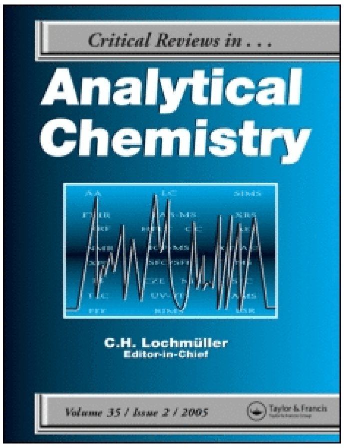

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ELECTROCHEMICAL INVESTIGATIONS OF IRON(0) AS A REDUCTANT FOR REDUCTIVE REMEDIATION OF CHLORINATED SOLVENTS IN THE ENVIRONMENT

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When considering the role of chemistry in environmental protection, there are two obvious points of attack: either before or after chemical species are introduced into the environment. One strategy is to design chemical processes from the ground up, to minimize the quantity and toxicity of pollutants released into the environment (Green Chemistry). Although this is obviously a preferable strategy, it is frequently not feasible, particularly in situations where the environmental damage has already been done. An alternative strategy is to devise environmental *in* situ processes to transform the pollutants into less toxic or harmful species. This *in situ* approach may either exploit or augment natural chemical or biological processes in the environment, or introduce new chemical or biological reagents to promote the transformation of target species. We will focus on the latter approach, with an emphasis on chemical processes.

"Bioremediation", which relies on the exploitation of populations of microorganisms to clean up environmental pollution, has received a lion's share of the press about environmental cleanup. However, there are also viable chemical approaches to the cleanup of certain types of environmental pollution. The two most important classes of environmental transformations of organic pollutants include reactions with nucleophiles (particularly hydrolysis and β-elimination) and redox reactions[1]. In fact, a number of important classes of pollutants are susceptible to reduction reactions in the environment. Halogenated (particularly chlorinated) compounds, which include ten of the twenty-five most frequently encountered pollutants on the United States Environmental Protection Agency's National Priorities List, represent one particularly important class. Other important classes include nitroaromatic compounds, azo dyes, and chromate species. Attention will focus here on reductive transformations.

Key questions include the fundamental chemical behavior of the target compounds in the environmental setting, and the characteristic features of the environmental system itself that will promote the transformation of these compounds. A major concern in evaluating possible *in situ* treatment technology is ensuring that the products of the transformation processes are not more hazardous than the parent compounds.

Clear evidence is available for a significant role of abiotic, principally chemical reductive transformation of many of these compounds. A proper understanding of such processes may enable the exploitation of so-called "natural attenuation" schemes, relying entirely on natural *in situ* environmental processes to effect cleanup. We have investigated both fundamental and empirical aspects of these processes in environmental sediments. Key questions include assessment of the intrinsic reactivity of selected pollutant classes, and estimation of the effective reduction potential (thermodynamic driving force) and quantity of environmental components capable of reacting with the pollutants (redox capacity). Semiempirical quantum mechanical calculations have been applied to predict the intrinsic outer-sphere electron transfer rates of the first, rate-limiting one-electron transfer reaction in the reduction of a series of nitroaromatic compounds[2]. We have also investigated the "redox capacity" of sediment material. We found surprisingly high redox capacity for a specific pond sediment material ("Beaver Dam" sediment from near Athens, Georgia). The very low equivalent molecular weight clearly established that abiotic species of low equivalent weight are involved. We also established, consistent with the work of several other groups, that inorganic iron species can play a major role as reactants in environmental redox processes[3].

In many cases, however, these natural processes may be too slow to be practical on a reasonable time scale. In such cases additional chemical treatment technology may help to alleviate the problem. Some of these engineered solutions can be very labor and capital intensive. So-called "Pump and treat" systems fall in this category. This approach can be very effective in cases where the total loading of organic pollutant is below the saturation level. However, it may require extremely long-term treatment in cases where significant loads of relatively water-insoluble materials, e. g. many chlorinated solvents, are released into the soil environment. In such cases, the groundwater may become saturated with the compound, and a large reservoir of the compound may remain in the ground in an ill-defined location. Even if pump and treat technology completely purifies the ground water extracted from such a site, the water will again become re-saturated with the pollutant when reintroduced to the site. Such cases may require decades of continuous treatment to achieve a substantial permanent improvement.

