Development of a spectrophotometric method for on-site analysis of peroxygens during *in-situ* chemical oxidation applications

Lars Rønn Bennedsen, Erik Gydesen Søgaard and Jens Muff

ABSTRACT

Activated peroxygens are frequently used as active agents in *in-situ* chemical oxidation (ISCO) contaminated site remediation applications, and fast and simple quantitative analysis of these species on site is necessary. In this work, the use of a spectrophotometric method based on classic iodometric titration is studied for quantitative analysis of $S_2O_8^{2-}$ and H_2O_2. Instead of a back-titration step, the absorbance of the yellow iodide colour was measured at 352 nm in the presence of a bicarbonate buffer. A linear calibration curve was obtained from 0 to 0.1 mM for both $S_2O_8^{2-}$ and H_2O_2. By dilution, the method can be used for all concentrations typically applied in the field. Concerning pH dependence, neutral pH levels caused no significant error whereas pH levels above 8 caused a 9% and 6% deviation from the theoretical peroxygen concentrations. Furthermore, the method showed little dependence on other matrix components, and absorbance was stable ($<2\%$ change) for more than a week. Overall, the method proved to be fast and simple, which are important features for a field method.

Key words | activated persulfate (ASP), *in-situ* chemical oxidation (ISCO), modified Fenton's reagent (MFR), on-site analysis, peroxygens
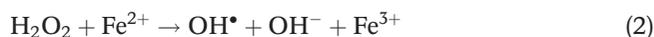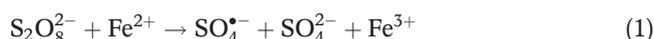
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INTRODUCTION

Even after decades of research on remediation technologies (Watts *et al.* 1999, 2007), contamination of the subsurface by persistent organic contaminants remains a significant problem. In the 1990s, the first reports were published on *in-situ* chemical oxidation (ISCO), and researchers and practitioners have since explored the possibilities of multiple oxidant systems. Activated hydrogen peroxide known as modified Fenton's reagent (MFR) and activated persulfate (ASP) are two of the more recent and most frequently used oxidant systems studied and used at full scale. Persulfate and hydrogen peroxide (jointly known as peroxygens) have standard reduction potentials of $E_o = 2.01$ V and $E_o = 1.78$ V, respectively. However, although they are strong oxidants, their rate of direct oxidation of most hazardous organics is mostly too slow to be applicable in remediation. For this reason, persulfate and hydrogen peroxide are activated in order to produce free radicals: sulfate radicals ($E_o = 2.4$ V) and hydroxyl radicals ($E_o = 2.76$ V). For ISCO application, iron is often used to activate the peroxygens in accordance with

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \tag{1}$$

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

Over the past 10 years, ISCO has been used increasingly for the remediation of contaminated sites. Therefore, simple and rapid methods are needed in order to conduct quantitative measurements of these oxidants in the field as part of monitoring the stability and distribution of oxidant in the subsurface during and after injections. Several methods have already been suggested and described in the literature; these include spectrophotometric (Bader *et al.* 1988; Shuiundu *et al.* 1990; Volk *et al.* 1993; Gulyas *et al.* 1995; Roche & Prados 1995; Benitez *et al.* 1996; LeLacheur & Glaze 1996; Leitner & Dore 1997; Sunder & Hempel 1997; Tanner & Wong 1998; Zhang *et al.* 2000; Huang *et al.* 2002;

Nogueira *et al.* 2005; Liang *et al.* 2008; Luo *et al.* 2008), reductometric (Kolthoff & Stegner 1947; Kolthoff & Carr 1953), polarographic (Kolthoff & Woods 1966; Amin & Hareez 1981), fluorometric (Echigo *et al.* 1996; Schick *et al.* 1997; Li & Townshend 1998; Taniai *et al.* 1999), electrochemical (Evans *et al.* 2002; Li *et al.* 2007; Salimi *et al.* 2007) and chemiluminescent (Hu *et al.* 2007; Tahirovic *et al.* 2007) methods. Furthermore, available semi-quantitative methods using test strips can be valuable during field work, but the accuracy might not be acceptable for all projects.

