LABORATORY TESTING OF THE POTENTIAL FOR THE INFLUENCE OF SUSPENDED SEDIMENTS ON THE ELECTROCHEMICAL REMEDIATION OF KARST GROUNDWATER

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Abstract

Due to the complicated nature of karst aquifers, many groundwater treatment technologies are difficult to implement successfully. A particular challenge arises because sediments are ubiquitous and mobile in karst systems and may either facilitate contaminant transport or act as long-term substrates for storage via sorption. However, electrochemical remediation is a promising technology to be optimized for karst aquifers due to easy manipulation and control of groundwater chemistry as well as low cost, ability for in situ application, and performance under alternative power sources. This study investigates the effects of suspended karst sediments on the electrochemical remediation of groundwater via electro-Fenton (EF) mechanism. The EF mechanism relies on direct electrolysis (i.e., water electrolysis and ferrous iron release) and indirect, electrochemically-induced processes (i.e., Pd catalyzed H_2O_2 production). These processes can be optimized for H_2O_2 generation and support of its activation to hydroxyl radicals – a powerful oxidant capable of degrading and transforming a wide range of contaminants (e.g., chlorinated solvents). In this study, we tested sediments varying in concentrations of Fe, Mn and buffering capacities. When the sediments were

introduced into the EF experiments, there were adverse effects on the H_2O_2 content: at steady state (120 min), Pd catalyzed formation of H_2O_2 decreased by 60%, 57%, and 75% in the presence of suspended sediment collected from three separate karst locations. Presented results imply that sediments' presence influences EF mechanism in electrochemical systems, but given the flexibility of the technology, it can be optimized in terms of electrode materials, current intensities and current regimes to address these challenges.

Introduction

Groundwater pollution is one of the greatest and most challenging environmental problems around the world. Toxic pollutants, defined by the EPA as those that cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions in reproduction) or physical deformations, are introduced into the environment through a variety of mediums, including mining activities, agriculture, manufacturing, vehicle emissions, improper disposal of chemicals, and more. (USEPA). As of 2009, an estimated two billion people drank polluted groundwater or breathed in toxic gases daily (Kuppusamy et al., 2016).

In response to rising pollution levels, groundwater remediation technologies continue to evolve to remove contaminants in a safe, efficient, and cost-effective manner. One emerging technology that appears favorable is that of electrochemical groundwater remediation, due to its versatility, ability to be easily controlled, cost-effectiveness, and ability to be performed in situ. The electrochemical cells can be optimized to treat a wide range of contaminants, including chlorinated compounds such as trichloroethylene (Acar et al., 1993; Rajic et al., 2016; Yuan et al., 2012). Recent field work using electrolytic reactive barriers to degrade chlorinated solvents has found their use effective, as electrode materials (titanium MMO) lifetimes are long-lasting, necessary power supplies are low (6 amps/m²), polarity reversal removes buildup of precipitates, and ultimately 90% of TCE in the field study was degraded without the formation of VC and DCE (Gilbert et al., 2010).

In particular, karst aquifers are susceptible to pollution due to direct recharge from sinkholes and other areas while challenges in implementing conventional remediation methods arise from complexity of terrain and geochemistry (Vesper et al., 2000). While electrochemical remediation implementation in karst systems requires additional investigation due to their complex nature and high flow volumes, electrochemical systems are being considered for karst aquifers, due to ease of manipulation and control of groundwater chemistry. Moreover, this technology has the potential to be modified for ex situ point-of-use treatment in locations where complex or heterogeneous aquifers make in-situ treatment difficult.

One mechanism currently studied for contaminant degradation through the electrochemical systems is oxidation via hydroxyl radicals ($\bullet$ OH). Oxygen gas produced at the anode (Eq. 1) of the reactor reacts with hydrogen gas produced at the cathode (Eq. 2), catalyzed by the presence of palladium. H_2O_2 is formed (Eq. 3), which is then catalyzed to form $\bullet$ OH in the presence of ferrous iron at low pH values (Eq. 4), in a process known as the Fenton reaction. The hydroxyl radicals, which are strong oxidants, non-discriminately degrade organic contaminants (Yuan et al., 2012).

Though the electrochemical mechanism can be optimized for maximum degradation efficiency in laboratory settings for given flow rates, electrode materials, currents, and electrolytic solutions, advanced oxidation processes are found to be influenced by naturally occurring substances (Austin et al., 2013). Specifically, Sra et al. (2010) found that, though the reaction rates were low, the presence of natural aquifer materials affected the concentrations of persulfate, a highly oxidizing chemical oxidant, relative to laboratory controls.

