

**BASE-ACTIVATED PERSULFATE TREATMENT OF CONTAMINATED
SOILS WITH pH DRIFT FROM ALKALINE TO CIRCUMNEUTRAL**

By

MICHAEL ANDREW MIRAGLIO

A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

WASHINGTON STATE UNIVERSITY
Department of Civil and Environmental Engineering

May 2009

To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation/thesis of Michael Andrew Miraglio find it satisfactory and recommend that it be accepted.

Richard Watts, Ph.D., Chair

Amy Teel, Ph.D.

Balasingam Muhunthan, Ph.D.

ACKNOWLEDGMENTS

The culmination of my research with the completion of this thesis paper symbolizes the apex and conclusion of my fantastic though sometimes academically strenuous career at Washington State University. First and foremost, I would like to thank my advisor Dr. Rick Watts, who generously allowed me join his research team. I am truly grateful for the steady support, guidance, and patience he has shown me throughout my graduate career.

I graciously appreciate the encouragement and guidance I have received from the entire faculty, professors, and my friends in the Civil Engineering department. I would like to thank Dr. Balasingam Muhunthan and Dr. Amy Teel for being on my committee. I am very grateful for all the help I received from Rob, Joseph, Josh, Olga, Ana, Jeremiah, Chase, and Mushtaque; thank you guys for always keeping the mood light, and helping me overt disaster with your guidance and kindness.

Any acknowledgement would not be complete without mentioning my family. My love and appreciation go to my mother and father, Mike and Carol, whom I draw inspiration from and owe everything to for supporting and encouraging me throughout my academic career. I also am grateful to have two loving sisters, Sophia and Angelina. Thank you all!

**BASE-ACTIVATED PERSULFATE TREATMENT OF CONTAMINATED
SOILS WITH pH DRIFT FROM ALKALINE TO CIRCUMNEUTRAL**

ABSTRACT

by Michael Andrew Miraglio, M.S.
Washington State University
May 2009

Chair: Richard J. Watts

Recent empirical evidence suggests that base-activated persulfate must be conducted at $\text{pH} > 10$ to be effective. However, other data suggests that persulfate reactivity remains as the pH drifts below pH 10. The potential for persulfate activation after base addition as the pH drifts from alkaline to circumneutral was investigated in four soil systems of varying soil organic matter (SOM) contents. Two probe compounds, nitrobenzene and hexachloroethane, were used to quantify the relative reactivity of hydroxyl radical and reductants, respectively. Hydroxyl radical activity was greatest in persulfate-soil slurries at pH 12 with decreasing hydroxyl radical activity in the systems in which the pH had drifted to pH 10 and pH 8. Furthermore, greater rates of hydroxyl radical generation were found with decreasing SOM contents, which is likely due to a lower degree of hydroxyl scavenging by SOM.

Superoxide radical and reductant generation also occurred at all pH systems with lower rates as the pH drifted toward circumneutral. In all pH systems, hexachloroethane degradation was greatest in soil systems with greater SOM content. Considerably less reductant formation occurred for the systems at pH 10 and pH 8 once the SOM was removed, but reductants were still formed.

Persulfate decomposition and pH drift were also monitored in conjunction with hydroxyl radical and reductant experiments. Persulfate decomposition occurred most rapidly in the soil slurries with greater SOM. Persulfate decomposition was minimal in all other slurries with the least decomposition occurring once SOM was removed. pH drift was approximately parallel to persulfate decomposition in all four soil systems with the most rapid decline in the higher SOM soil systems. The results of this research demonstrate that base-activated persulfate may be more active than previously thought as the pH drifts towards neutral. From a practical treatment perspective, application of base-activated persulfate in situ may potentially extend treatment longer than previously thought making it a more efficient ISCO technology.

TABLE OF CONTENTS

	Page
ABSTRACT.....	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
1. Introduction.....	1
2. Methodology	3
2.1 Materials.....	3
2.2 Soils.....	3
2.3 Probe Compounds.....	4
2.4 Screening of Base Dosages.....	4
2.5 Experimental Procedures	5
2.6 Analysis.....	6
3. Results and Discussion.....	6
3.1 Persulfate decomposition and pH changes in soil slurries.....	6
3.2 pH drift in soil slurries.....	8
3.3 Hydroxyl radical generation as pH drifts to circumneutral	10
3.4 Superoxide radical and reductant generation as the pH drifts to circumneutral...	11
4. Conclusion	12
References	14
Tables	16
Figures.....	17

LIST OF TABLES

Table 1. Physical properties of soils KB1 and KB2.....	16
Table 2. Chemical properties of soils KB1 and KB2.....	16

