RUI: An Innovative Hybrid Technology for the Removal and Destruction of Perchlorate from Aqueous Systems Using Polymeric Ligand Exchange Technology and a Packed Bed Bio-Reactor

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ABSTRACT: This IREE research project is the beginning of a collaboration between the PI, Dr. Steven Mylon, and Dr. David Waite, Head of the Civil and Environmental Engineering School at the University of New South Wales, Sydney, Australia. The research extends the scope of study of a current NSF grant (NSF-0553654) that seeks a novel solution to perchlorate contamination through the separation and destruction of perchlorate from ground waters. The goals of this IREE project were: 1) To examine the potential for zero valent iron nanoparticles (nZVI) to reduce perchlorate in ion-exchange regenerate solutions, and to optimize the process, and 2) To establish additional productive collaborations between Drs. Mylon and Waite. As a result of time spent at UNSW by both Dr. Mylon and undergraduate research student, both of these goals have been met and will be discussed herein.

INTRODUCTION : As outlined in the original proposal, the PI, three co-PIs, and a number of undergraduate students at Lafayette College in Easton, PA have been investigating two individual processes that will eventually be joined to realize the effective separation of perchlorate from contaminated waters followed by its destruction in a packed bed reactor (PBR). The first process is based on separation of perchlorate through a novel approach using trace metal loaded DOW3N-based (Dow Chemical Dowex M4195) polymeric ligand exchangers (PLEs) to sequester perchlorate. After regeneration of the perchlorate loaded PLEs, the remediation of perchlorate is planned through microbial reduction in a packed bed bio-reactor. We expect the second step for this process to affect the complete biological reduction of perchlorate using a yet-to-be determined species of perchlorate reducing bacteria.

While the primary proposal has one focus on the biological reduction of perchlorate, alternative processes have examined the abiotic reduction of perchlorate [1,2] through the application of zero valent iron (ZVI). Based on a room temperature standard free energy of reaction, $\Delta G^o = -1,387\ kJ/mol$ [1], for the reduction of perchlorate by zero valent iron, we anticipate that the abiotic reduction of perchlorate from ion-exchange regenerate solutions may be more appealing (based on technical simplicity, cost, and kinetics) than a biological process. Despite the potential for abiotic perchlorate reduction, little is known about the rates, mechanisms, and optimum conditions for these processes, and much of the publishable data is contradictory [1-3]. Therefore, a study of the kind is essential, not only as a complement to our original NSF proposal, but also to fill the gap in existing research regarding abiotic perchlorate reduction.

To this end, Dr. Steven Mylon and senior undergraduate chemistry major, Alexander Goergen, traveled to the University of New South Wales, Sydney, AU to begin a collaboration with Dr. David Waite and his research group. Dr. Waite is the current head of the school of civil and environmental engineering at UNSW. Dr. Waite's group is experienced in both surface chemical processes and, more recently, have been investigating the kinetics of natural and remediation processes. Alex Goergen (AG) spent 10 weeks (June 5- August 15, 2007) at UNSW learning how to manufacture nanosized ZVI (nZVI) through a process patented by Dr. Waite. Additionally he began learning methods for the design of batch experiments to measure the effectiveness and optimal conditions of perchlorate reduction by nZVI. Dr. Mylon spent nearly 6 months (June 5- November 30, 2007) working with Dr. Waite and his group at UNSW. Mylon began by working alongside AG and on methods for nZVI functionalization. Drs Mylon and Waite also established additional productive collaborations in areas where they have common interests. Specifically, Drs Mylon and Waite began new research projects in the area of advanced oxidation processes. This research seeks to develop kinetic models for the application of nZVI to oxidative degradation of contaminants.

RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

As part of the visit to UNSW, Dr. Mylon was accorded the status of Visiting Research Fellow and received all the benefits of a UNSW staff member whilst at UNSW (office, computer support, library access, etc). Alex Goergen

enrolled in the UNSW Practicum Program and, as such, received benefits that accrue to all UNSW students (library and computing access and access to UNSW sporting and recreational facilities).

