^{2+} : 10 mg L⁻¹, different Pd concentrations, current: 60 mA, Na_2SO_4 : 10 mM, flow rate: 2 mL min⁻¹)

Fig. 6.

a) Effect of different current on the degradation of chlorobenzene b) correlation between chlorobenzene removal efficiency and applied current (Conditions: Fe²⁺: 10 mg L⁻¹, different currents, Pd: 10 mg L⁻¹, Na₂SO₄: 10 mM, flow rate: 2 mL min⁻¹)