In 2008, Liang *et al.* proposed a spectrophotometric method for the determination of $S_2O_8^{2-}$ based on modifications of the iodometric titration method (Liang *et al.* 2008). However, from our point of view, the approach used in the method has, in addition to $S_2O_8^{2-}$, the potential to apply to H_2O_2. The objective of this research was thus to investigate the procedure further regarding H_2O_2 quantification and the influence of matrix effects on its validity. Matrix effects include change in pH, the concomitant presence of different iron species, and the presence of natural soil and groundwater components in real contaminated soil from a site with a complex mixture of organics ranging from pharmaceutical waste to chlorinated solvents. As a basis for comparison to Liang *et al.* and our H_2O_2 experiments, $S_2O_8^{2-}$ was also included in this study.

The chemistry of the studied spectrophotometric method is a modification of the traditional iodometric titration developed by Kolthoff & Stegner (1947) (Kolthoff & Stegner 1947), where oxidants (peroxygens) react with iodide in accordance with

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \qquad (3)$$

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-} \qquad (4)$$
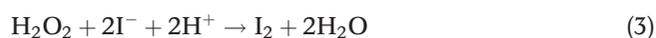
The ideal reaction stoichiometry between oxidant and iodide is 1:2, and the iodine product is back-titrated with the thiosulfate, $S_2O_3^{2-}$, as reductant

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad (5)$$

The approach studied in this paper omits the back-titration step and aims for spectrophotometric measurement of the yellow-coloured iodine as a signal (Liang *et al.* 2008).

In ISCO applications, monitoring H_2O_2 and $S_2O_8^{2-}$ concentrations is important for the evaluation of radius of influence and stability of oxidant at the site, but the modified iodometric method cannot be used for detecting radicals. For this purpose, a few field-suitable methods have been proposed to measure some of the radicals generated in MFR (Satoh *et al.* 2007) and ASP (Hoag *et al.* 2009).

MATERIALS AND METHODS

Chemicals

All chemicals in the experiment, excluding hydrogen peroxide and sodium hydroxide, were analytical reagent grade chemicals and were used as received. Dilutions and stock solutions were prepared with demineralized water produced in-house with a Silex II ion exchanger from SILHORKO (Skanderborg, Denmark). The following chemicals were used: potassium persulfate (>99% Merck (Darmstadt, Germany)), hydrogen peroxide (technical grade 33% VWR (Søborg, Denmark)), potassium iodide (>99.5% Merck), potassium bicarbonate (100% J. T. Baker (Deventer, The Netherlands)), sulfuric acid (96% Bie & Berntsen (Søborg Denmark)), sodium hydroxide (technical grade 30% VWR), ferrous sulfate heptahydrate (>99% J. T. Baker), and citric acid monohydrate (>99% Merck).

A $K_2S_2O_8$ stock solution (5 mM) was prepared for every test by dissolving 1.3517 g of $K_2S_2O_8$ in 1,000 ml demineralized water. An H_2O_2 stock solution (5 mM) solution was also prepared for each test. A 5 mM $FeSO_4$ solution was prepared by dissolving 1.390 g $FeSO_4 \cdot 5H_2O$ in 1,000 ml demineralized water. A 1.0 M citric acid solution was prepared by dissolving 10.51 g of citric acid monohydrate in 50.00 ml demineralized water. Solutions of 1.0 M H_2SO_4 and 1.0 M NaOH were used to adjust the pH value of the solutions.

Apparatus

Spectrophotometric measurements were made with a Varian Cary 50 UV-visible light spectrophotometer (Palo Alto, California, US) equipped with quartz cuvettes of 1 cm light path, and all samples were measured at least 4 times. Solution pH was monitored using a Radiometer PHM210 pH meter (Lyon, France).