In particular, suspended sediments have been shown to be present in natural karst groundwater in turbidities from 0 NTU up to 200 NTU during storm events, and can reach up to 1000 NTU in sinkhole vicinities (Dussart-baptista et al., 2003; Pronk et al., 2006; Pronk et al., 2009). Due to the abundance of suspended sediments in natural karst systems, their presence during electrochemical treatments must be considered if the technology is to be used for the remediation of karst systems.

The purpose of this paper is to determine the effects that suspended sediments play on the creation of oxidizing species in an electrochemical flow-through reactor.

Materials and Methods

Materials

All chemicals used in this study were above analytical grade. $CaSO_4$ was purchased from J T Baker. Na_2SO_4 and H_2SO_4 were purchased from Fisher Scientific. NaOH was purchased from ACROS. Palladium pellets (0.5% wt. Pd on alumina pellets) were purchased from Alfa Aesar. Titanium sulfate ($TiSO_4$) was purchased from GFS Chemicals. Deionized water (18.0 m Ω cm) obtained from a Millipore Milli-Q system was used in all the experiments.

Simulated groundwater was created by mixing 3 mM Na_2SO_4 and 0.5 mM $CaSO_4$ in deionized water. Carbonates and bicarbonates were excluded from this study to decouple their effects on the electrochemical processes from the effects of suspended sediment, although H_2O_2 formation and the Fenton reaction are also expected to be affected by the high buffering capacity of karst groundwater.

Three sediment samples were collected from karst deposits in West Virginia. The samples, denoted as MC, DLC, and CTS, were sifted through 1.18 mm mesh before introducing into the reactor. Suspended sediment mixtures were mixed for two days before use; this is the amount of time necessary to reach chemical equilibrium.

Electrochemical Setup

A vertical acrylic column (Figure 1) was used as plug flow electrochemical reactor. Three titanium/ mixed metal oxide (Ti/MMO) electrodes were assembled in a sequence of anode, cathode 1, and cathode 2, from the bottom to the top of the reactor. Directly on the top of cathode 1 was one layer of glass beads, to prevent palladium/electrode direct reactions, on top of which was placed 10 g of palladium pellets ($\text{Pd}/\text{Al}_2\text{O}_3$). A constant current of 90 mA was supplied to the electrodes by DC source. Current was split between cathode 1 and cathode 2 at a corresponding ratio of 2:1 to optimize H_2O_2 production, based on prior experimental tests (data not yet published).

A constant flow rate of 5 mL/min was maintained by a peristaltic pump during 2 hours of experiment, when steady state was reached. The simulated groundwater with or without 2 g/L of suspended sediment (roughly between 100 and 1000 NTU, depending on the sediment sampling site) was supplied to the reactor. The samples

were taken from the defined sampling ports and analyzed for H_2O_2 content and pH. Experiments were conducted in duplicates.

Experimental Methods

H_2O_2 concentration was measured spectrophotometrically according to the method described by Eisenberg (1943). Samples containing suspended sediment were filtered through 0.22 μm Milipore filters prior to analysis. Excluding the removal of suspended sediment particles from solution, filtering revealed to have no additional effect on the H_2O_2 measurements (such as lowering H_2O_2 measurements relative to non-filtered samples).

Titration was performed by raising the pH of 100 mL of 2 g/L of suspended sediment samples to 10 by the addition of <1 mL 0.1 M NaOH. The pH was brought to 3 using 0.01 M H_2SO_4 .

Specific conductance (SC) and pH were measured on slurries shaken at 100 rpm for 1 hour. Following the methods of Kalra (1995) and Hanlon (2015), 1:1 sediment-water ratio was used for pH and a 1:2 ratio for SC; replicates of six samples were measured.

Instruments

H_2O_2 concentration was measured using a Shimadzu UV-1800 spectrophotometer. The pH of the solution during electrochemical experiments was measured using a portable Orion 3-Star pH meter. SC and pH of intrinsic sediment samples were measured using calibrated Hanna Instruments laboratory electrodes. Metal concentration was determined through inductively coupled plasma mass spectrometry (ICP-MS, Bruker Aurora M90) Turbidity was measured using a HACH 2100N turbidity-meter.

Results and Discussion

Sediment Chemistry

Prior to running the column experiments, sediment samples were examined for all relevant intrinsic characteristics. Specific conductance was determined to be an average of 44.78, 69.63, and 86.12 $\mu\text{S}/\text{cm}$ for MC, DLC, and CTS, respectively. The pH was determined to be an average of 7.70, 7.74, and 6.77 for MC, DLC, and CTS, respectively. Both SC and pH data are depicted in Figure 2.

