Electrokinetic Remediation: Electrolysis of Iron Anodes for Treatment of Contaminants

RET Participants: Susan Agger (Maynard Ecology Center, Cambridge Public Schools) and Jessica Quinn (Revere High School)
Faculty Mentor: Dr. Akram Alshawabkeh (Department of Civil and Environmental Engineering)

Abstract

Granular (micro-scale) zero valence iron is used for chemical reduction of contaminants in groundwater. However, the rate of transformation reactions that involve iron and the contaminants are not controlled. In this study, we propose to replace the granular iron by solid iron and use electrolysis to induce the reaction between iron and the contaminants. This allows controlling the rate of reactions by controlling the electric current. Experiments were conducted to assess changes in batch volume of water as a result of electrolysis with iron anodes. The results were compared with those using non-reactive (MMO) electrodes. In one set of experiments the anodes and cathodes were separated by a membrane. In another set, the anode and cathode solutions were mixed. A constant current of 1 mA was applied. The results demonstrated that using an iron cathode and anode in a mixed environment reduces the environment while maintaining a neutral pH. Although there is a greater reducing environment in a separated chamber, a mixed chamber allows for greater reduction due to the presence of iron, thus the most optimum condition for treatment.

Introduction

It has been estimated that remediation of the nearly 1,450 contaminated sites in the United States will cost $350 Billion[1]. Techniques such as pump-and-treat, physical and chemical treatment, and bioremediation are both costly and ineffective in many heterogeneous soils. Electrokinetic remediation techniques are proposed to be more cost effective and efficient processes.

Electrokinetic remediation has been implemented using inert electrodes, titanium coated mixed-metal oxide. While this technique has proven successful, an even more inexpensive material such as iron may be used as electrodes. Scrap steel is widely accessible, thus potentially decreasing the cost of remediation at many sites. Oxidation-Reduction reactions at the anode and cathode:

At the anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (iron anodes)

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ (inert anodes)

At the cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

The project consisted of solving two unique problems: 1) how will implementing the use of iron electrodes affect the major parameters of the solution (specifically ORP, generally a function of pH) and 2) will reduction be more effective in a chamber when the cathode and anode are mixed or when they are separated? Oxidation occurs at the anode and the cathode becomes a reducing environment.

A current of 1mA/L was incorporated and pH, oxidation-reduction potential (ORP), and electric conductivity (EC) were monitored accordingly. The electrolyte selected for this experiment was 5mL 0.5M NaCl/650mL distilled H2O.

Methods

Batch electrolysis experiments were performed in the lab using Lucite chambers fitted with titanium coated mixed-metal oxide mesh electrodes. Batch electrolysis experiments were also run using iron (Fe+) electrodes. Wires were connected directly to the top of electrodes by wrapping method.

The experimental chambers included two mixed (undivided) chambers containing magnetic stir bars and two separated chambers containing a permeable Nafion™ membrane. The electrolysis chambers were filled with 1300 ml distilled water with 10 ml 0.5 M NaCl added as electrolyte.

Experiments were run with time points taken at various intervals. The DC power supplies were run at 1 mA. During each reading the following data was recorded: time interval, voltage, pH, ORP and EC (µS/cm).

Methods used to standardize and calibrate probes:

- pH buffers 4, 7 & 10 to calibrate the pH probe
- Zobell Solution was used to standardize the ORP (oxidation/reduction probe)
- Probes were rechecked every few days using standard buffers.

For each experiment, the initial concentration of hydrogen ion was calculated based on the initial pH reading: $-pH = \log [H^+]$. Using the initial concentration of [H+], the [OH-] concentration was determined. These values, in addition to time, gave the theoretical values for the reaction over time. The theoretical data points were plotted as pH over time and the graph of actual time points and experimental pH readings were over-layed to compare actual pH with theoretical.

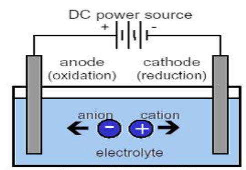

Figure 1. Basic Electrolysis Set-up[2].

