Report for 2004AL25B: Development and Characterization of a New Class of High-Capacity Ion Exchangers and and Environmentally Benign Process for Removal of Perchlorate in Water

- Articles in Refereed Scientific Journals:
  - Xiong, Z., Zhao D., and W. Harper (2005) "Sorption and Desorption of Perchlorate With Conventional and Non-conventional Ion Exchangers" Water Research. (to be submitted)
  - An, B., Z. Xiong, Z. FU, Donge Zhao, (2005) "preparation and Application of a New Class of Polymeric Ligand Exchangers for Selective Separation of Trace Contaminants" Separation Science and Technology, (to be submitted)
- Conference Proceedings:
  - Dimick, P., D. Zhao, A. Kney, J. Tavakoli (2005) Regeneration of a Perchlorate Loaded Polymeric Ligand Exchanger, DOW 3N-Cu" 2005 Spring National Meeting Proceedings, April 10-14, Atlanta, GA.
  - Xiong, Z. and D. Zhao "Removal of Perchlorate From Drinking Water Using a New Class of Ion Exchangers" 2004 Alabama Water Resources Conference, Environmental Institute, Auburn University, AL

Report Follows

PROJECT SYNOPSIS

TITLE: DEVELOPMENT AND CHARACTERIZATION OF A NEW CLASS OF HIGH-CAPACITY ION EXCHANGERS AND AN ENVIRONMENTALLY BENIGN PROCESS FOR REMOVAL OF PERCHLORATE IN WATER

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a) Problem statement and research objectives

In the recent years, perchlorate has been widely detected at dangerous levels in drinking water in at least 22 states including Alabama. Drinking water for more than 20 million Americans is contaminated with this toxic legacy of the Cold War. The chemical has been demonstrated to pose a variety of serious health risks relating to thyroid function, especially in newborns, children, and pregnant women. It can cause both physical and mental retardation and has been linked to thyroid cancer. Based on long-term epidemiological data, the draft assessment proposed a reference dose (RfD) of 0.00003 mg/kg/day. Translated to a drinking water equivalent level (DWEL), EPA recommended a provisionary a maximum contaminant level (MCL) of 1 ppb (part per billion) in drinking water. While a final MCL is under deliberation, eight states have established various action levels for perchlorate in drinking water ranging from 1 ppb to 14 ppb. California, where at least 7 millions of people are affected, has adopted a 4 ppb action level. Given the extremely high mobility and persistency of perchlorate, there is an urgent need for developing cost effective and environmentally friendly processes to remove perchlorate from drinking water and to safeguard the health of affected Alabama citizens.

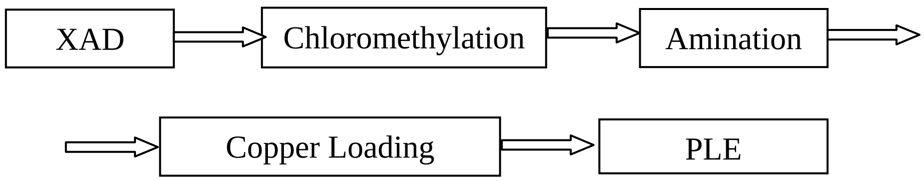
This research aims to develop an environmentally benign, cost-effective process for effective removal and complete destruction of perchlorate in drinking water from affected Alabama sources. A new class of novel sorbents, referred to as polymeric ligand exchangers or PLE's will be prepared, characterized and compared with other sorbents. The specific research **objectives** are to:

1) Develop a new class of ion exchangers that can treat perchlorate and compare them with commercially available adsorbents;
2) Develop a novel regenerative, and environmentally benign fixed-bed process based on the new materials; and
3) Explore new strategies to completely destroy perchlorate in water.

b) Research Methodology

The proposed research was carried out by executing the following tasks:

Task 1: Preparation of PLEs. A number of new polymeric ligand exchangers (PLE's) were synthesized through functionalizing commercially available polystyrene polymer adsorbents, XAD resins (XAD7HP, XAD16, and XAD1180) in accord with the following general scheme:



For comparison, an earlier PLE, DOW 3N-Cu, was used as a benchmark sorbent. In addition, two strong base anion (SBA) exchangers (IRA 958 and IRA 900), two modified SBA resins (Purolite 520 and Purolite 530), a fiber resin, and two weak base anion (WBA) exchangers (DOWEX22 and Diaion®WA21J) were also studied for comparison.

