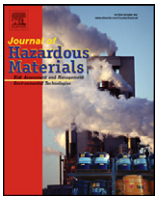
Journal of Hazardous Materials 199–200 (2012) 128–134

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Mobilization of metals during treatment of contaminated soils by modified Fenton's reagent using different chelating agents

Lars R. Bennedsen[a,b], Anne Krischker[c], Torben H. Jørgensen[b], Erik G. Søgaard[a,*]

[a] *Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Niels Bohrs Vej 8, DK-6700 Esbjerg, Denmark*
[b] *Rambøll Denmark A/S, Lystholt Allé 10, DK-7100 Vejle, Denmark*
[c] *University of Applied Sciences Jena, Carl-Zeiss-Promenade 2, 07745 Jena, Germany*

ARTICLE INFO

Article history:
Received 29 April 2011
Received in revised form 8 October 2011
Accepted 23 October 2011
Available online 29 October 2011

Keywords:
In situ chemical oxidation
Modified Fenton's reagent
Metal mobilization
EDTA
Citrate
Pyrophosphate

ABSTRACT

Changes in pH and redox conditions and the application of chelating agents when applying in situ chemical oxidation (ISCO) for remediation of contaminated sites can cause mobilization of metals to the groundwater above threshold limit values. The mechanisms causing the mobilization are not fully understood and have only been investigated in few studies. The present work investigated the mobilization of 9 metals from two very different contaminated soils in bench and pilot tests during treatment with modified Fenton's reagent (MFR) and found significant mobilization of Cu and Pb to the water in mg/l levels. Also Fe, As, Mn, Ni, Zn, Mg, and Ca mobilization was observed. These findings were confirmed in a pilot test where concentrations of Cu and Pb up to 52.2 and 33.7 mg/l were observed, respectively. Overall, the chelating agents tested (EDTA, citrate and pyrophosphate) did not seem to increase mobilization of metals compared to treatment with only hydrogen peroxide and iron. The results strongly indicate that the mobilization is caused by hydrogen peroxide and reactive species including oxidants and reductants formed with MFR. Based on these results, the use of chelating agents for ISCO will not cause an increase in metal mobilization.

1. Introduction

Mobilization of metals to the groundwater when applying in situ chemical oxidation (ISCO) for remediation of contaminated sites has been observed [1,2] and transport of these metals may cause a release of metals to ecosystems, areas with water catchment, etc. at concentrations above threshold limit values. One of the most common ISCO technologies applies hydrogen peroxide activated by an iron catalyst. The Fe(II) mediated decomposition of hydrogen peroxide is known as modified Fenton's reagent (MFR) or catalyzed H_2O_2 propagation (CHP) and produces hydroxyl radicals according to reaction (1). These radicals react with more than 95% of contaminants of concern (COC) at near diffusion-controlled rates, i.e. $k > 10^9\,M^{-1}\,s^{-1}$ [3]. Depending on the catalyst used and the hydrogen peroxide concentration, MFR also generates the reactive oxygen species perhydroxyl radical ($HO_2^\bullet$), superoxide radical anion ($O_2^{\bullet-}$), hydroperoxide anion (HO_2^-) and organic radicals [4] according to reactions (2)–(6).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{1}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{2}$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \tag{3}$$

$$HO_2^\bullet \leftrightarrow O_2^\bullet - + H^+ \quad pK_a = 4.8 \tag{4}$$

$$HO_2^\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \tag{5}$$

$$OH^\bullet + RH \rightarrow H_2O + R^\bullet \tag{6}$$

The acidic properties of Fe(II) lowers pH to 3–4 in classical Fenton's system, when Fe(II) is added to deionized water. In soils and groundwater the influence on pH is more complicated since most of these systems possess a strong buffering capacity that will maintain pH in the neutral domain and result in iron precipitation as oxides and ineffective catalysis of hydrogen peroxide. As an alternative to lowering pH in the entire treatment area to 2–4 with e.g. sulfuric acid, several other methods have been used to catalyze the hydrogen peroxide. These include soluble iron [5–7], iron minerals [6,8–13], and chelated iron [14–18]. The main advantages of using chelated iron as catalysts are that the process can be conducted at neutral pH and that chelates may travel farther in the subsurface compared to soluble iron [4]. However, the dosage of oxidants has to be increased since the oxidation capacity of MFR will be lowered due to oxidation of the chelating agents. Studies have shown that the widespread used chelating agents for consumer products and industrial processes combined with poor biodegradability of

---

[*] Corresponding author. Tel.: +45 99407622; fax: +45 99407710.
E-mail address: egs@bio.aau.dk (E.G. Søgaard).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.10.068

Table 1
Characteristics of the used natural soils.

	Soil A	Soil B
Properties		
Organic matter	Low	Low
Sand	87%	92%
Clay and silt	13%	8%
Soil texture	Loamy sand	Sand
Contaminants	Fuel oil	Chlorinated solvents, hydrocarbons, pharmaceuticals, other
Buffer capacity	High	Low
Depth	3.5 m bgs	4–14 m bgs
Metals [μg/g]		
As	0.5	1.6
Co	2.3	<0.3
Cr	20.1	4.7
Cu	6.8	13.4
Fe	8060.0	189.0
Mn	213.0	2.4
Ni	4.2	36.9
Pb	4.6	20.6
Zn	19.7	3.0
Mg	1690.0	28.0
Ca	458.0	454.0

these chemicals have lead to accumulation of chelating agents in the environment and EDTA is now among the highest concentrated anthropogenic compounds in European surface waters [19]. An important issue is that chelating agents may enhance the mobility and transport of heavy metals once released into the environment and high concentrations are also able to remobilized metals out of sediments [20].