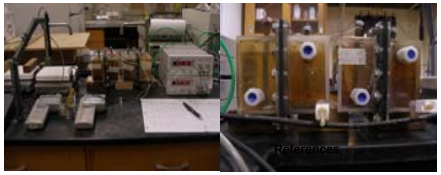

Figure 2. Experimental Set-up: a) Separated Chambers and Power Source and b) Close-up View of Separated Chambers

Figure 3. Experimental Iron Electrodes, used in Open Chambers.

Figure 4. Taking Measurements: a) Susan recording pH b) Jessica recording ORP

References

1. http://www1.coe.neu.edu/~aalsha/shortcourse.pdf
2. http://www.envirotools.org/factsheets/Remediation/electrokinetics_remediation.shtml

Acknowledgements

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Results

Figure 5. a shows that when the anode and cathode are in a mixed chamber a somewhat neutral pH is maintained. In Figure 5. b, ORP levels for the mixed-metal electrodes increases as the pH remains constant. The iron electrodes maintain a lower ORP with the neutral pH.

Using iron electrodes resulted in a great increase in pH at the cathode and a decrease in pH at the anode in the separated chambers. The mixed chambers maintained a somewhat neutral environment (see Figure 5. c). Figure 5. d shows that the cathode creates a reducing environment as a function of the pH. A reduction environment is also created within the mixed chamber.

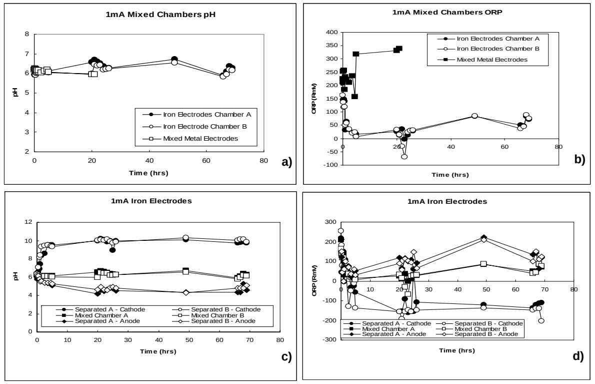

Figure 5. Results: a) pH over time in the mixed chambers using iron and mixed-metal electrodes b) ORP over time in the mixed chambers using iron and mixed-metal electrodes c) pH over time comparing separated and mixed chambers using iron electrodes d) ORP over time comparing separated and mixed chambers using iron electrodes

Conclusions

One of the goals of the experiment was to determine if using iron electrodes versus the standard mixed-metal electrodes would create an optimum reducing environment. Our results show that while the pH in the mixed chambers remains relatively neutral and constant over time, the corresponding ORP readings (see Figure 5. a and b) for iron electrodes show a decrease in ORP due to the iron. This creates a greater reducing environment than the mixed metal electrodes. Although reduction is increased with higher pH, the experimental difference seen here in ORP is not due to higher pH but is due to the presence of iron in solution. The higher ORP for mixed metal electrodes is due to the mixed metal oxides producing O2 during the electrolysis reaction resulting in an oxidizing environment. These results demonstrate that iron electrodes create the most optimum reducing environment which will lead to the degradation of contaminants requiring reduction.

The second goal of the experiment was to determine whether the cathode and anode should be separated or in a mixed solution. Our results show that while the reaction at the cathode created an extreme reducing environment this is a function of a high pH. Though there is a lower reduction condition in the mixed chamber, this is the optimum environment because the ORP is decreased due to the presence of iron rather than as a function of pH (see Figure 5. c and d).0

Classroom Connections

As part of the RET program, participating teachers are required to develop relevant lessons utilizing content and skills acquired during the RET laboratory assignment. Listed below are curriculum areas enriched by this learning experience in Dr. Akram Alshawabkeh's Civil and Environmental Engineering lab.

High School (9-12)	Chemistry – electrochemistry, electrolysis, pH, the use of electronic probes to collect scientific data Biology – bacteria, nutrient cycling, trophic levels, bioremediation
Middle School (6-8)	Earth Science – earth processes over time, soil erosion and deposition, watersheds, topographical and contour map reading skills Water Cycle – the inter-relationship of surface and groundwater Technology and Engineering – bioengineering
Elementary (K-5)	Soils - soil composition and characteristics

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