The on-site work was an extension of the primary NSF award and no experiments that were proposed in the primary NSF proposal were performed at UNSW. The day-to-day research program was much like a typical research program in the United States. While in Australia, all experimental work was performed in one of Dr. Waite's research laboratories or at other laboratories on the UNSW campus. Alex Goergen began working closely with a graduate student, Quan Sun, from Dr. Waite's group learning the process of manufacturing the nZVI. Following this, he was taught the methods for running batch experiments using some well characterized compounds as targets for reduction. He became quite familiar with new methods of detection such as HPLC, fluorescence and UV-VIS spectroscopy. All these skills will assist him in his senior year as a major in chemistry at Lafayette College when he takes advanced laboratory courses. Upon returning to Lafayette College, Goergen was able to continue his research using perchlorate as the target compound for reduction. This work will be the basis for his senior honors thesis. Future experiments for him include assessing the effect of nZVI on the reduction of perchlorate.

As a visiting research fellow, Dr. Mylon was welcomed into Dr. Waite's research group. In addition to following the progress of AG, Dr. Mylon extended the research coupled to the primary proposal by working on methods for functionalizing the nZVI. Primary particles formed during the synthesis of nZVI are known to aggregate thus decreasing the reactive surface area. Through functionalization of nZVI, the degree of aggregation should diminish at little cost to the total reactive surface area. In other words reactive surface lost due to functionalization is made up for through decreasing the extent of aggregation. The most successful functionalization schemes employ high molecular weight molecules such as alginate, starch and carboxy methyl cellulose (CMC). Both transmission electron microscopy (TEM) and laser diffraction particle sizing were employed to examine the effects on nZVI functionalization. Figures 1 illustrates the effect that alginate and starch functionalization have on particle size distribution of nZVI.

As mentioned earlier, a portion of Dr. Mylon's time at UNSW was also spent developing new areas of collaboration between his group and Dr. Waite's. In addition to a reductive pathway for contaminant remediation in the presence of oxygen nZVI can be used to affect oxidative transformations as well. The mechanism relies on the two electron transfer according to:

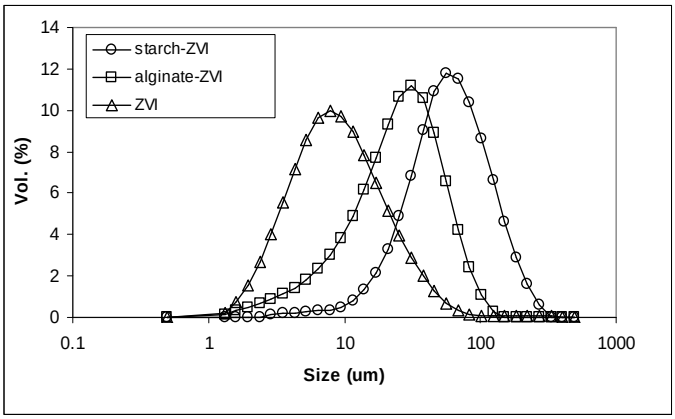

Figure 1: Particle size distribution for ZVI (open triangles), alginate functionalized ZVI (open squares) and starch functionalized ZVI (open circles).

$$Fe + H_2O \longrightarrow H_2O_2 + Fe^{2+}$$

The products of the above reaction, Fenton's reagent, react to form hydroxyl radicals and other oxidizing species. Dr. Waite and Mylon have begun a collaboration to study the oxidizing ability of nZVI and to develop kinetic models for substrate oxidization using simple model substrates.

BROADER IMPACTS OF THE INTERNATIONAL TRAVEL

The IREE opportunity fostered a strong project-based partnership between Dr. Mylon and Dr. Waite. This partnership extended beyond Drs. Mylon and Waite to include the other junior scientists (postdocs and graduate students) who make up Dr. Waite's research group as well as AG, an undergraduate research student from Lafayette College. This research collaboration joins scientists from two different disciplines (chemistry and environmental engineering) to focus on important environmental concerns.

In addition to enhancing partnerships and interdisciplinary research, this IREE opportunity also served to enhance the infrastructure of research education. Lafayette College, like many highly selective small colleges, values scholarship and has high research expectations of its faculty. Faculty are strongly encouraged to develop ongoing research programs that involve undergraduate students and produce publications in high impact peer-reviewed journals. The IREE opportunity provided support for one

undergraduate student researcher to not only work with the PI but also with Dr. Waite and his group of postdocs and graduate students. The development of the undergraduate research student in this way, is unlike conventional opportunities available, and has made a positive impact on his development as a future scientist. Additionally, the opportunity for Dr. Mylon to extend his stay at UNSW has helped expand the scope of his research program which will allow him to offer a greater number of research opportunities to Lafayette College undergraduates.

