Remediation of metal-contaminated aqueous systems by electrochemical peroxidation: an experimental investigation

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Abstract

An innovative technology, electrochemical peroxidation (ECP), was investigated for remediation of mixed metal-contaminated aqueous systems by application of direct electric current to steel electrodes and of dilute H_2O_2 solution to promote Fenton's reactions, forming sparingly soluble solid hydrous ferric oxides (HFO). Bench scale experiments evaluated the sorption and distribution of As, Be, Cd, Cr, Cs, Cu, Li, Ni, Pb, Se, V, and Zn among the soluble and solid state HFO formed as part of the ECP process. The effects of pH, hydrogen peroxide concentrations and electric current process times on the efficiency of metal removal were studied. The potential of this technology was demonstrated by effective removal at pH 3.5–4.6 and within 3 min of 0.25 A dc + 100 mg H_2O_2 l^{-1}, of As, Cr, Pb, Se and V with complete removal of As and Cr, >95.0%. On increasing the pH of the solution to 6.0, the retention of Be and Cu by HFO increased from 0.9–1.9% at pH 3.5 to 76.8–80.7% at pH 6.0 while concentrations of other metals, such as Pb, decreased due to precipitation of Pb hydroxy-complexes. Experiments in the absence of H_2O_2 revealed that metals were adsorbed by HFO with the same order of affinity, As > Cr > Se > V > Be, as in the presence of H_2O_2, but, with the exception of Cr, to a lesser extent. H_2O_2 used in the ECP process was fundamental to increase the adsorption capacity of HFO for As, from 79.2 to 99.2%, due to the oxidation of As(III) to As(V), which has a stronger affinity for HFO. The reduced adsorption may be related to the formation of poorly ordered crystalline akaganeite, which has a lower surface area than ferrihydrite formed when H_2O_2 was used. The optimal operating conditions were pH < 6.0, an H_2O_2 concentration of 100 mg l^{-1} and a current process time not exceeding 3 min. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Remediation of contaminated groundwater remains one of the most intractable problems of environmental restoration. Contaminants typically enter groundwater at concentrations that are thousands or even millions of times above risk-based action levels and then disperse as they are carried through aquifers in flowing groundwater. Chemical phenomena, such as slow dissolution of contaminant sources or slow desorption from the aquifer matrix, further limit the success of remedial efforts.

The magnitude of the groundwater contamination problem is immense: 300,000–400,000 sites in the US contain contaminated soil and/or groundwater [1]. Of the Superfund sites for which Records of Decision have been issued, 75% contained some form of metal contamination [2]. Federal expenditure on the cleanup of contaminated sites is expected to be between US$ 234 and 389 billion over the next 75 years, with combined expenditure for the cleanup of all private and public US sites projected to be between US$ 500 billion and 1 trillion [3].

Although available techniques for the cleanup of these sites can be highly effective, all have high costs that limit their utility for specific applications. For example, pump-and-treat technology flushing water from an aquifer until contaminant concentrations drop below target cleanup levels is effective at containing groundwater plumes. However, a recent evaluation of 77 pump-and-treat systems found that regulatory standards had been achieved at only about 10% of the sites evaluated [1]. The failure of pump-and-treat remediation to meet cleanup goals can be attributed to ineffective containment of point sources, or to the slow release of contaminants from the aquifer itself by desorption and diffusion out of dead-end pore spaces. Electrokinetic separation techniques, which induce the migration and recovery of ions in groundwater using electrical currents [3], have limited effectiveness due to the production of H^+, which has high ionic mobility relative to most metals. Permeable reactive subsurface walls are becoming an accepted technology [1,4] and have been used to achieve in situ immobilization of U, Mo, Cr(VI), Sr, Tc and Ni using various adsorption, reduction, and precipitation reactions [5–7]. In practice, few of the reactive wall materials currently used can be cost-effectively regenerated in place, and thus may require periodic excavation and renewal. Newly developed techniques for containing contamination through in situ aquifer permeability reduction, such as grouting with supersaturated gypsum solutions [8] or microbially produced polysaccharides [9], seem promising for controlling point sources but are less practical for dispersed plumes.