LIST OF FIGURES

Figure 1. pH profiles of various molar ratios of sodium hydroxide:sodium persulfate for soils KB1 (a) and KB2 (b).	17
Figure 2. pH profiles of chosen molar ratios of sodium hydroxide:sodium persulfate for soil slurries KB1 and KB2 indicating approximate spike times of probe compounds.	18
Figure 3. pH profiles of the selected molar ratio of 0.375:1 sodium hydroxide:sodium persulfate for soil slurries KB1-No SOM and KB2-No SOM.	18
Figure 4. Persulfate concentrations in soil slurries KB1(a) and KB2(b) in conjunction with hydroxyl radical generation experiments.	19
Figure 5. Persulfate concentrations in soil slurries KB1-No SOM(a) and KB2-No SOM(b) in conjunction with hydroxyl radical generation experiments.	20
Figure 6. Persulfate concentrations in soil slurries KB1(a) and KB2(b) in conjunction with reductant generation experiments.	21
Figure 7. Persulfate concentrations in soil slurries KB1-No SOM(a) and KB2-No SOM(b)) in conjunction with reductant generation experiments.	22
Figure 8. pH profiles for soil slurries KB1(a) and KB2(b) in conjunction with hydroxyl radical generation experiments.	23
Figure 9. pH profiles for soil slurries KB1-No SOM(a) and KB2-No SOM(b) in conjunction with hydroxyl radical generation experiments.	24
Figure 10. pH profiles for soil slurries KB1(a) and KB2(b) in conjunction with reductant generation experiments.	25
Figure 11. pH profiles for soil slurries KB1-No SOM(a) and KB2-No SOM(b) in conjunction with reductant generation experiments.	26
Figure 12. Hydroxyl radical generation quantified through nitrobenzene degradation in soil slurries KB1(a) and KB2(b).	27
Figure 13. Hydroxyl radical generation quantified through nitrobenzene degradation in soil slurries KB1-No SOM(a) and KB2-No SOM(b).	28
Figure 14. Reductant generation quantified through hexachloroethane degradation in soil slurries KB1(a) and KB2 (b).	29
Figure 15. Reductant generation quantified through hexachloroethane degradation in soil slurries KB1-No SOM(a) and KB2-No SOM(b).	30

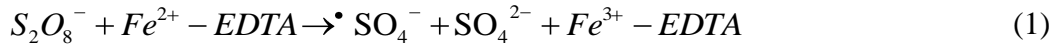
1. Introduction

Soils and groundwater contaminated with hazardous organic chemicals can often present threats to public health and the environment. Therefore, continued efforts are needed to develop remediation technologies. Many of the remediation technologies that have evolved over the past 30 years have limitations. For example, pump-and-treat systems are limited by rates of contaminant desorption and non-aqueous phase liquid dissolution (Watts, 1998) and are characterized by high costs due to continued pumping over long time periods (ITRC, 2005). Bioremediation may take significant time due to difficulties in obtaining effective treatment, contaminant toxicity, insufficient nutrients, and desorption and dissolution limitations (ITRC, 2008). Thermal remediation can be heat transfer limited; furthermore, there are high costs involved with the transfer of heat through the subsurface (Lighty et al., 1990).

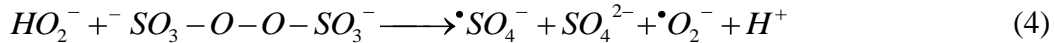
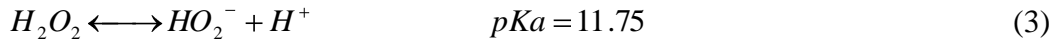
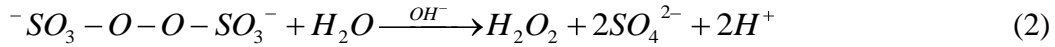
An increasingly popular method for treating subsurface contamination is the use of in situ chemical oxidation (ISCO), which involves the injection of strong oxidants into the subsurface. Four ISCO oxidants have been developed over the past 20 years: modified Fenton's reagent, or catalyzed H_2O_2 propagations (CHP), permanganate, ozone, and activated persulfate (Hulling and Pivetz, 2006). Permanganate is a relatively stable and specific oxidant that reacts primarily with alkenes by addition to the C=C double bond (Siegrist et al., 2001). CHP, ozone, and persulfate serve as oxidant sources for radical based reactions that are relatively non-specific, providing the basis to destroy most organic contaminants (Watts and Teel, 2006). Hydrogen peroxide and ozone are short-lived in the subsurface, while persulfate can persist in the subsurface for months (Brown et al., 2003). Therefore, the use of persulfate can be advantageous because it is a

nonspecific oxidant and has the potential to promote contact between the oxidant and contaminants.

Two methods commonly used to activate persulfate are chelated iron and base. One of the most commonly used chelated forms of iron is iron(II)-ethylenediaminetetraacetic acid (Fe(II)-EDTA) (Block et al., 2004). Chelated iron promotes the decomposition of persulfate to sulfate radicals:



Base-activated persulfate is the most popular formulation currently used in field applications. Furman et al. (2009) postulated that sulfate, hydroxyl, and superoxide radicals are formed in base-activated persulfate systems:



The generation of the suite of reactive oxygen species shown in equations 2-5 provides widespread reactivity of base-activated persulfate formulations.

The effectiveness of base-activated persulfate in the subsurface is dependent on pH. Empirical data from field investigations suggest that the reactivity of persulfate formulations decreases dramatically at pH < 10. Although Block et al. (2004), suggested that base-activated persulfate is only effective at pH > 10, some results suggest that contaminant oxidation may proceed at pH systems < 10, especially in the presence of

subsurface solids. The objective of this research was to investigate the reactivity of base-activated persulfate formulations as the pH drifts from alkaline to circumneutral pH.