Finally, for both Dr. Mylon and Alex Goergen, this IREE offered a unique educational experience, specifically, a global perspective and an appreciation of the societal implication of their work. This was achieved through travel, formal meetings, informal discussion and immersion into Australian society. In Australia, Dr Mylon and his student developed a familiarity with history (natural and social) and current cultures of the Australia, as well as a more complete understanding of the local environmental issues. Some issues that Dr. Waite and his group were addressing specifically include: The effects of agricultural practices on acid sulfate soils in coastal New South Wales and the potential impact a proposed desalinization plant in Sydney, AU might have on coastal zone biogeochemistry.

DISCUSSION AND SUMMARY

The opportunity provided to scientists early in their career for travel and collaboration with senior colleagues is arguably the most important benefit of the IREE program. One should differentiate the important accomplishments of the international research experience between those directly related to science and an ongoing project and those more likely to provide results and research opportunities in the future. While the application of nZVI to perchlorate reduction in regenerate brines has not been fully optimized, the research to date indicates that its promise is clear. Undertaking such a research task with only undergraduate assistance and watching ongoing progress is highly significant and it demonstrates the possibilities.

Perhaps equally important are the new research programs developed by Drs Mylon and Waite. In this work, they have developed a system that models the oxidative remediation of contaminants through the application nZVI. Armed with this model, they can begin to examine the effects of external factors such as solution chemistry, functionalization scheme and the addition of dopants to the nZVI on the rate and efficiency of oxidative degradation. In addition to research based on the initial NSF proposal, this research will be

published in peer reviewed journals, presented at scientific conferences and will be the basis of further collaboration between the two laboratories. Already, both Mylon and Waite have sought additional funding opportunities to maintain this collaboration and keep a foothold in this exciting area of research.

One possible area to explore in the future could be to better leverage the experiences and knowledge of past IREE participants. An "alumni database" of sorts would provide accessible data and contact information to future generations of award recipients about the experiences of living abroad. Given the time spent in preparing for this trip in Australia, I believe that my student and I would have benefited from such a database. Another idea for the IREE program would be to create an additional fund pool for extended academic collaborations. These monies would be used to support and sustain academic partnerships that have been established through the IREE program. For example, as an extension of my work with Dr. Waite at UNSW in Australia, I would be thrilled about having funding to host him and his research team at my own teaching institution for follow-up research, conferences or a speaker series. Finally, there are minor programmatic components of the program that could be improved. For example, increasing the allowable time for visits to host countries would better enable the creation of long lasting collaborations as opposed to only opportunistic collaborations. To this end, additional funds will be required to allow researchers from US institutions to spend a longer period of time abroad. Additionally, some mechanism should be developed to adjust the original complement for the fluctuations of world currencies. The experience of travel to Australia over this past year highlights this need. Budgeting was done nearly one year prior to travel, and the US dollar lost greater than 10% of its value to the Australian dollar over that time. For housing and other budget items, changes like this can have significant unintended financial consequences for those who propose international travel.

ACKNOWLEDGEMENTS

The majority of this work was funded by a National Science Foundation grant (NSF-0553654). Additional institutional support for Dr. Mylon was provided by Lafayette College. Support for Alexander Goergen was also provided by Lafayette College's EXCEL Scholars research program and the office of the Provost of Lafayette College. Finally, we acknowledge support from Dr. David Waite and the Civil and Environmental Engineering School at UNSW.

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BRIEF BIOGRAPHIES OF RESEARCHERS

Steven E. Mylon received both a BS in engineering and B.A. in Soviet Eastern European Studies from Tufts University in 1988. Following five years of teaching at a private secondary school, Mylon entered the graduate program in chemistry at Dartmouth College. Under the supervision of Dr. Charles Braun he received his Ph.D. degree in Physical Chemistry in 1998. Following two additional years of teaching, he was awarded the Camille and Henry Dreyfus Postdoctoral Fellowship in Environmental Chemistry at Yale University. His co-advisors at Yale were Dr. Menachem Elimelich in the Chemical Engineering department and Dr. Gaboury Benoit in Yale's Environment School. Since 2004, he has been an Assistant Professor of Chemistry at Lafayette College in Easton, PA. As a recipient of an NSF-IREE award, Mylon was a Visiting Fellow at the University of New South Wales in Sydney, AU.

Alexander Goergen is currently a senior chemistry major at Lafayette College. Goergen has been working with Steven Mylon as a Lafayette College EXCEL Scholar since the summer of 2005. Thanks to the NSF- IREE award Goergen spent 10 weeks at the University of New South Wales enrolled as a practicum student. Alex worked in the research group of Professor David Waite who is the head of the school of Civil and Environmental Engineering at UNSW.