Several other technologies are based on the use of iron oxides to remove metals from waste water and liquid hazardous waste [10,11]. Removal has been attributed to ion exchange, specific adsorption to surface hydroxyl groups, coprecipitation, multinuclear complex or mixed-cation hydroxide complex formation at the surface or precipitation as the discrete oxide or hydroxide. Ferrous iron injection has been shown to be a potentially effective approach to immobilizing Cr(VI) by inducing its reduction to less soluble Cr(III) [12]. Laboratory tests have demonstrated that in situ emplacement of hydrous ferric oxides (HFO) in aquifers by injecting an acidic Fe(III) solution or by simple oxygen injection alone [13] produces an adsorptive substrate with minimal decrease in aquifer permeability. In several water treatment plants [14], the pH of the waste water is raised with $Ca(OH)_2$ solution which leads to the precipitation of heavy metals as their hydroxides. At the same time,

Fe(III) chloride which is added to the waste water also precipitates as ferrihydrite and binds all the heavy metals. The precipitate is then filtered off and is dumped in storage valleys and pits.

In this paper, we investigate a potential new ex situ/in situ method for remediating metal-contaminated water by an electrochemical peroxidation process, (ECP), a proprietary process developed by researchers at the Environmental Research Center at the State University of New York at Oswego, USA. ECP is an enhancement of Fenton's reagent (FR). FR is a wide applied oxidative technology which utilizes the reaction of hydrogen peroxide with ferrous iron (generally added as $FeCl_2$ or $FeSO_4$) to produce free radicals which are capable of oxidizing aqueous phase contaminants. Because the addition of ferrous salts containing chlorine or sulphur to water is undesirable, electrochemistry provides an environmentally preferred method to introduce ferrous iron into solution.

ECP utilizes sacrificial steel electrodes [15] and stoichiometrically balanced additions of dilute hydrogen peroxide solutions to promote FR reactions. HFO are produced as dissolved iron (Fe^{2+}), generated by direct current applied between high surface area electrodes, reacts with the hydrogen peroxide. In laboratory trials, ECP has been successful in reducing to non-detectable levels polychlorinated biphenyls, petroleum hydrocarbons, chlorinated solvents, MTBE and BTEX in various aqueous matrices, septic tanks, groundwater, slurries, pulp and paper waste [15].

The objectives of this work were to evaluate the extent of removal of As, Be, Cd, Cr, Cs, Cu, Li, Ni, Pb, Se, V, and Zn(III) from water by adsorbing colloidal HFO produced during the ECP process, and to assess the effects of operational ECP parameters like time application of current, pH of the water, hydrogen peroxide dosage and the optimum operating conditions for water treatment.

2. Materials and methods

Stock standard solutions of Be, Cd, Cr, Cs, Cu, Li, Ni, Pb, Se, V, and Zn ($1 \, g \, l^{-1}$) were obtained from Fisher Scientific, Pittsburgh, PA. Reagent grade $NaAsO_2$ as the As(III) source and H_2O_2 (30% v/v) were also provided by Fisher Scientific. Reagent grade, HNO_3 (Fisher Scientific, Pittsburgh, PA) was used as purchased. Stock solutions of arsenite and of Cr(VI) were prepared by dissolving a predetermined amount of $NaAsO_2$ and potassium dichromate in tap water to give an As concentration of $1 \, mg \, l^{-1}$.

From an environmental standpoint, Li is reported as non-critical, V is presumed to have ecological significance, whereas all the remaining elements are considered very toxic and environmentally hazardous [16]. Cs was included due to its increasing presence in water from nuclear power sources. A simulated metal-contaminated groundwater was obtained by diluting and mixing aliquots of the stock standard solutions with tap water to give a final metal concentration of $2.5 \, mg \, l^{-1}$ which is 250 (Cd) to 50 (As, Cr, Pb) times greater than the USEPA regulatory limit in drinking water [17] and up to 36,000 times (Cd) greater than the background concentration in freshwater [18].

The effect of pH on the sorption of metals by hydrous ferric oxide was evaluated at a pH range of 3.5–6.0. Before applying current the background solutions were adjusted with either dilute nitric acid (HNO_3) or sodium hydroxide (NaOH) to obtain the pH range from

3.5 to 6.0. Solution pH was measured using a pH meter equipped with an Accu-pHast micro-combination glass electrode (Fisher Scientific).