Procedure

Standard solutions for calibration were prepared daily by adding 40 ml of demineralized water into 50 ml measuring glasses. Then, 0.2 g of $KHCO_3$ (resulting in 40 mM), 4 g of KI (resulting in 482 mM) and 0–1 ml of either 5 mM H_2O_2 or 5 mM $K_2S_2O_8$ stock solution (resulting in 0–0.1 mM) was added to measuring glasses that were filled with

demineralized water to the 50 ml mark. After the glasses were shaken by hand, the reactions were allowed to equilibrate for 30 min before measuring the absorbance at 352 nm. The resulting concentrations in the measuring solutions were 0.00–0.10 mM of oxidant (0–3.4 mg/l H_2O_2 or 0–27 mg/l $K_2S_2O_8$). $Na_2S_2O_8$ was also tested and behaved identically to $K_2S_2O_8$.

Dependent on the expected concentration to be determined in the sample, different sample volumes can be added to the 50 ml measuring solution in order to obtain concentrations within the calibration area of 0–0.1 mM. Concentration, C_{sample} [mM], of oxidant in the sample solution can be calculated from the expression

$$C_{sample} = C_{measured} \frac{0.050l}{V_{sample}} \tag{6}$$

where $C_{measured}$ [mM] is the measured concentration and V_{sample} [L] is the sample volume added to the measuring solution, e.g., if 1 ml of sample is added, the dilution factor (DF) will be 50. The method was tested with DF from 50 to 10,000 (0–34 g/l H_2O_2) and if needed, higher DF will also work. All zero measurements were made on demineralized water.

RESULTS AND DISCUSSION

Absorbance and calibration

Individual UV-visible absorption spectra for the maximal concentrations of the single and combined reagents used in the analytical method are presented in Figure 1. It is clear that the single reagents persulfate, hydrogen peroxide, potassium bicarbonate, potassium iodine, citric acid, sulfuric acid, and sodium hydroxide do not absorb light at the analytical wavelength of 352 nm, where the maximum absorbance is seen for the combined oxidant, potassium iodide and potassium bicarbonate solution.

From the prepared stock solutions, calibration curves for both H_2O_2 and $S_2O_8^{2-}$ were made. Figure 2 shows a linear correlation between absorbance and concentration at final concentrations of 0–0.1 mM oxidant in the measuring solution with a regression coefficient R^2 of 0.9992 for both H_2O_2 and $S_2O_8^{2-}$. The slopes of the curves ($\alpha_{H2O2} = 0.5523$ and $\alpha_{S2O82-} = 0.5385$) are comparable, which suggests that the method can be further simplified by measuring both oxidants based on a single calibration curve. The convergence between the slopes also suggests that this method can be
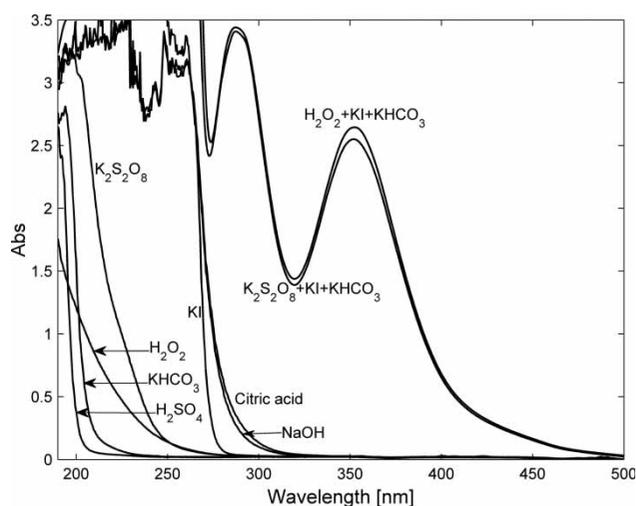