The suspended sediment samples were additionally tested for turbidity and metal concentrations (Mn and Fe) using 2 g/L of the sample. The turbidity measurements

Figure 1. Electrochemical column setup.

indicated that CTS sample contains the largest number of smaller size fractions (Table 1). This is consistent to grain size analyses, not included in this study. CTS also contains the largest concentration of dissolved manganese, while DLC contains the largest concentration of dissolved iron. Both metals could play a role in the conversion of H_2O_2 in the reactor to hydroxyl radicals (Oturán et al., 2010).

As shown in Figure 3, all sediment types followed similar titration trends, although CTS was slightly dissimilar to the other two sediment types due to its increased resistance to pH changes throughout the entire titration. This increased buffering capacity could lead to greater pH resistances in the plug flow reactor, as is discussed in the following section.

Plug-Flow Experiments

The results of the plug flow H_2O_2 tests are displayed in Figure 4. The results show that the suspended sediments have a negative effect on the amount of H_2O_2 in the reactor during the experiments (Figure 4). At steady state (120 minutes), the H_2O_2 concentrations in solutions containing 2 g/L of MC, DLC, and CTS were 60%, 57%, and 75% lower than the control tests, respectively.

Figure 2. Specific conductance and pH of sediment samples MC, DLC, and CTS.

Sediment site	Mn (ppb)	Fe (ppb)	Turbidity (NTU)
MC	4.1	31.8	140
DLC	2.35	37.5	52
CTS	47.8	32.5	1254

Table 1. Leached Mn and Fe, and Turbidity of 2 g/L of suspended sediments from MC, DLC, and CTS sampling sites

Figure 3. Titrations of CTS, DLC, and MC sediment samples from pH 10 to pH 3.

The pH of the solution above the anode, cathode 1, and cathode 2, is displayed in Figure 5. Though the pH of the solution is more variable in the vicinity above cathode 1 for all sediment types, it appears that the buffering capacities of the differing sediment types do not affect their respective pH values in the cathode or the variability of the pH values.

Discussion

Suspended sediment in high concentrations has a negative impact on H_2O_2 formed during the electrochemical process used to oxidize contaminants, and can lower the production up to 75% relative to a control.

Possible sources of suspended sediment interference in H_2O_2 production include: (1) covering of the palladium and electrodes with fine particles of sediment, impeding H_2O_2 formation, (2) the catalyzed breakdown of H_2O_2 into water due to the presence of suspended sediments, and (3) increasing the production of hydroxyl radicals from H_2O_2 , catalyzed by manganese and iron from the sediments.

Based on the preliminary tests (not included in this paper) suspended sediments accumulate on the electrodes during the course of the experiments but the coverage of the anode and cathode negligibly change H_2O_2 content.

The pH of the solution in the column ranged between ~2.5 above the anode to ~10.5 above cathode 2. Maintaining the pH zones within the reactor is of great importance for efficient electro-Fenton reaction (optimum pH is 3). While the sediment samples displayed differing buffering capacities in relevant pH values, the spatial variability

Figure 4. Concentration of H₂O₂ at the steady state flow rate condition measured after 120 minutes using 2 g/L of suspended sediment. Error bars depict one standard deviation from average values.

Figure 5. Column experiment pH values above the anode, cathode 1, and cathode 2. Error bars depict one standard deviation from average values.

of pH values throughout the column in the presence of different sediment types did not differ significantly from the control (maximum of ± 1.2 pH units in cathode 1 vicinity). Therefore, the influence of innate buffering capacities of sediments appears to negligibly affect the pH profile of solution in the electrochemical column.

An additional influence of pH relates to the breakdown of H₂O₂ in the presence of suspended sediment, where at pH 10, H₂O₂ decreases up to 35%, while at pH 4 changes are negligible. These data (not shown here) are part of an ongoing study on the effects of sediments on batch experiments, and may be a factor in the lower concentrations of hydrogen peroxide measured in the column reactor in the presence of sediments.

Future work will include investigation into concentrations of redox species (Mn and Fe) catalyzing H₂O₂ degradation into hydroxyl radicals. Though the concentrations of redox species from the suspended sediments samples were low (Table 1), further tests including the direct measurement hydroxyl radicals will confirm if this metal presence due to the presence of suspended sediments contributes to the production of these highly oxidizing species.

Ongoing and future work focuses more thoroughly on the mechanisms affected by the suspended sediments in order to identify weak spots and optimize the electrochemical oxidation/reduction of contaminants in the presence of large amounts of suspended sediments. Future work will include breakdown of contaminants such as trichloroethylene and pesticides in the presence of suspended sediments to determine if the presence of sediments affects contaminant degradation.

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