Two mild steel electrodes, $15 \, cm \times 10 \, cm$, were placed 1 cm apart in a 1.5 l beaker. Before use, the electrodes were abraded with 400 A grade dry sanding paper (Eagle Abrasive, US) and then washed with tap water, deionized water and with three successive rinses of 1 N HNO_3. The total surface area of the electrodes was $600 \, cm^2 \, l^{-1}$ with a submerged surface area of $500 \, cm^2 \, l^{-1}$. Direct current (0.25 A) was applied for 3 min and regulated by an EG&G potentiostat/galvanostat and solution mixed on a stirring plate at a speed of 400 rpm, using a teflon-coated magnetic stir bar. Aqueous H_2O_2 and Fe^{2+} concentrations were monitored every minute using E.M. Quant Test Strips (EM Science, Gibbstown, NJ) and a Reflectance Meter, whereas total aqueous iron concentrations were measured using a Perkin-Elmer 5100 atomic absorption spectrometer equipped with a deuterium-arc background correction. At the end of each 3 min experiment, the generated Fe(III) HFO, operationally defined as particles $> 0.45 \, \mu m$, was allowed to settle and water suspension filtered through Gelman 0.45 glass whool filters. The extract was acidified with concentrated nitric acid, stored at $4°C$ until analyzed. Fe(III) oxyhydroxide material was rinsed with deionized water to remove halite, dried at $50°C$ and digested in aqua regia (5:3 $HCl:HNO_3$) in a Milestone microwave digestion unit. Using 2 M HCl, the resulting digest was transferred to a 25-ml volumetric flask and made up to volume. Concentrations of As, Be, Cd, Cr, Cs, Cu, Li, Ni, Pb, Se, V, and Zn were determined in the extracts and in the digested HFO phase by inductively coupled plasma (ICP) spectrophotometric analysis (ACME Analytical Labs, Vancouver, BC). The background concentration of all the studied metals in the HFO material was found to be negligible throughout the pH range of 3.5–9.5. All measurements were duplicated. The mineralogy of the HFO flock was studied by X-ray diffraction (XRD). XRD patterns of oriented materials were recorded with a Rigaku Geigerflex D/Max IIIC diffractometer using iron-filtered Co $K\alpha$ radiation generated at 40 kV and 30 mA, at a scan speed of $1° \, 2\theta \, min^{-1}$ with a $1°$ divergence slit, a 0.15 receiving slit and a $1°$ scatter slit.

3. Results

3.1. Effect of pH on metal removal by HFO

The effect of pH (from 3.5 to 6.0) on the removal of As, Be, Cd, Cr, Cs, Cu, Li, Ni, Pb, Se, V, and Zn by suspended HFO generated during immersion of steel electrodes for 3 min with 0.25 A dc and $100 \, mg \, H_2O_2 \, l^{-1}$ and metal mass balances are shown in Table 1. The total mass of metals recovered was calculated by summing the mass of metal remaining in solution and that captured on the HFO solids (Table 1). Generation during the experiments of the suspended orange-brown flocculent mainly consisting of HFO probably proceeds in three steps.

1. Electrochemical corrosion of the zero-valent iron of the cathode, in which Fe^0 is oxidized to Fe^{2+}

$$Fe^0(s) \rightarrow Fe^{2+} + 2e^- \tag{1}$$

Table 1
Mass balance and percentage recovery of metals on HFO with variable pH 3.5, 4.6, 6.5, and 3 min of 0.25 A dc[a]

Metal	As	Be	Cd	Cr	Cs	Cu	Li	Ni	Pb	Se	V	Zn
pH 3.5												
Mass balance (%)	92.1 (98.5)	97.3 (113.2)	114.6 (93.8)	92.7 (117.2)	99.5 (93.0)	111.9 (103.5)	128.8 (119.5)	85.9 (116.1)	144.5 (93.3)	136.3 (106.8)	141.0 (109.4)	111.3 (106.5)
Recovery on HFO (%)	99.5 (1.53)	0.9 (0.0)	0.0 (6.2)	95.5 (0.0)	0.1 (7.0)	1.9 (0.0)	0.0 (0.0)	0.8 (0.0)	75.7 (6.73)	84.7 (0.0)	71.3 (0.0)	2.9 0.0
pH 4.6												
Mass balance (%)	91.7 (95.9)	104.2 (107.2)	115.0 (102.7)	81.1 (92.2)	99.7 (100.7)	124.7 (103.5)	128.6 (110.8)	85.2 (105.7)	115.6 (104.2)	122.7 (105.8)	125.8 (119.4)	111.1 (103.5)
Recovery on HFO (%)	99.2 (9.5)	7.4 (0.5)	0.4 (0.2)	94.9 (2.6)	0.1 (0.03)	12.0 (1.7)	0.0 (0.0)	2.0 (0.0)	94.6 (95.3)	78.6 (5.4)	70.0 (17.5)	2.6 (1.0)
pH 6.5												
Mass balance (%)	91.0 (99.2)	138.7 (97.2)	123.4 (97.9)	67.4 (98.1)	94.6 (99.4)	130.2 (98.2)	140.3 (97.9)	103.7 (99.7)	110.2 (99.9)	123.0 (98.7)	146.0 (101.1)	124.9 (104.3)
Recovery on HFO (%)	99.7 (0.94)	76.8 (0.74)	4.3 (4.2)	93.2 (1.4)	0.3 (10.1)	80.7 (13.5)	0.3 (14.3)	7.1 (2.9)	99.6 (99.4)	74.6 (12.1)	60.0 (14.6)	13.3 (11.3)