2. Methodology

2.1 Materials

Sodium persulfate (>98%) and hexachloroethane (99%) were purchased from Sigma-Aldrich. Mixed hexanes, nitrobenzene (99%), sodium hydroxide, sodium bicarbonate, and sodium carbonate were obtained from J.T. Baker. Sodium thiosulfate (99%) and n-hexane were purchased from Fisher Chemical. Potassium iodide (99%) was purchased from Alfa Aesar. Deionized water was purified to >18.0M Ω •cm with a Barnstead Nanopure II deionizing system.

2.2 Soils

Two horizons of a surface soil, collected from an open slope near Kamiak Butte, WA, were used in base-activated persulfate reactions. The two horizons (KB1 and KB2) were chosen because of their varying soil organic carbon contents but similar mineralogy (Table 1). The soils were crushed using a soil grinder and sieved through a 1.65 mm sieve. Organic carbon content was determined by the Walkley-Black method (Walkley and Black, 1934). Particle size distribution was analyzed using the pipette method (Gee and Bauder, 1986). The citrate-bicarbonate-dithionite extraction method was used to determine amorphous and crystalline iron and manganese oxyhydroxides content (Jackson et al., 1986). Cation exchange capacity was analyzed by saturation with sodium acetate at pH 8.2 (U.S. Soil Conservation Service, 1972). Physical and chemical properties for the KB1 and KB2 soils are listed in Tables 1 and 2.

Soil organic matter (SOM) was removed from the two soils by addition of 20% hydrogen peroxide (H_2O_2) (Robinson, 1927). Soil slurries received periodic additions of H_2O_2 and were heated to 60°C until a visible color change of dark to light in the soil occurred indicating that the SOM was removed. Soils were dried at 55°C , pulverized, and sieved with a 1.65 mm sieve.

2.3 Probe Compounds

The probe compounds were selected based on their relative reactivities with each of the reactive oxygen species. Nitrobenzene (NB) was used to detect hydroxyl radicals ($k_{\text{OH}\cdot} = 3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) but not sulfate radicals ($k_{\text{SO}_4\cdot-} \leq 10^6 \text{ M}^{-1}\text{s}^{-1}$) (Buxton et al., 1988; Neta et al., 1977). Hexachloroethane (HCA) was selected as a probe for superoxide and other reductants ($k_{\text{O}_2\cdot-} = 400 \text{ M}^{-1}\text{s}^{-1}$) because it has negligible reactivity with oxidants; e.g., hydroxyl radicals are nonreactive with perchlorinated aliphatic compounds ($k_{\text{OH}\cdot} \leq 1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) (Haag and Yao, 1992; Afanas'ev, 1989).

2.4 Screening of Base Dosages

Several persulfate formulations of varied sodium hydroxide to persulfate molar ratios were added to the KB1 and KB2 soils to obtain a base dosage that would drift from basic to circumneutral (Figure 1a-b). Using a sodium persulfate concentration of 0.5 M, molar ratios of 0.375:1 to 2.5:1 hydroxide:persulfate were prepared; 20 mL of each were added to 10 g of soil in 40 mL volatile organic analysis (VOA) vials. The pH was monitored over time to obtain pH profiles for each molar ratio; each vial was mixed prior to pH measurements. The vials were incubated in a water bath at 25°C ($\pm 2^\circ\text{C}$) between measurements.

From the results in Figure 1a-b, molar ratios of 1.25:1 were used in the KB1 soil slurries and 0.375:1 were used in the KB2 soil slurries to evaluate persulfate reactivity as the pH drifted from basic to circumneutral. Approximate spike times for the probe compounds were determined from these profiles at pH levels of 12, 10, and 8 (Figure 2). Furthermore, molar ratios of 0.375:1 were used once the SOM was removed for soils KB1-No SOM and KB2-No SOM because a smaller ratio would not bring the starting pH above 12 in these soil slurries. Changes in pH in these soil slurries with approximate spike times are shown in Figure 3.

2.5 Experimental Procedures

VOA vials were prepared with 10 g of the KB1, KB2, KB1-No SOM, or KB2-No SOM soils. Each vial received 18 mL of the sodium hydroxide:sodium persulfate solution; the vials were mixed, and then incubated in a water bath at 25°C ($\pm 2^\circ\text{C}$).

Once the pH in the reactors declined to 12, a series of vials received 2 mL of one of the concentrated probe compounds (10 mM NB or 0.005 mM HCA) which yielded final solution concentrations of 1 mM NB or 0.0005 mM HCA, respectively. Probe degradation was then monitored by periodically extracting the entire vial contents with 5 mL of hexane and analyzing the extract by gas chromatography. All vials were mixed before samples were extracted to ensure homogeneity and minimize volatilization.

The pH in the remaining reactors was monitored until it decreased to 10 and then to 8; these vials then received 2 mL each of the concentrated probe stock solution. Due to lack of drift, the pH in the KB2-No SOM reactors had to be artificially lowered to pH 10 and pH 8 through the addition of dilute sulfuric acid. Control systems were

established in parallel using deionized water in place of base-activated persulfate for each soil slurry system.