Figure 1 | UV-visible absorption spectra for the single reagents used in this study including $[K_2S_2O_8]$ = 5 mM, $[H_2O_2]$ = 5 mM, $[KI]$ = 482 mM, $[KHCO_3]$ = 40 mM, $[H_2SO_4]$ = 1 M, $[NaOH]$ = 1 M, $[citric acid]$ = 1 M and combined reagent solutions in accordance with the method description with concentrations in the measuring solution of $[H_2O_2]_0$ = 0.1 mM, $[K_2S_2O_8]_0$ = 0.1 mM, $[KI]_0$ = 482 mM, and $[KHCO_3]_0$ = 40 mM.
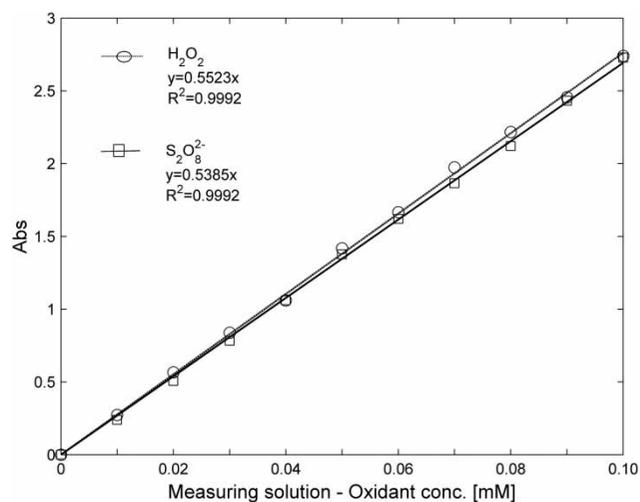

Figure 2 | Calibration curves for both H_2O_2 and $K_2S_2O_8$ as presented in materials and methods. DF for this calibration was 50.

used as a dual oxidant measurement method for quantifying the sum of H_2O_2 and $S_2O_8^{2-}$ in mixed solutions.

Effect of solution pH

In ISCO, pH adjustments are commonly used to enhance the process, e.g., pH is lowered with sulfuric acid to avoid precipitation of iron, or pH is raised by adding sodium hydroxide for alkaline activation of $S_2O_8^{2-}$. In low buffered aquifers, $S_2O_8^{2-}$ alone can cause a significant decrease in pH to
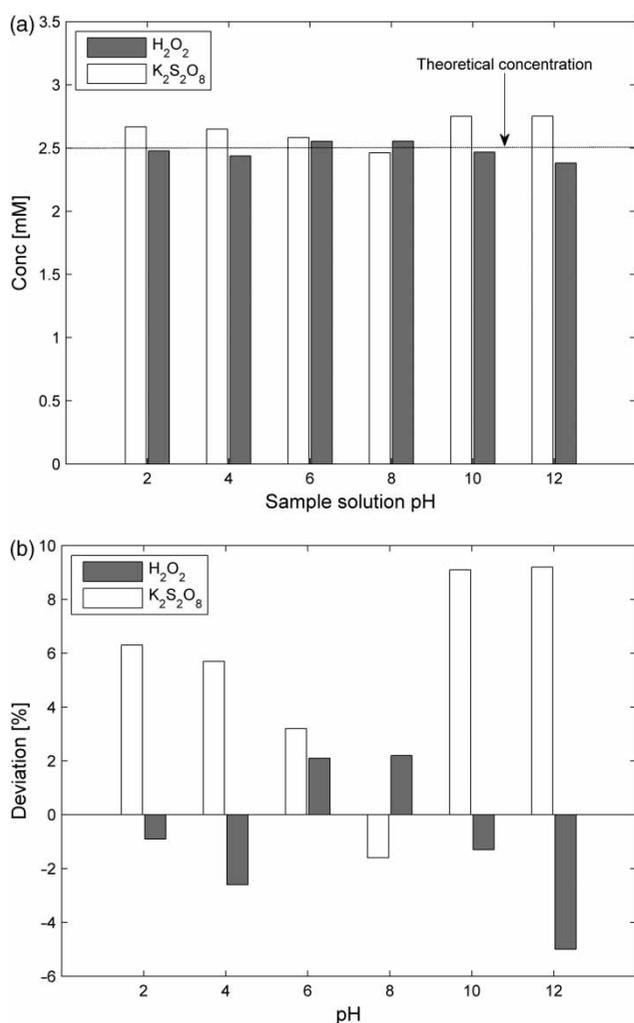
Figure 3 | (a) Measurement of H_2O_2 and $K_2S_2O_8$ at different sample solution pH compared to the theoretical concentration of 2.5 mM. (b) The calculated deviation of the experimentally determined value from the theoretical.