[a] Values in parentheses refer to corresponding thesis without electric current application.

2. Oxidation of Fe^{2+} by

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + OH^- + OH^\bullet + Fe(II) \tag{2}$$
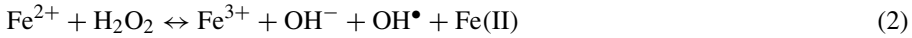
$OH^\bullet$ may be scavenged by reaction with another Fe^{2+} (Eq. (3)) or with a metal (M^{2+}), or it may react with an organic compound

$$OH^\bullet + Fe^{2+} + M^{2+} \rightarrow OH^- + Fe^{3+} + M^{3+} \tag{3}$$
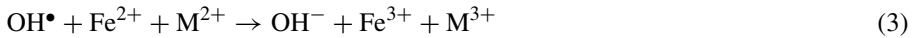
3. Once Fe^{3+} is produced, precipitation of HFO (Eq. (4)) is nearly instantaneous

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \tag{4}$$

Dissolution of Fe^{2+} (Eq. (1)) from the cathode may be enhanced by lowering the pH of the solution (Eq. (5))

$$Fe^0 + 2H^+ \leftrightarrow Fe^{2+} + H_2 \tag{5}$$

However, besides Fe(III) oxyhydroxide, other oxidation products including $M(OH)_3$, $AsO(OH)_3$ and Fe(III) arsenates, and arsenites can form during the ECP process. The amount of colloidal iron does not seem significantly affected by the initial pH of the water, varying between $151 \, mg \, l^{-1}$ at pH 3.5 and $136 \, mg \, l^{-1}$ at pH 6.0. HFO is, in fact, sparingly soluble at groundwater pH greater than 4–5 s.u. ($K_{sp} = 10^{-38}$) [19] provided that conditions remain sufficiently oxidizing to prevent reduction of Fe^{3+} back to Fe^{2+}.

The metal mass balance calculations indicate an average recovery in the analyzed water–HFO suspension above 90% (Table 1). Of all the studied elements, As, Cr, Pb, Se and V show the highest affinity for HFO, with an extent of adsorption at pH 3.5 which varied according to the following order: As > Cr > Se > Pb > V, with percentages of removal at pH 3.5 ranging between 71.3% for V and 99.5% for As. The results obtained for As and Cr suggest that these elements compete more effectively than Zn or Cd with Fe for complexation sites in the HFO system and under the conditions adopted during the ECP process. By contrast, for metals like Be, Cd, Cs, Cu, Li, V and Zn, removal percentages are lower and do not exceed 2.9% (Zn). Although limited, studies have shown that sorption of heavy metals to hydrous oxides is a two-step process: rapid adsorption of metal ions to the external surface is followed by slow intraparticle diffusion along the oxide micropore walls. This intraparticle diffusion is the rate-limiting mechanism in the sorption process of Zn and Cd to microporous oxides [20].