2.6 Analysis

Probe compound concentrations were quantified using Hewlett-Packard 5890A gas chromatographs with an electron capture detector (for HCA) and a flame ionization detector (for NB), each fit with 10 m × 0.53 mm DB-1 capillary columns. Program conditions for HCA analysis included injector temperature of 220°C, detector temperature of 270°C, initial oven temperature of 100°C, program rate of 30°C min⁻¹, and final temperature of 240°C. Program conditions for NB analysis included injector temperature of 200°C, detector temperature of 250°C, initial oven temperature of 60°C, program rate of 30°C min⁻¹, and final temperature of 180°C. Persulfate concentrations were measured by iodometric titration using 0.01 N sodium thiosulfate (Kolthoff and Stenger, 1947). The pH was quantified using a Fisher Accumet Basic AB15 pH meter.

3. Results and Discussion

Four different soil systems were investigated for hydroxyl radical and reductant activity as basic persulfate formulations were allowed to drift toward circumneutral pH: soils KB1 and KB2 with 1.01% and 0.24% organic carbon, respectively, and soils KB1-No SOM and KB2-No SOM on which the SOM was removed. Persulfate concentration, pH, and either hydroxyl radical or reductant generation were quantified concurrently as the reactions proceeded.

3.1 Persulfate decomposition and pH changes in soil slurries

Persulfate decomposition was monitored as the pH drifted toward neutral during the experiments that tracked hydroxyl radical and reductant generation. Persulfate

decomposition in the KB1 and KB2 soil slurries in which hydroxyl radical generation was tracked is shown in Figure 4a-b. The persulfate concentration decreased from 0.5 M to 0.27 M as the pH in the KB1 reactors reached pH 12, likely due to persulfate consumption by SOM. Initial persulfate concentrations for the three starting pH regimes of pH 12, pH 10, and pH 8, were 0.27 M, 0.25 M, and 0.22 M, respectively. Persulfate decomposed an additional 33%, 28%, and 23% in these systems over the 30 d reactions. The bulk of the persulfate loss occurred in the first few days with less consumption over the remaining 30 d.

The persulfate concentration decreased from 0.5 M to 0.48 M as the pH in the KB2 reactors reached pH 12. Initial persulfate concentrations were 0.48 M, 0.47 M, and 0.46 M for the starting pH regimes of pH 12, pH 10, and pH 8. Persulfate decomposed an additional 17%, 15%, and 13% in the three pH regimes over 30 d.

Persulfate concentrations in the KB1-No SOM and KB2-No SOM soil slurries in which hydroxyl radical generation was tracked are shown in Figure 5a-b. Rates of persulfate decomposition in persulfate slurries containing KB1-No SOM and KB2-No SOM were less than in the slurries containing SOM; persulfate consumption was <2% in these slurries once the pH reached 12. Initial persulfate concentrations in the KB1-No SOM were 0.50 M, 0.48 M, and 0.45 M for the three pH regimes. Persulfate decomposed an additional 10%, 8%, and 7% over 30 d. The rates of persulfate consumption in the three pH regimes were relatively constant over the 30 d reactions compared to the KB1 and KB2 soil slurries.

Initial persulfate concentrations in the KB2-No SOM slurries were 0.48 M, 0.47 M, and 0.47 M; the initial persulfate concentrations in these systems were nearly identical

at pH 10 and pH 8 because the pH in these reactors had to be artificially lowered through the addition of dilute sulfuric acid. Only 4% persulfate decomposition was observed in the KB2-No SOM soil slurries over each reaction period for all three pH systems; 6 d for pH 12 system, and 14 d for the pH 10 and pH 8 systems.

Persulfate concentrations monitored in conjunction with reductant generation experiments are illustrated in Figure 6a-b for soil slurries KB1 and KB2, and Figure 7a-b for soil slurries KB1-No SOM and KB2-No SOM. The persulfate decomposition trends are nearly the same as the persulfate decomposition in the hydroxyl radical generation experiments (Figure 4a-b and Figure 5a-b).

3.2 pH drift in soil slurries

pH was monitored in the four different soil systems in conjunction with hydroxyl radical and reductant activity as basic persulfate formulations drifted from alkaline circumneutral pH. The rate of pH change followed a pattern similar to persulfate decomposition and decreased most rapidly in the early stages of the reactions. pH drift in soil slurries is due to the generation of sulfuric acid as the persulfate decomposed; based on reaction stoichiometry, two moles of sulfuric acid are produced from one mole of persulfate;



Changes in pH over time for the KB1 and KB2 soil slurries during the hydroxyl radical generation experiments is shown in Figure 8a-b. In parallel to rapid persulfate consumption, the pH dropped most rapidly in the early stages of persulfate decomposition in the KB1 soil systems because of the greater SOD; e.g., the pH in the KB1 soil slurries declined from pH 12 to pH 10 over 24 hours after addition of

nitrobenzene probe. After 24 hours, the rate of pH change in the KB1 soil slurries continued to change somewhat rapidly but with a lower rate of change until day 15. At that time, the rate of pH change in the three soil systems slowed and was nearly identical for the remaining 30 d.

