Modified Fenton oxidation of diesel fuel in arctic soils rich in organic matter and iron

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HIGHLIGHTS

- Modified Fenton chemistry treated aged diesel fuel in three arctic soils.
- Soil organic matter (SOM) was a more effective Fe chelate than EDTA.
- SOM-Fe(III) stability constant is 20 orders of magnitude lower than EDTA-Fe(III).
- Modified Fenton chemistry selectively oxidized diesel fuel over SOM.
- Modified Fenton treatment can be effective for in SOM-rich soils.

ARTICLE INFO

ABSTRACT

Modified Fenton (MF) chemistry was tested in the laboratory to treat three diesel fuel-contaminated soils from the Canadian arctic rich in soil organic matter (SOM) and Fe oxides. Reactors were dosed with hydrogen peroxide (HP), and treatment was compared in reactors with SOM as the only chelate vs. reactors to which ethylenediaminetetraacetate (EDTA) was added. Concentrations of diesel fuel and HP were measured over time, and the oxidation of both diesel fuel and SOM were quantified in each soil. A distinct selectivity for oxidation of diesel fuel over SOM was observed. Reactors with EDTA showed significantly less diesel fuel oxidation and lower oxidant efficiency (diesel fuel oxidized/HP consumed) than reactors with SOM as the only chelate. The results from these studies demonstrate that MF chemistry can be an effective remedial tool for contaminated arctic soils, and challenge the traditional conceptual model that SOM reduces the efficiency of MF treatment through excessive scavenging of oxidant.

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1. Introduction

The lack of an electrical grid in the Arctic makes petroleum-based fuels the main source of energy. In recent years there has been an increase in the exploration and extraction of mineral and petroleum resources, and in other commercial, industrial, military, and touristic activities. These operations result in the contamination of soil and groundwater. Options for soil remediation in arctic regions are limited because of the difficulty and expense of transporting specialized equipment to remote sites and the need for low-maintenance solutions implemented on-site or in situ. Bioremediation has been the most common method (Paudyn et al., 2008), but often requires years to achieve cleanup levels because low temperatures limit rates of microbial activity.

Chemical oxidation using Modified Fenton (MF) chemistry is a promising alternative for remediation of arctic and subarctic soils, capable of achieving cleanup limits within days to weeks. MF chemistry is based on the catalysis of hydrogen peroxide (HP) by Fe. A review of how MF chemistry in soils differs from conventional Fenton treatment of wastewaters is provided by Watts and Teel (2005), Pignatello et al. (2006). The most important difference is that conventional Fenton chemistry acidifies to keep the pH at or below 2.8, whereas MF reactions take place near the natural pH of the soil. Soils from arctic and subarctic regions are often rich in Fe oxides (Foscolos and Kodama, 1981; Konhauser et al., 1994; Rutherford, 1995; Nicholson and Moore, 1997). Native Fe oxides participate in MF treatment (Lin and Gurol, 1998; Watts and
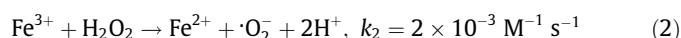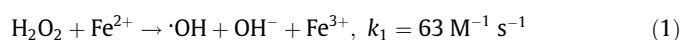
Teel, 2005), making Fe supplements unnecessary. HP can be applied with the same simple techniques used for bioremediation (i.e., tilling into surface soil, or spraying onto piles). In areas where transportation of liquid HP may be problematic, solid peroxygens (e.g., sodium percarbonate, calcium peroxide) that release HP upon contact with water can be used instead.

There are many HP propagation reactions involved in Fenton systems (Watts and Teel, 2005). However, the most critical are Reactions 1 and 2, which are provided below with second-order rate constants k_1 and k_2, respectively. Reaction 1 is the Fenton reaction, which describes the catalysis of HP by Fe(II) (Haber and Weiss, 1934; Walling, 1975). The hydroxyl radical (·OH) is a strong oxidant ($E_0 = 2.73$ V) with a high reactivity towards petroleum hydrocarbons and most other contaminants. The superoxide radical anion (·O_2^-) is a weak reductant and nucleophile, and does not react directly with hydrocarbons. Reaction 2 completes the cycle by reducing Fe(III) back to Fe(II) so that more ·OH can be generated via Reaction 1. This reaction is critical when native Fe oxides are used as catalysts, because the Fe is predominantly present as insoluble Fe(III). Note that k_2 is four orders of magnitude less than k_1. Reaction 2 is the rate-limiting step in conventional Fenton chemistry (Lewis et al., 2009), and is even more rate-limiting in MF systems because Fe(III) is insoluble above pH 2.8 (Stumm and Morgan, 1996).