At acid pH and with the exception of Pb, metals do not tend to form insoluble complexes, mainly hydroxides (Table 1). As Pb has a very low solubility product, $K_{sp} = 1.43 \times 10^{-20}$ [21] precipitates from solution at the amount of 6.73% at pH 3.5 and almost completely at pH 4.6 (95.3%) and 6.0 (99.4%). Formation of Pb^{2+} hydroxy complexes is also helped by decomposition of H_2O_2 which is total at pH 3.5 and almost complete at higher pH (90%). At pH 4.6 and in the extreme oxidizing conditions created by H_2O_2, most of the Cr(VI), because of its anionic nature, precipitates (78%) as $Cr(OH)_3$ or with other metal cations like Pb [22] and the remaining is adsorbed onto the positive surface of HFO (Table 1). On increasing the pH of the aqueous solution, a considerable increase may be observed in Be adsorption on the surfaces of HFO, rising from 0.9% at pH 3.5 to 76.8% at pH 6.0

and of Cu, from 1.9 to 80.7%. At pH 6.0, metals are adsorbed according to the order: As > Be > Cr > Cu > Se > V. As was efficiently removed from solution by the HFO, suggesting high efficiency of iron oxide and mixed iron oxide in reducing As concentrations in solution.

Adsorption of arsenic on the HFO is extremely high, rapid and apparently independent of the initial pH of the water, with percentage removal of As on HFO superior to 99%. After only 3 min of generating an electric direct current in the reacting water system, about 4150 μg of arsenic out of an initial mean concentration of 4300 μg As(III) are retained by the HFO and very small traces of the element, approximately $10.0 \mu l^{-1}$, remain in solution. Arsenate and arsenite normally behave in opposite ways with regard to the influence of pH on the adsorption of arsenic on iron oxyhydroxides [23–26]. In dual anion systems and in the pH range of 3–10, which is also the pH range of our tests, adsorption of arsenate normally decreases with increasing pH, while arsenite adsorption increases with increasing pH, with maximum adsorption at approximately pH 9.0. Due to the role of H_2O_2, whose decomposition is enormously accelerated by the presence of other metals, it is likely that in our experiments arsenic is adsorbed as As(V) at pH 3.5–6.0. This result from an environmental point of view means that the ECP process creates the most appropriate conditions for the removal of As(III), the most toxic form of arsenic usually found in groundwater. These observations also seem confirmed by background experiments in the absence of H_2O_2 (Table 3) where As adsorption at pH 4.6 was lower than that in the presence of peroxide (79.2% versus 99.5%).

Dissolution of Fe^{2+} from the cathode in the absence of peroxide and at pH 3.5 is a function of effective surface area, increasing Fe(II) levels form $18 \, mg \, l^{-1}$ at 1 min to $33 \, mg \, l^{-1}$ at 3 min. In our experiments, H_2O_2 is far in excess of Fe(II) which is converted almost instantly to Fe^{3+} ($k = 53 \, l \, mol^{-1} \, s^{-1}$). Jain and Loeppert [27] report that the interaction of arsenate and arsenite with HFO was highly dependent on pH and initial arsenic concentration. The quantitative adsorption of As(V) at low pH is attributable to the relatively high adsorption capacity of HFO for As [25] and the stronger electrostatic attraction of the positively charged surface sites for $H_2AsO_4^-$, the predominant As(V) species. As(III) is less adsorbed onto HFO surfaces than As(V) [28]. Recent data [29–31] indicate that the $H_2AsO_4^-$ forms inner sphere Fe–As(V) complex relative to surface complex of As(III). The stronger adsorption of Be (76.8%) onto HFO at pH 6.0 can be imputed to the fact that the element, having a great affinity for OH^- [32], forms more stronger complexes with the OH^- ions of the HFO surfaces.

3.2. Effect of H_2O_2 concentration on metal removal

The effect is shown (Table 2) of increasing amounts of H_2O_2, from 100 to $1000 \, mg \, l^{-1}$, combined with 3 min of direct current at pH 4.6, upon metal removal from aqueous solution and relative mass balance during ECP. Mass balance calculations reveal an overall recovery of metals superior to 86%. Removal of metals does not seem significantly affected by the concentration of peroxide and in several cases, with the sole exception of V (from 60 to 74.3%), decreases with the H_2O_2 concentration. Indeed, the results show, for example, that Zn recovery on HFO decreased from 130% to 6.12 and Se from 74 to 45.1%. This could be related to limited metal decomposition of H_2O_2 occurring in excess of the metals in solution

Table 2
Mass balance and percentage recovery of metals on HFO with variable application of H_2O_2, 100, 1000 mg $H_2O_2 l^{-1}$, and 3 min of 0.25 A dc at pH 6.5