The rate of pH change in the KB2 soil slurries was less than the rate in the KB1 soil slurries. The pH declined most rapidly in the first 6 d in all three pH systems; e.g., the pH in the KB2 soil slurries declined from pH 12 to pH 10 over 48 hours after addition of nitrobenzene probe. After 6 d, the rate of pH change in the three soil systems slowed significantly and was nearly identical for the next 18 d. After 24 d, the rate of pH change increased slightly as the pH in all three systems decreased below pH 6.

Changes in pH over time for the KB1-No SOM and KB2-No SOM soil slurries in which relative hydroxyl radical generation was quantified is shown in Figure 9a-b. The rate of pH change in both of these systems was less than in the soil systems with SOM; in addition, less persulfate decomposed which decreased the rate of pH drift. The rates of pH drift in the KB1-No SOM soil systems were slightly greater than the KB2-No SOM soil systems, which may be due to the degree to which the SOM was removed; slightly more SOM remained in the KB1-No SOM soil (0.12%) than in the KB2-No SOM soil (0.06%) after SOM removal. The pH then declined linearly for both KB1-No SOM and KB2-No SOM soil slurries throughout the reactions. A small pH increase was observed in the early stages of the pH 8 and pH 10 systems of the KB2-No SOM after the injection of the probe compounds (The probe solutions were added at acidic pH to obtain the desired pH in the system).

pH drift monitored in conjunction with the reductant generation experiments is shown in Figure 10a-b for soil slurries KB1 and KB2, and Figure 11a-b for soil slurries KB1-No SOM and KB2-No SOM. These results are nearly the same as the pH profiles in the hydroxyl radical generation experiments (Figure 8a-b and Figure 9a-b).

3.3 Hydroxyl radical generation as pH drifts to circumneutral

Relative rates of hydroxyl radical generation were quantified by the oxidation of nitrobenzene as the pH drifted toward neutrality. Nitrobenzene concentrations in the KB1 and KB2 soil slurries are shown in Figure 12a-b. Nitrobenzene degradation in the KB1 soil slurries was 67% in the pH 12 system, 60% in the pH 10 system, and 34% in the pH 8 system over 30 d. Minimal nitrobenzene loss occurred in parallel control systems. Initial rates of hydroxyl radical generation were greater in early stages of the reactions, with a more constant degradation rate occurring after 3 d. Since less persulfate remained in the KB1 soil slurries due to the large SOD, less persulfate was available to react with nitrobenzene. Furthermore, due to the high amount of SOM, the hydroxyl radicals, catalyzed from the remaining persulfate, were likely scavenged by the SOM.

Nitrobenzene degradation in the KB2 soil slurries was 97% in the pH 12 system, 96% in the pH 10 system, and 94% in the pH 8 system over the 30 d. Initial rates of hydroxyl radical generation were greater in the higher pH systems, with near constant degradation rates occurring after 6 d in the three different pH regimes. Minimal nitrobenzene loss occurred in parallel control systems. In general, hydroxyl radical generation was greater in the KB2 systems compared to the KB1 systems likely due to a combination of more persulfate available for catalysis and less scavenging of hydroxyl radicals by SOM. These results demonstrate that relative rates of hydroxyl radical

generation decreased as the pH drifted from alkaline toward circumneutral conditions, but hydroxyl radicals were still generated.

Relative rates of hydroxyl radical generation quantified through the oxidation of nitrobenzene in the KB1-No SOM and KB2-No SOM slurries are shown in Figure 13a-b. Nitrobenzene was oxidized to nondetectable concentrations in all KB1-No SOM pH slurries after 30 d and after 14 d for the KB2-No SOM slurries with minimal nitrobenzene loss in parallel soil control systems. The differing rates of hydroxyl radical generation in these two systems may be partly from oxidant scavenging by lingering SOM; slightly more SOM remained in the KB1-No SOM soil (0.12%) than the KB2-No SOM soil (0.06%) after SOM removal. Another possible explanation may be varying mechanisms that are activating persulfate in these two systems, which include catalysis by the soil minerals or a radical chain reaction that is initiated at high pH.

3.4 Superoxide radical and reductant generation as the pH drifts to circumneutral

Relative rates of superoxide radical and reductant generation were quantified by the reduction of hexachloroethane (HCA) as the pH drifted toward neutrality. HCA concentrations in the KB1 and KB2 slurries are shown in Figure 14a-b. HCA in the KB1 soil slurries was degraded to near-nondetectable concentrations after 2.5 d in the pH 12 system, 6 d in the pH 10 system, and 8 d in the pH 8 system. Reductant generation also occurred in parallel control systems with 62% HCA degradation after 8 d. The apparent reductant formation observed in the three soil slurries plus the control system indicate that SOM promoted reductive dechlorination in all four systems; SOM provides reducing conditions that likely degrade HCA by different pathways. Nevertheless, HCA degraded more rapidly in base-activated persulfate systems than in control systems.