Figure 4 | Absorption spectra for iron in different solutions. $[H_2O_2 + KI + KHCO_3]_0 =$ 0.1 mM, 482 mM, and 40 mM, $[FeSO_4 + H_2SO_4]_0 = 0.1$ mM and 20 mM. $[FeSO_4 + H_2O_2]_0 = 0.1$ mM and 5 mM.

about 2 (Block *et al.* 2004; Bennedsen *et al.* 2010). Figure 3 shows the effect of different pH levels (adjusted with either 1.0 M H_2SO_4 or 1.0 M NaOH) in the sample solutions on the measured peroxygen concentrations, compared to the experimentally made theoretical value realised from the sample preparation. The largest deviations from the theoretical value were observed at high pH (10–12), where deviations up to 5% and 9% were observed for H_2O_2 and $K_2S_2O_8$ sample solutions, respectively. At low pH (2–4), the concentration in the $K_2S_2O_8$ solutions deviated by 6%. In the remaining samples, deviations were 1–3%. Overall, the lowest deviations were seen for H_2O_2, but at neutral pH, acceptable results were obtained for both oxidants with only small deviations. Compared to some of the methods mentioned in the introduction, this method is more accurate (max. 9% deviation) over a wide pH range (2–12), which is
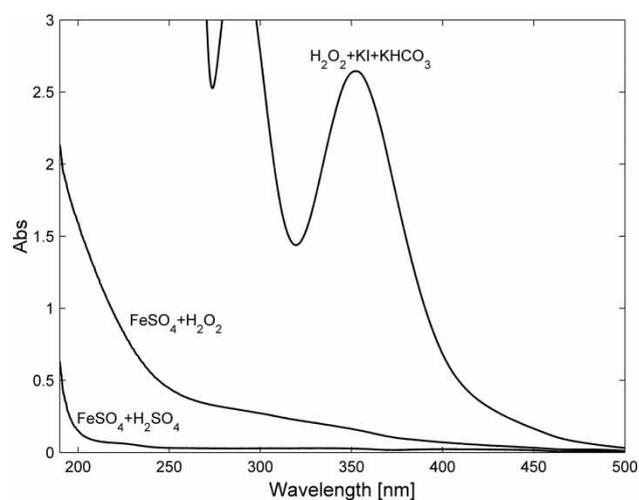
ascribed to the buffering effect of $KHCO_3$ in the measuring solution. These results are in agreement with results obtained by Liang *et al.* (2008) who reported a maximum deviation of 8% for $Na_2S_2O_8$ measurements at pH 7–10.