Metal	As	Be	Cd	Cr	Cs	Cu	Li	Ni	Pb	Se	V	Zn
H_2O_2 100 mg l^{-1}												
Mass balance (%)	91.01	138.7	123.4	67.4	94.6	130.2	140.3	103.7	110.2	123.0	146.0	124.9
Recovery on HFO (%)	99.7	76.8	4.3	93.2	0.3	80.7	0.3	7.1	99.6	74.6	60.0	130.3
H_2O_2 1000 mg l^{-1}												
Mass balance (%)	91.7	126.9	92.19	101.7	97.90	95.6	86.7	90.92	103.6	81.8	106.2	90.2
Recovery on HFO (%)	99.2	61.4	1.29	90.0	0.42	64.7	1.25	3.12	99.1	45.13	74.3	6.18

as well as a limited increase in available surface areas for adsorption since by increasing the amount of H_2O_2 from 100 to 1000 mg l^{-1}, the amount of HFO floc increases by only 2% at pH 4.6. The residual H_2O_2 concentration was low, below 10 mg l^{-1} at pH 4.6, in the experiment with an H_2O_2 rate of 100 mg l^{-1}, due to reaction [2,3] with various metals and remains of the same order of magnitude, 900 mg l^{-1}, in the experiment with an H_2O_2 rate of 1000 mg l^{-1}. Thus, it does not seem beneficial to use H_2O_2 rates in excess of 100 mg l^{-1}.

3.3. Effect of time current application

The results from Table 3 show that, in the absence of peroxide, metals were adsorbed by HFO with the same order of affinity (As > Cr > Se > V > Be) as that shown in the presence of 100 mg H_2O_2 l^{-1}, (Table 3) but, with the exception of Cr, to a lesser extent. This holds for As, that was 79.2% removed with 3 min of plain current compared with 99.2% by adding 100 mg l^{-1} of H_2O_2. Thus, H_2O_2 appears to be fundamental for the oxidation of As(III) to As(V) with more than 99% of the applied As(III) adsorbed on HFO. Hexavalent dichromate was successfully removed with an adsorption of 99.9% of the initial pool just after 3 min of application of 0.25 A dc. On doubling the current time exposure, from 3 to 6 min, removal of metals increased as in the case of As, from 79.2 to 89.6%, nonetheless remaining below percentage removals obtained in the presence of H_2O_2 (99.2% for As). For other metals like Be, removal increased from 53.7 to 66.8% and by more than 100% for Ni and Zn. The greater removal of metals also seems to be related to the greater amount (~80%) of HFO available surface sites doubling the current time application. Freshly precipitated HFO has a specific surface area of 600 m^2 g^{-1} [19] and an exchange capacity of 10–25 meq, 100 g^{-1}.

3.4. Mineralogy of the HFO solids

The solid phase was characterized to test for the presence of iron oxide in the ECP generated solids. X-ray diffraction provided evidence for the formation of non-crystalline iron oxide identified as the least ordered form of ferrihydrite (2-line) (Fig. 1a). The two broad diffraction bands at ca. 0.26 and 0.15 nm can be attributed either to the distance between the Fe layers [33] or to the oxygen arrangement [34]. Cornell and Schwertmann [35] report that

Table 3
Mass balance and percentage recovery of metals on HFO with variable time, 3–6 min, 0.25 mA dc application at pH 6.5[a]

Metal	As	Be	Cd	Cr	Cs	Cu	Li	Ni	Pb	Se	V	Zn
3 min, 0.25 mA dc												
Mass balance (%)	91.7	160.8	89.6	99.5	101.3	88.05	93.2	92.5	99.5	79.3	102.7	77.9
Recovery on HFO (%)	99.2	93.7	16.1	99.9	0.24	88.32	0.62	42.3	97.9	98.1	99.9	63.8
6 min, 0.25 mA dc												
Mass balance (%)	95.4	104.8	89.3	101.5	101.2	92.6	96.6	90.7	100.3	84.15	100.6	82.6
Recovery on HFO (%)	99.6	96.8	26.1	99.9	0.42	91.7	1.46	57.6	99.7	99.5	99.9	98.9