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+}, \ k_1 = 63 \ M^{-1} \ s^{-1} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot O_2^- + 2H^+, \ k_2 = 2 \times 10^{-3} \ M^{-1} \ s^{-1} \quad (2)$$

Native Fe oxides can participate in MF reactions via heterogeneous catalysis (Watts et al., 1990; Valentine and Wang, 1998). However, chelates are usually added to increase the participation of these insoluble species in Reaction 2 (Watts and Teel, 2005; Pignatello et al., 2006). The reactivity of a chelated-metal varies inversely with stability constant (Sheldon and Kochi, 1981). The higher the stability constant the more rate-limiting Reaction 2 becomes. An ideal chelate has a low stability constant so that Fe(III) is readily released for Reaction 2, but is resistant to chemical oxidation (Sun and Pignatello, 1992). Fe(III) reactivity also increases as chelate dose increases. Lewis et al. (2009) showed that increasing the chelate:Fe(III) ratio increased HP stability and oxidant efficiency. Ethylenediaminetetraacetate (EDTA) is a common chelate in MF applications (Watts and Teel, 2005; Pignatello et al., 2006).

Because short summers in the arctic and subarctic limit the biodegradation of plant debris, many soils have a high content of soil organic matter (SOM) (Jobbágy and Jackson, 2000; Hossain et al., 2007; Simpson, 2010), providing a built-in chelate for MF treatment. The humic acid (HA) and fulvic acid (FA) fractions of SOM are excellent and well-studied metal chelates (Kerrdorff and Schnitzer, 1980; Tipping, 2002). The log of the stability constant for HA–Fe(III) at circum-neutral pH is 2.8 (Tipping, 1998), compared with 27.7 for EDTA–Fe(III) (Martell et al., 2003), a difference of 22 orders of magnitude. The greater stability constant indicates that Fe(III) chelated with EDTA is less available for Fenton reactions than Fe(III) chelated with SOM. If both chelates are present, Fe(III) will preferentially chelate with EDTA rather than SOM, and EDTA can be expected to control Fe(III) reactivity.

Another property of SOM which can enhance MF treatment is its ability to reduce Fe(III) to Fe(II). This reduces the amount of HP used for this purpose in Reaction 2, leaving more to generate ·OH via Reaction 1. Chen and Pignatello (1997) demonstrated Fe(III) reduction to Fe(II) in Fenton systems by constituents of HA (quinones and hydroquinones). Paciolla et al. (2002) used spectroscopy to show that HA reduced Fe(III) to Fe(II), and that

the reduction of molecular oxygen by Fe(II) actually produced HP and ·OH.

SOM, like all organic chelates, also reacts with ·OH, which reduces oxidant efficiency. The traditional conceptual model is that ·OH has the same affinity for SOM as for organic contaminants, rendering soils high in SOM unsuitable for MF treatment. Because of this common misconception, there have been few attempts to treat contaminated soils high in SOM with MF chemistry. However, the results of several studies challenge this model, and have reported that SOM can actually enhance contaminant oxidation. Vione et al. (2004) reported that that the Fenton degradation of phenol with added Fe(III) was faster in the presence of humic acids. Voelker and Sulzberger (1996) reported that, although FA scavenged some ·OH, the effective rate constant of Fenton reactions increased with increasing FA concentration at pH 5. Li et al. (1997) observed that MF oxidation of 2,4,6-trinitrotoluene was enhanced when HA was added, which they attributed to its ability to reduce Fe(III) to Fe(II). Huling et al. (2001) demonstrated that peat enhanced the production of ·OH in Fenton reactions. Bissey et al. (2006) observed that SOM increased the stability of HP and the yield of ·OH in MF treatment of soils. Georgi et al. (2007) showed that addition of HA to MF systems enhanced the production of ·OH and the degradation of hydrocarbons. However, none of these studies quantified the HA and/or SOM oxidized in MF reactions, which is critical to understanding its resistance to chemical oxidation. A significant aspect of this research is that SOM degradation during MF treatment was actually quantified.

Only two studies have been found on treatment of contaminated arctic or subarctic soils using MF chemistry, or indeed any other oxidant. Stow (1997) reported that MF treatment achieved significant degradation of polychlorinated biphenyls in fill material from northern Labrador (58 °N latitude) with a very low SOM content. Fe(II) was added without a chelate, and multiple applications of HP were required. Ferguson et al. (2004) tested MF treatment of diesel fuel in a soil from Antarctica. No chelates were added, but the SOM and Fe content was not measured. No contaminant degradation was observed.

This paper describes laboratory studies of MF treatment in three soils from arctic Canada with a high content of SOM and Fe oxides, and diesel fuel contamination aged at least 10 y. Performance was compared for reactors with SOM as the only chelate vs. added EDTA. The general purpose of these studies was to assess MF treatment of arctic soils rich in both SOM and Fe oxides. The specific goals of the experiments were to; (1) compare SOM and EDTA as chelates for MF treatment, (2) quantify the mass of both diesel fuel and SOM oxidized, and (3) determine the oxidant efficiency (mass of diesel fuel oxidized/mass of HP consumed).

2. Materials and methods

2.1. Chemicals

Liquid HP (50%) was provided *gratis* from Solvay (Deer Park, Texas). Solid sodium salts of HA were purchased from Sigma–Aldrich (St. Louis, Missouri), and EDTA disodium salt was purchased from Sigma–Aldrich (Milwaukee, Wisconsin).

2.2. Soils

Three soils with aged diesel fuel contamination were collected from different locations in the Canadian Arctic. Table 1 lists the location and latitude of the soils, and the approximate age of contamination with diesel fuel. The soils were collected from areas of permafrost and supported tundra vegetation.