Influence of Fe^{2+} and Fe^{3+}

When ferrous iron is oxidized from Fe^{2+} to Fe^{3+} it absorbs light at 352 nm, but when ferrous iron is in an acidic environment, no significant absorption is observed. The influence of iron on the absorbance measured therefore depends strongly on the oxidation state. In Figure 4, absorbance spectra were recorded for ferrous iron solutions in both sulfuric acid and H_2O_2 and compared to the spectrum of the H_2O_2, potassium iodide and potassium bicarbonate solution. In H_2O_2, ferrous iron was oxidized to ferric iron, and Figure 4 shows the absorbance of ferric iron at the measurement wavelength of 352 nm. In the worst case, with ferrous iron and oxidant concentrations added 1:1, the ferric iron accounted for an absorbance error of plus 6% (Fe^{3+} absorbance was 0.16 and absorbance by the oxidant measuring solution was 2.60, $(0.16/2.76)*100\% =$ 5.8%). In practical ISCO applications, ferrous iron is commonly added in lower molar concentrations (often around 100 mg/l, 1.8 mM) compared to H_2O_2 (often 2–12%, 590–3,500 mM (Watts & Teel 2005)) or $S_2O_8^{2-}$ (often 10–30% $Na_2S_2O_8$, 420–1,260 mM (Block 2008)) for activation of the oxidants, which means the effect can often be neglected. When subsurface concentrations of oxidants decrease due to activation and decomposition, it becomes more important

to account for background absorbance from oxidized iron and other components in groundwater that absorb light at the analytical wavelength.

Effect of reaction time

For $S_2O_8^{2-}$ measurements, a reaction time of 15 min was suggested by Liang et al. (2008). In the present study, absorbance was measured over time in order to evaluate whether this was also applicable for H_2O_2. Furthermore, different amounts of KI were tested to reduce the amount of chemicals used. Figure 5 shows that the rate of production of iodine was higher with H_2O_2 than $S_2O_8^{2-}$, where the absorbance was stable after 4 and 20 min for H_2O_2 and $S_2O_8^{2-}$, respectively. However, a lower amount of KI not only resulted in slower reactions, but also in reduced absorbance and hence a lower measured peroxygen concentration. This demonstrated the importance of using the same amount of KI for every measurement. Potassium iodide was added in greater volume compared to the oxidant (121 to 482 mM KI to 0.05 mM oxidant) but equilibration of the reaction resulted in measurably different iodine concentrations despite constant oxidant concentration. Further investigations showed that the absorbance of the solutions were stable (<2% change) for more than a week.

Results from measurements in soil slurry batch reactors containing a complex contaminant mixture