An alternative technology which has received considerable attention lately is the introduction of permeable reactive barriers into the path of a plume of pollutant in relatively shallow aquifers. These reactive barriers can induce an *in situ* chemical reaction to transform the pollutant to new products during its residence time in the permeable reactive barrier. This approach is deceptively simple. In principle it involves simply excavating a suitable site in the groundwater flow pattern, filling a trench with the permeable barrier material, and then covering it with soil. Thereafter, the barrier should function as a purely passive reactor with minimal maintenance or external intervention. Considerable laboratory and field work has been carried out on such systems. Numerous field-scale tests are underway at present, particularly in Canada and the United States, to evaluate the feasibility of one of the most promising applications of this technology. This approach uses zero-valent metals such as iron.

A key concern about these zero valent iron permeable barriers is the identification of the transformation products, to insure that a pollution problem is not transformed into an even worse problem. Additional concerns involve the long-term susceptibility of the reactive barriers to plugging (e. g. by soil material or biofilm development), or to poisoning and deactivation by species encountered in the soil, the groundwater, or the pollutant plume.

We have applied simple electrochemical methodology to the laboratory investigation of some of the processes involved in the reduction of one specific chlorinated compound, chloroform, at iron(0). One set of experiments was aimed at better understanding of the long-term loss of reactivity that might occur if the iron is subjected to periodic oxidation processes to form various iron (hydr)oxide species. A second set of experiments was aimed both at developing methodology for successful observation of the reduction of chloroform in predominantly aqueous media, and at identifying some initial steps in the reaction process. We performed both cyclic voltammetry at small electrodes, and steady-state potentiostatic flow-through experiments on a porous iron column electrode with on-line gas chromatographic detection of reactants and initial products.

The cyclic voltammetric responses of various types of iron metal electrodes are complex and rather diffuse, reflecting numerous iron (hydr)oxide surface species, as well as multiple electrochemical reactions including hydrogen evolution. Difference experiments enabled extraction of useful information about the surface state and surface reactivity of iron metal samples, even when the process of interest contributed only a minor component of the total reaction current.

The reactivity and stability of response of the iron surface were probed by investigating the cyclic voltammetric response of methyl viologen, which undergoes an uncomplicated electron transfer reaction at iron electrodes. Voltammetric response at initially clean iron electrodes was measured as a function of progressively increasing surface blockage effected by oxide formation during repeated oxidative cycles. This response was compared with that at commercially available bulk granular iron of the type used in field test beds. The behavior at initially clean iron electrodes gradually progressed from a simple, uncomplicated, predominantly mass-transfer-controlled process under planar diffusion conditions toward a more steady-state response. The behavior at the commercial granular iron electrodes exhibited a strongly pronounced steady-state behavior even in the initial voltammogram.

We interpret the results as arising from the effective behavior of iron metal as a partially blocked electrode or microelectrode array. Theoretical fits of voltammograms obtained at partially oxidized surfaces agreed well with experiment. When the surface of the iron is progressively blocked by repetitive generation of oxide layers that inhibit electron transfer, the iron remains surprisingly active. Although the response falls off with increasing surface blockage, the reactivity still retains a surprisingly large fraction of that for an initial, pristine surface, because of the effects of lateral diffusion between active sites. The results indicate that these iron surfaces will retain a significant degree of activity even after substantial surface deactivation.

Voltammetric investigations also provided clear evidence that chloroform could be reduced at an iron electrode, in an irreversible process. As with methyl viologen, the reactivity with chloroform was partially diminished after repeated oxidation of the iron surface, but remained clearly evident after many cycles. Difference measurements were essential to enable clear detection of the reaction of chloroform, to distinguish it from a high background current due to hydrogen evolution.

We applied a new approach, voltachromatography, for characterization of these reactions in a flow-through electrode reactor based on the commercial bulk granular iron used in environmental field clean-up sites. The approach is applicable to reactions that can be electrochemically driven or modulated, but which occur at a rate too slow to be detected amperometrically by direct voltammetric means. The approach allowed chromatographic monitoring of the dependence of reactant and product concentrations in a flow reactor on the electrochemically controlled potential (chromatographic response rather than current vs. applied potential). Results showed significant production of methylene chloride, the first stable reduction product of chloroform reduction, at potentials more positive than those at which hydrogen evolution is evident. These results suggest that one postulated pathway involving reduction by active hydrogen is not necessary for the reaction to occur.

Interestingly, however, a mass balance shows that the concentration of methylene chloride when 90 % of chloroform has been reacted is only several percent of the initial concentration of chloroform. This result suggests that methylene chloride is an intermediate rather than final reaction product. Further investigations are continuing to identify additional steps and products of this reaction. These results should be useful in the further characterization and development of groundwater remediation technology for chlorinated solvents based on *in situ* beds of iron(0)[4].

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