The coexisting occurrence of organic contaminants and heavy metals in soil is a significant factor complicating remediation of contaminated sites, as the enhanced desorption of organic contaminants by the MFR reactions may lead to mobilization of heavy metals [1,2]. Also, chelating agents are used directly for extraction of heavy metals from contaminated soils [21–27] and to enhance phytoextraction of heavy metals from contaminated soils [28–30]. These fields of application indirectly suggest that using chelating agents for ISCO may increase metal mobilization.

Only few studies have investigated metal mobilization during treatment of contaminated soils with MFR. In these studies mobilization of Cd, Cu, Ni, Pb, Zn [1] and Pb [2] was investigated. Both studies used nitrilotriacetic acid (NTA) to keep Fe(III) in solution. The objective in this work is to investigate the mobilization of different metals from contaminated natural soils treated with MFR and to study the influence of pH, oxidation, and different chelating agents to obtain a better understanding of the mechanisms causing the mobilization of metals during MFR. Also, the results from bench scale experiments were compared to results obtained in a field scale pilot test. The present study focused on EDTA, a widely used non-biodegradable synthetic chelating agent. Attempts have been made to find more environmental compatible chelating agents to keep the iron catalyst in solution [17,31] and in the present study the performance of EDTA was compared to a biodegradable organic chelating agent (citrate) and an inorganic chelating agent (pyrophosphate) that is not degraded by MFR.

2. Materials and methods

2.1. Soil samples

Sandy soils from two different contaminated sites in Denmark were used for the experiments. The characteristics of the soils, referred to as soils A and B, are presented in Table 1 with average concentrations of different metals in the soils. The analysis by ICP-AES was based on triple determinations of 1 g of digested soil sample and hence results deviated up to 30% for the different metals due to the heterogeneous nature of the soil samples.

2.2. Chemicals

Technical grades of hydrogen peroxide (33% H_2O_2) and sodium hydroxide (30% NaOH) were purchased from VWR international, LLC. Analytical grades of ferrous iron sulfate heptahydrate (>99% $FeSO_4 \cdot 7H_2O$), citric acid (>99% $C_6H_8O_7$), sodium pyrophosphate decahydrate (99% $Na_4P_2O_7 \cdot 10H_2O$) and ethylenediaminetetraacetic acid, EDTA (99% $C_{10}H_{16}N_2O_8$) were purchased from Merck and Sigma–Aldrich. Sulfuric acid (96% H_2SO_4) and nitric acid (65% HNO_3) were purchased from Bie & Berntsen.

2.3. Analytical methods

As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Mg, and Ca were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry, ICP-AES (Perkin Elmer Optima 3000DV) with detection limits of about 0.01 mg/l. All water samples were passed through a 0.45 μm filter and then immediately acidified with HNO_3 before analysis. Soil samples were digested in HNO_3 at 120 °C before analysis of the aqueous phase with ICP-AES. Solution pH was monitored using a Radiometer PHM210 pH meter.

2.4. Test setup

Each batch reactor consisted of a 100 ml Erlenmeyer flask with 50 ± 0.05 g of soil suspended in deionized water. 0.90 ml 0.10 M catalyst stock solution and 1.50 ml 33% hydrogen peroxide (1.13 g/cm^3) was added to the reactors to initiate the reactions, resulting in a total aqueous volume in each flask of 50.00 ml. Fe concentrations in all catalyst stock solutions were 0.10 M and in the chelated iron catalyst stock solutions the Fe(II):chelate molar ratio was 1:1. pH in all stock solutions were adjusted to 7.0 with NaOH or H_2SO_4.

All tests were performed in duplicate in two identical reactors. Control reactors receiving only deionized water, deionized water with hydrogen peroxide, and deionized water with hydrogen peroxide and iron were performed in parallel. For soil B it was necessary to prepare a pH control reactor due to a low buffer capacity of the soil. This reactor received only soil and deionized water and pH was adjusted to 2.8 using 0.9 M H_2SO_4. An overview of the reactors applied in the study is presented in Table 2. All samples were shortly stirred once a day. Reactions were carried out at 25 ± 1 °C in covered flasks and were allowed to proceed for 7 days. 10 ml aliquots were collected after 5 h and after 7 days. pH was monitored after 5, 24, 96, and 168 h. pH was not adjusted in the reactors and no buffer was used to maintain a constant pH. Varying pH may complicate interpretation of the results, but this was specifically chosen to simulate the conditions and results of a field scale application, where pH is not normally controlled through buffer addition. ICP-AES control analyses of all reagents showed that no metal impurities in these reagents could affect the results, hence the metal concentrations at time 0 could be assumed to be below detection limit of about 0.01 mg/l for the ICP-AES technique.

2.5. Pilot study

MFR was tested at the soil B site in pilot scale. A volume of about 110 m^3 of soil located 3–6 m bgs was treated with 20,500 l of stabilized 12.5% H_2O_2 and 10,250 l of chelated iron catalyst solution (ISOTEC^{SM} Cat 4260, patented catalyst from In-Situ Oxidative Technologies Inc.) in total over four injection events. Five injection points screened in two depths were used and the design radius