

FIELD TESTING AND MODELING OF THE FENTON FILTRATION PROCESS FOR ARSENIC REMOVAL

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Background

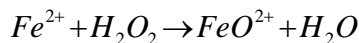
In Fenton's reaction, hydrogen peroxide (H_2O_2) reacts with ferrous iron (Fe^{2+}) to produce a powerful oxidant which converts As(III), the main form of arsenic in Midwest groundwater, to the more easily removed As(V) and also converts soluble Fe^{2+} to insoluble hydrous ferric oxide (HFO). Arsenic-containing groundwater also contains ferrous iron, so Fenton's reaction can be induced by adding hydrogen peroxide, an inexpensive chemical. As(V) readily sorbs to HFO and can therefore be removed by filtration. Previous research (MTAC Technical Reports 06-03, 06-11) showed that Fenton filtration with supplemental FeCl_3 can lower soluble As concentrations below the maximum contaminant level (MCL) of $10 \mu\text{g/L}$. The objectives of the present research were to compare Fenton-filtration with conventional chemical oxidation, characterize the stoichiometry of Fenton oxidation and the role of natural organic matter, develop a model of As sorption, and perform a full-scale test of Fenton filtration.

Comparison of Fenton Filtration with Conventional Chemical Oxidation

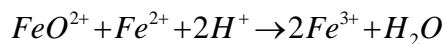
Jar tests were performed at the Danvers, Illinois water treatment. The source water contained approximately 2 mg/L Fe and $40 \mu\text{g/L}$ As. The plant used aeration and sand filtration to get good (90-95%) Fe removal but only 20-25% As removal. The jar tests used H_2O_2 , sodium hypochlorite (NaOCl) or potassium permanganate (KMnO_4) as oxidants and ferric chloride (FeCl_3) for supplemental Fe in some tests. In all tests, the oxidant and any FeCl_3 were added to freshly collected groundwater, stirred for 5 minutes, aerated, and filtered. The tests were intended to simulate oxidant addition upstream from the aerator and sand filter. In the controls (no oxidant or FeCl_3), Fe and As removal were similar to that in the plant. In tests with only 5 mg/L Fe added (aeration only, no other oxidant) there was no significant oxidation of As(III) and a modest improvement in As removal, but soluble As was still above the MCL. Similarly, in tests with addition of just the oxidant equivalent to the Fe^{2+} (H_2O_2 , KMnO_4) or $\text{Fe}^{2+} + \text{NH}_4\text{-N}$ (NaOCl), there was only a modest improvement in As removal. As(III) was almost completely oxidized by NaOCl and KMnO_4 , while for H_2O_2 As(III) was ~50% oxidized. Fenton filtration with 5 mg/L Fe reduced soluble As to $11 \mu\text{g/L}$, slightly above the MCL. Addition of NaOCl or KMnO_4 with the same Fe dose reduced soluble As to $1 - 2 \mu\text{g/L}$. Clearly, oxidation of As(III) and adequate sorption of As are both essential for effective As removal.

Reaction Pathways of the Fenton Filtration Process

In the first step of Fenton's reaction at the pH of groundwater, ferrous iron (Fe^{2+}) reacts with H_2O_2 to produce ferryl ion (FeO^{2+}), a very reactive species.



The ferryl ion can react with another Fe^{2+} ion to yield two ferric ions (Fe^{3+}), which precipitate as HFO.



The overall stoichiometry is therefore two Fe^{2+} oxidized for every H_2O_2 . The FeO^{2+} ion can also oxidize As(III) to As(V) but the As concentration in groundwater is typically less than 5% that of Fe^{2+} so the stoichiometry is still expected to be essentially two Fe^{2+} for every H_2O_2 . The FeO^{2+} ion may also react with natural organic matter (NOM) to produce H_2O_2 as a byproduct.

Therefore, deviations from the expected 2:1 stoichiometry in real groundwater may indicate that reactions with NOM significantly affect the Fenton reaction.

Experiments were performed in which varying amounts of Fe^{2+} were added to a fixed amount of H_2O_2 . For synthetic carbonate or phosphate solutions, the results were as expected. For increasing Fe doses up to two times the H_2O_2 dose, only decreasing concentrations of H_2O_2 were detected. For higher Fe doses only increasing Fe concentrations were detected. However, for Danvers groundwater, H_2O_2 was detected at concentrations similar to the initial concentration for all Fe doses. Clearly, H_2O_2 was produced in reactions involving NOM. This confirms earlier results which showed that Fe^{2+} is the limiting reactant in Fenton filtration. There is little or no improvement in As(III) oxidation for H_2O_2 doses in excess of the Fe^{2+} concentration. Clearly, the effects of NOM on Fenton oxidation deserve further study.

Modeling Arsenic Sorption

Arsenic removal in the pilot-scale tests (MTAC TR06-03) was modeled using the triple-plane option of Visual Minteq, a freely available computer program. It was assumed that sorption to HFO was the only reaction that could remove soluble As. The model has no adjustable parameters. The database of equilibrium constants and surface properties of HFO were all taken from the open literature. The model input was the concentrations of As(III) and As(V) (after oxidation), Fe (including added $FeCl_3$), and other ions in groundwater. The model qualitatively agreed with the data, although soluble As concentrations were generally over-estimated. Such modeling may be useful for roughly estimating the effects of Fe addition or changing pH on As removal.

Full-Scale Tests

Full-scale testing of Fenton filtration proved infeasible. Instead, sampling and analyses were performed in support of tests of $KMnO_4$ addition. The results were consistent with the jar tests. Oxidation of As(III) was better than 90% for $KMnO_4$ equivalent to 60% or more of Fe. There was some particulate Fe in the clearwell below the sand filter. However, the soluble As concentration in the clearwell was always above the MCL. That is, even if the sand filter removed all particulate Fe, the sorption capacity would be inadequate for As removal. Adding some $FeCl_3$ to increase the sorption capacity would probably be necessary to meet the MCL.