Task 2: Batch equilibrium and kinetic tests. This task includes a series of equilibrium and kinetic experiments. The equilibrium tests are designed to test and compare the equilibrium sorption capacity of PLEs and commercial resins for perchlorate removal. Sorption isotherms were constructed for PLEs and other resins in binary and multiple component systems. Perchlorate/co-solute binary ion exchange separation factors were calculated for each resin and then compared. Effects of solution pH, ionic strength, and concentration of competing anions such as sulfate on sorption capacity will be investigated in details. The kinetic tests are geared to study the sorption rates of PLEs compared to commercial resins for practical applications. Batch kinetic tests were carried out. Diffusion models were then applied to interpret the experimental kinetics data. The intraparticle diffusion coefficients for various resins were determined by fitting the models to experimental data and then compared.

Task 3: Column tests. Fixed-bed column runs were carried out to test the dynamic breakthrough behaviors of various resins. Breakthrough curves for perchlorate, other common anions (SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-), DOM and pH were measured using bench-scale column set-up.

Task 4. Regeneration. Regeneration tests are aimed to compare regeneration efficiencies of PLE's as compared to commercial resins. Perchlorate-saturated beds were regenerated in-situ using two regenerants 1) 4% (wt.) NaCl (brine) with 0~10 ethanol; and 2) brine plus various concentrations of NaOH with 0-30% ethanol. Subsequently, optimal conditions such as brine concentration, pH, hydrodynamic conditions, and solvent need were determined.

Task 5. **Ultimate destruction of perchlorate.** We tested the feasibility of destroying perchlorate in water or in the spent regenerant brine using biotic and abiotic methods. The biodegradation of perchlorate was carried out using microorganisms isolated from marine sediments; whereas the abiotic degradation of perchlorate was achieved using a newly synthesized nanoscale zero-valent iron particles.

c) Principal findings and significance

The major findings are summarized as follows:

(1) Three new PLEs were synthesized with varying matrix properties and hydrophobicity;
(2) The PLE's offer perchlorate sorption capacity comparable to that for standard SBA resins, but PLE's can be regenerated more efficiently at higher pH.
(3) Resins based on polystyrene matrix offer higher affinity and capacity for perchlorate than resins based on polyacrylic matrix. However, regeneration of the resins based on polyacrylic matrix is much more efficient.
(4) Although sorption of perchlorate is enhanced by hydrophobic interactions, the perchlorate uptake follows ion-exchange stoichiometry. The concurrent ion-pairing, Lewis acid-base interaction and hydrophobic interaction between PLE's and perchlorate are the underlying mechanism for perchlorate uptake.
(5) Despite completely different functionalities, the regenerability of PLE's and SBA resins is comparable at pH below 9.
(6) Fibrous ion-exchanger (Smopex 103) turns out to be a promising choice for perchlorate removal. It showed good perchlorate uptake capacity (117.78 mg/g), much better sorption kinetics than any other sorbents, and efficient regeneration. Over 85% its ion-exchange capacity was recovered using 38 bed volumes of a brine solution (12% NaCl at pH ~7.0)
(7) The regeneration efficiency of exhausted ion-exchangers can be improved by adding organics like methanol or ethanol into the regenerant and/or increasing the eluant pH.

These findings are instrumental for designers and decision makers to select the best sorbent for removal of perchlorate from contaminated waters.