HCA was degraded to nondetectable limits in the KB2 slurries after 5.5 d in the pH 12 system, and 8 d for both the pH 10 and pH 8 systems; 11% HCA degradation occurred in parallel control systems after 8 d. In general, reductant generation was greater in higher pH regimes for both the KB1 and KB2 soil systems. The pH 12 system of the KB1 soil slurries showed faster HCA degradation than the pH 12 system of the KB2 soil slurries with similar patterns for soil slurries in the pH 10 and pH 8 systems. Scavenging did not appear to affect the reductants as much as the oxidants; i.e., there was no significant difference in reductant formation between the KB1 and KB2 soils, with approximately 33% of the persulfate consumed before addition of the HCA probe.

Relative rates of reductant generation for the KB1-No SOM and KB2-No SOM slurries are shown in Figure 15a-b. HCA was degraded to nondetectable limits in the pH 12 system of the KB1-No SOM soil slurries after 6 d. HCA degradation of 90% occurred in the pH 10 system, and 25% in the pH 8 system after 8 d. HCA degradation in the KB2-No SOM soil slurries after 8 d was 83% in the pH 12 system, 27% in the pH 10 system, and 26% in the pH 8 system. Minimal HCA loss occurred in all parallel control systems. The pH 10 KB1-No SOM system showed significantly greater reductant generation than the parallel pH 10 KB2-No SOM system, which is likely due to slightly more organic matter remaining in the KB1-No SOM soil than the KB2-No SOM after the SOM removal procedure was completed. These results suggest that there is a minimum SOM concentration at which SOM can promote the generation of reductants.

4. Conclusion

The potential for persulfate activation after base addition as the pH drifts from alkaline to circumneutral was investigated in four soil systems with varying SOM

contents. Persulfate decomposition occurred most rapidly in the KB1 soil slurries due to the greater SOM content. Persulfate decomposition was minimal in the other slurries with the least occurring in the KB2-No SOM soil systems. pH drift was approximately parallel to persulfate decomposition in all four soil systems with the most rapid decline occurring in the presence of higher SOM.

In all soil slurries, hydroxyl radical and reductant formation occurred which was demonstrated by nitrobenzene and hexachloroethane degradation. In general, hydroxyl radical activity was greatest at higher pH systems, but still occurred in starting pH regimes of pH 10 and pH 8. Furthermore, greater rates of hydroxyl radical generation were found with decreasing SOM contents, which is likely due to a lower degree of hydroxyl scavenging by SOM.

Superoxide radical and reductant generation also occurred in all pH systems with lower generation rates as the pH drifted to circumneutral. In all pH systems, reductant generation was greatest in soil systems with greater SOM content. Considerably less reductant formation occurred for the systems at pH 10 and pH 8 once the SOM was removed, but reductants still formed.

The results of this research demonstrate that in the presence of subsurface solids, base-activated persulfate can generate reactive oxygen species in pH systems <10; these results differ from recent findings in which persulfate reactivity was negligible at pH <10. SOM plays a significant role in this process by lowering net oxidant generation rates but promotes higher reductant activity. From a practical treatment perspective, application of base-activated persulfate in situ may potentially extend treatment longer than previously thought making it a more efficient ISCO technology.

References

- Afanas'ev, I.B., 1989. Superoxide Ion: Chemistry and Biological Implications, vol. 1. CRC Press, Boca Raton, FL.
- Block, P.A., Brown, R.A., Robinson, D., 2004. Novel Activation Technologies for Sodium Persulfate In Situ Chemical Oxidation. Proceedings of the Fourth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds.
- Brown, R.A., Robinson, D., and Skladany, G., 2003. Response to Naturally Occurring Organic Material: Permanganate versus Persulfate. ConSoil, Ghent, Belgium.
- Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}^-$) in aqueous solution. *J. Phys. Chem. Ref. Data.* 17, 513–780.
- Furman, O. S., Teel, A. L., and Watts, R.J. 2009. Mechanism and Contaminant Destruction Pathways in Base-Activated Persulfate Systems. *Environ. Sci. Technol.* In preparation.
- Gee, B.W., Bauder, J.W., 1986. Particle size analysis in: A. Klute (Ed), Methods of soil analysis; part 1. physical and mineralogical methods, American Society of Agronomy, Madison, WI, p. 399.
- Haag, W.R., Yao, C.C.D, 1992. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. and Technol.* 26, 1005-1013.
- Huling, S.G., Pivetz, B.E., 2006. In-Situ Chemical Oxidation. United States Environmental Protection Agency.
- ITRC (Interstate Technology & Regulatory Council). 2008. *In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones*. BioDNAPL-3. Washington, D.C.: Interstate Technology & Regulatory Council, Bioremediation of DNAPLs Team.
- Interstate Technology Regulatory Council., (ITRC) 2005. Overview of Groundwater Remediation Technologies for MTBE and TBA.
- Jackson, M.L., Lim, C.H., Zelazny, L.W., 1986. In: A. Klute et al. (Eds.), Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods. American Society of Agronomy and Soil Science Society of America, Madison, WI, p. 124
- Kolthoff, I.M., Stenger, V.A., 1947. Volumetric Analysis, second Revised ed Titration Methods: Acid-base, Precipitation, and Complex Reactions, vol. II Interscience Publishers, Inc., New York.