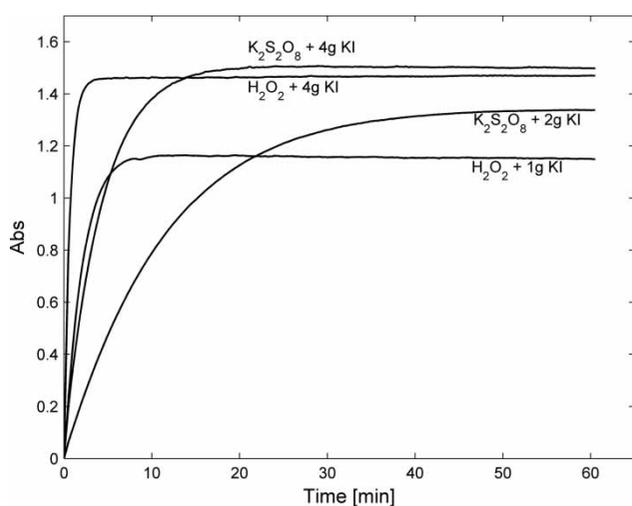The presented analytical method was tested in several water and slurry bench test experiments where the primary aim was to compare MFR and ASP for the remediation of soil and groundwater contaminated with a complex mixture of chlorinated solvents, petroleum hydrocarbons, pharmaceuticals, mercury, cyanide and several other compounds. The removal efficiencies with respect to contaminants from this study are presented in Bennedsen et al. (2010). With respect to analysis of aqueous oxidant concentrations, the method presented in this paper provided fast and reliable results in all tests. An example is showed in Figure 6, where H_2O_2 decomposition (initially 2.3%) was measured in a soil slurry batch reactor (50 g soil and 100 ml groundwater). The soil was course-grained sand with a low content of natural organic matter, small concentrations of metals and the presence of residual free-phase tetrachloroethylene. The site groundwater contained benzene (22 mg/l), toluene (29 mg/l), tetrachloroethylene (120 mg/l), sulfonamides (660 μg/l), barbiturates (420 μg/l), and several other contaminants. Initially, the pH was 5.0 but it decreased to 3.1 during treatment with H_2O_2. Redox conditions were sulfate reducing and methanogenic prior to treatment. Except for dilution with demineralized water to adjust expected H_2O_2 concentrations to the calibration range, no preparation of the collected water samples from the reactor was performed before H_2O_2 analysis. As seen in Figure 6, the measured H_2O_2 starting concentration (672 mM) was acceptably close to the theoretical (679 mM) and decomposition was followed for 5 days, where all H_2O_2 had reacted. The visible decay in H_2O_2
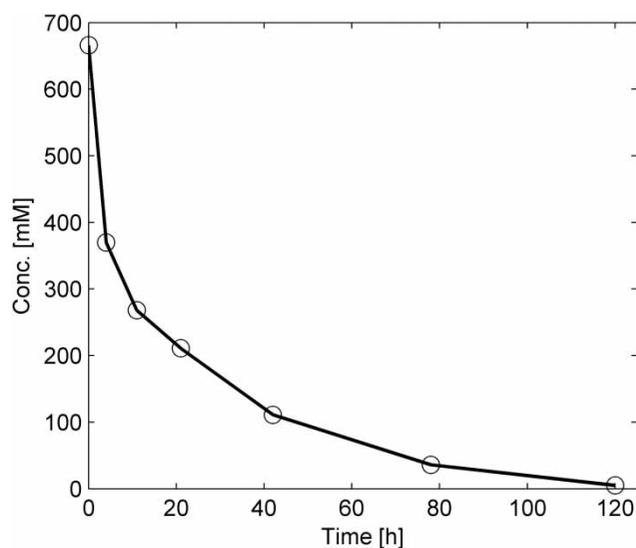
Figure 5 │ Kinetics of the oxidation of iodide to iodine by 0.05 mM H_2O_2 and $S_2O_8^{2-}$ with different concentrations of potassium iodide.

Figure 6 │ An example where the analytical method was used with contaminated soil and ground water. H_2O_2 concentration was measured daily for 5 days to investigate the stability of the oxidant. 1.8 mM citric acid chelated iron catalyst was added to the water in the bench test reactor.

followed the expected pattern with respect to its consumption primarily through activation and organic degradation. DFs of 1,000 to 10,000 was necessary to reach the calibration range, and this demineralized water dilution minimized the influence of ferric iron in particular, but also other potentially interfering species from the contaminated matrix. Humic compounds that can be concentrated in some groundwater may absorb at wavelengths close to the 352 nm used in the method presented here, but the chemical oxidation process itself can be expected to minimize this interference together with the inherent standard dilution required by the method. Based on these results obtained in the presence of a highly contaminated soil and groundwater matrix in soil slurry reactors, the method was shown to be applicable for potential on-site use.

CONCLUSIONS

The analytical method investigated in this paper can be used to measure the concentration of H_2O_2 and $S_2O_8^{2-}$ in contaminated water and also, to a certain extent, the sum of these peroxygens. The ease of the method makes it applicable to on-site field measurement when performing ISCO operations. Extreme pH conditions can influence the results, but the found deviation was less than 6% and 9% for H_2O_2 and $S_2O_8^{2-}$, respectively. Background absorbance from groundwater constituents potentially needs to be taken into account, but no significant interference was observed in this study. The method was tested for the measurement of peroxides in contaminated soil and groundwater matrices and showed the anticipated relative decay in accordance with the amount of peroxygen added.

ACKNOWLEDGEMENTS

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