[a] H_2O_2 was added at 100 mg l^{-1} rate.
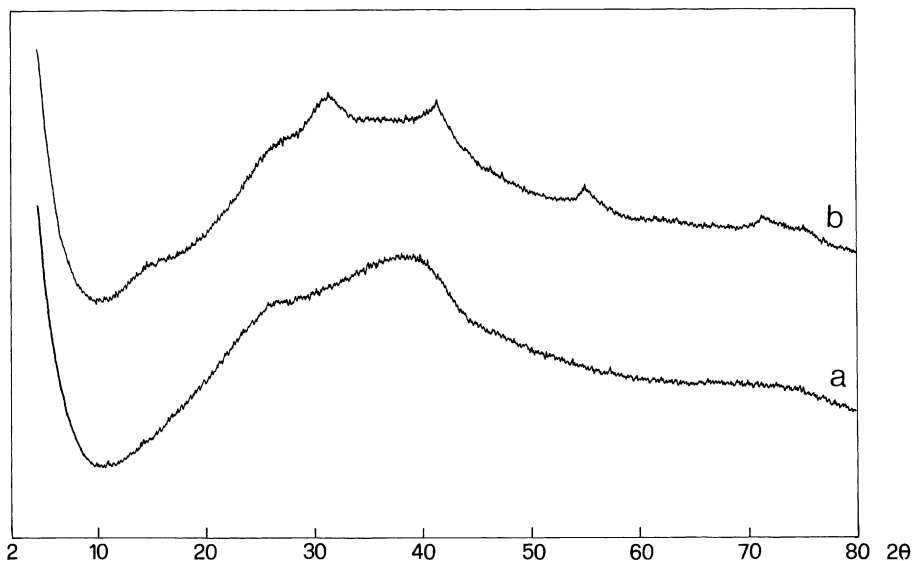
Fig. 1. XRD diffractogram of ECP solids generated after 3 min of 0.25 A dc in the (a) presence of 100 mg H_2O_2 l^{-1} and in the (b) absence of H_2O_2.

formation of poorly ordered ferrihydrite can be enhanced by intense rates of oxidation from H_2O_2 additions as may well occur during ECP experiments. In the absence of peroxide, the XRD chromatogram (Fig. 1b) revealed the presence of a poorly crystalline akaganeite, β-FeOOH, with three main reflections (0.74, 0.33 and 0.16 nm) whose formation is favored by the presence in solution of Cl^- [35] that can derive in our experiments from the use of tap water in the liquid phase.

For the duration of our studies, we observed no crystallization of the formed HFO during ECP. Although non-crystalline materials spontaneously transform to more crystalline phases, the adsorption of several metals, like Be, Cr, Pb, Cu, in the strong salt matrixes tested for ECP, may inhibit the transformation of HFO into crystalline structures, as also evidenced by Trivedi and Axe [20] who found that hydrous metal oxides remain amorphous when Cd or Zn is sorbed to their surfaces. This is important since even though the transformation from the amorphous to crystalline state is advantageous for the long-term stability of the iron oxides, crystalline solids have diminished capacity to bind heavy metals [36].

4. Conclusions

The ECP process may therefore be used not only to reduce organic contaminant concentrations but also to adsorb and recover valuable or toxic metals. The HFO phase consisting of various Fe forms from meta-stable amorphous freshly precipitated to crystalline mineral phases can form very thin layer of Fe-oxyhydroxides on sediment grains [37]. In subsurface in situ treatment, the iron hydroxides can be trapped in rocks and sediments pores and be

immobilized. In situ application of ECP may allow the oxidation of As(III) to As(V) and the adsorption with the removal from otherwise potable groundwater sources. Complete removal of hexavalent Cr by ECP may be an alternative to conventional water treatment based on the reduction to Cr(III) and precipitation as $Cr(OH)_3$ at high pH or use of expensive ion-exchange resins. The energy consumption was calculated to be low and not exceeding $10 \, Wh^{-1} \, l^{-1}$. The ECP process may represent a potential new in situ method for remediating metal-contaminated groundwater by coating contaminated aquifers with an HFO substrate which is adsorptive, insoluble and non-toxic. The oxidizing environment provided by H_2O_2 in the saturated zone maintains under kinetic control the redox state of the aquifer, avoiding release of metals in solution and ensuring long-term remediation of metal-contaminated groundwater. In an ex situ application undesirable levels of hydrogen and oxygen can be controlled by providing adequate ventilation and minimizing headspace build-up throughout the reactor. Further research on the kinetic of metal removal will be performed to optimize the overall performance of the ECP process.

Acknowledgements

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