- Lighty, J.S., Silcox, G.D, Pershing, DW., 1990. Fundamentals for the Thermal Remediation of Contaminated Soils. Particle and Bed Desorption Models. *Environ. Sci. and Technol.* 24, 750-757.
- Neta, P., Madhavan, V., Zemel, H., Fesseden, R.W., 1977. Rate Constants and Mechanism of Reaction of SO_4^- with Aromatic Compounds. *J. Amer. Chem. Soc.* 99, 163-164.
- Robinson, W.O., 1927. The determination of organic matter in soils by means of hydrogen peroxide. *J. Agric. Res.* 34, 339-356.
- Siegrist R L, Urynowicz M A, West O R, Crimi M L and Lowe K S 2001 Principles and Practices of In Situ Chemical Oxidation Using Permanganate (Columbus, OH: Battelle)
- U.S. Soil Conservation Service., 1972. Soil Survey Investigation: Report 1. U.S. Government Printing Office, Washington, DC. Cation exchange capacity
- Walkley A. and Black I. A., 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method *Soil Sci.* 37, 29–38.
- Watts , R.J., Teel, A. L., 2006. Treatment of Contaminated Soils and Groundwater using ISCO. *Prac. Period Hazard Toxic, and Radioact. Waste Manage.* 10(1), 2-9.
- Watts , R.J., 1998. Hazardous Wastes: Sources, Pathways, Receptors. Wiley and Sons Inc. pp 553-554,

Tables

Table 1. Physical properties of soils KB1 and KB2.

Soil	Textural Classification [*]			Texture	Cation Exchange Capacity (Cmol(+)/kg) ^{**}
	% Sand	% Clay	% Silt		
KB1	31.5	10	58.5	Silt Loam	34
KB2	39.5	11.1	49.8	Loam	19

* Method analyzed: Hydrometer

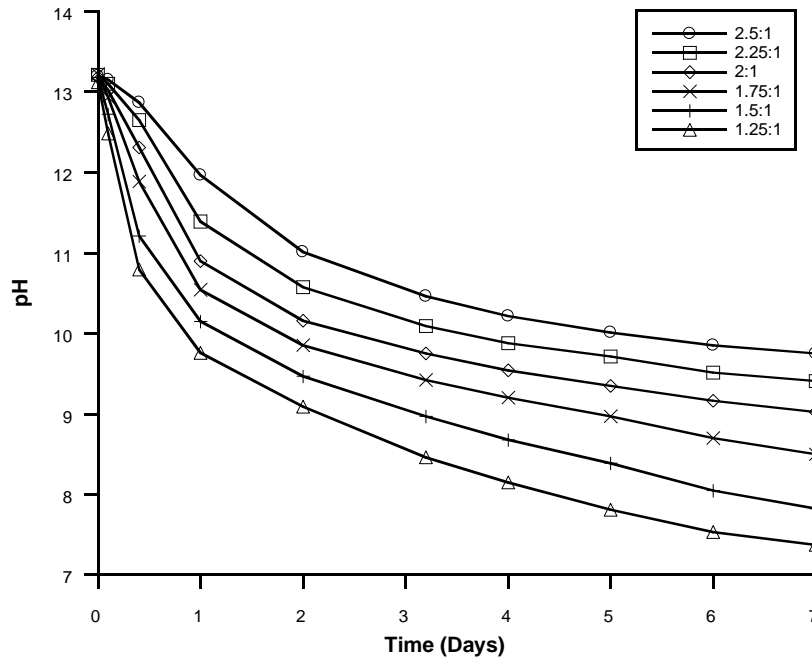
**Method analyzed: EPA 9081

Table 2. Chemical properties of soils KB1 and KB2.

Soil	Amorphous Mn (µg/g)	Total Mn (µg/g)	Amorphous Fe (µg/g)	Crystalline Fe (µg/g)	% Organic Carbon	% Organic Carbon After H ₂ O ₂ Treatment
KB1	194	380	4656	2789	1.01	0.12
KB2	296	510	2196	1697	0.24	0.06

Figures

a



b

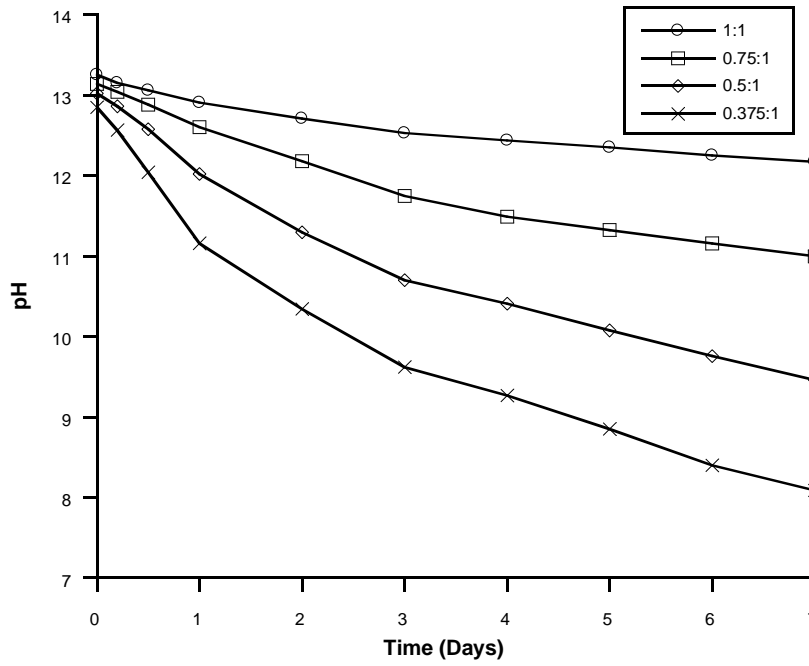


Figure 1. pH profiles of various molar ratios of sodium hydroxide:sodium persulfate for soils KB1 (a) and KB2 (b).

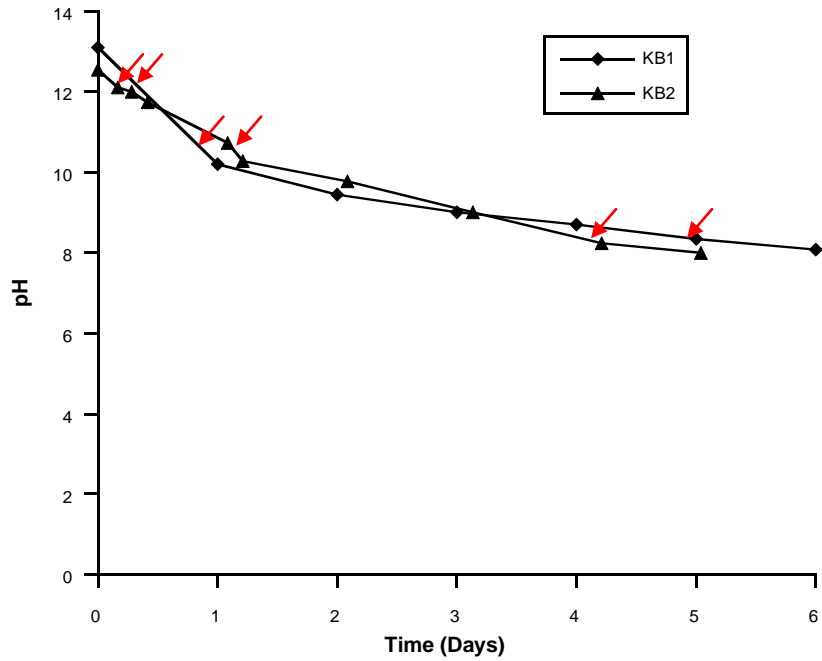
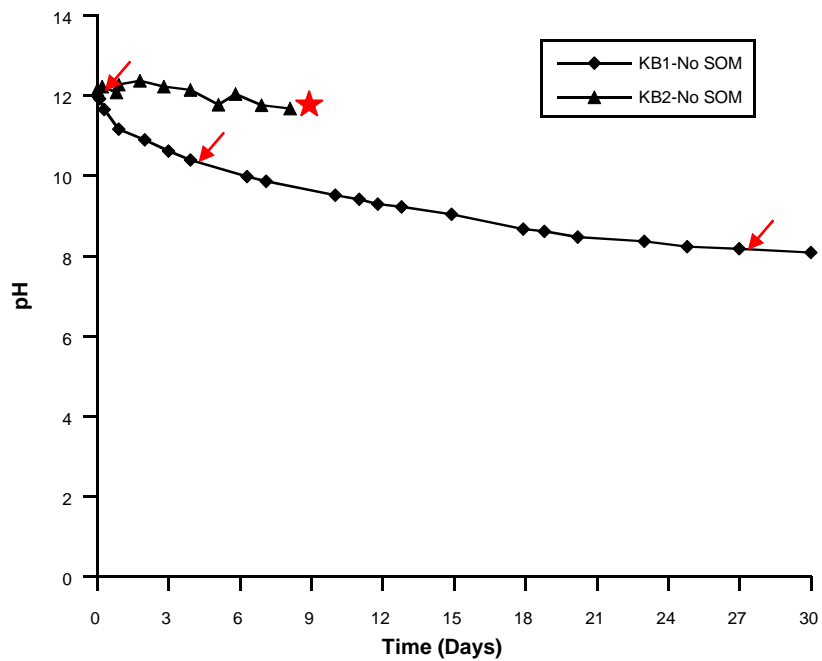


Figure 2. pH profiles of chosen molar ratios of sodium hydroxide:sodium persulfate for soil slurries KB1 and KB2 indicating approximate spike times of probe compounds.



* Approximate spike times of probe compounds indicated by arrows.
 **Star indicates that pH in KB2-No SOM soil system would not drift sufficiently fast.

Figure 3. pH profiles of the selected molar ratio of 0.375:1 sodium hydroxide:sodium persulfate for soil slurries KB1-No SOM and KB2-No SOM.

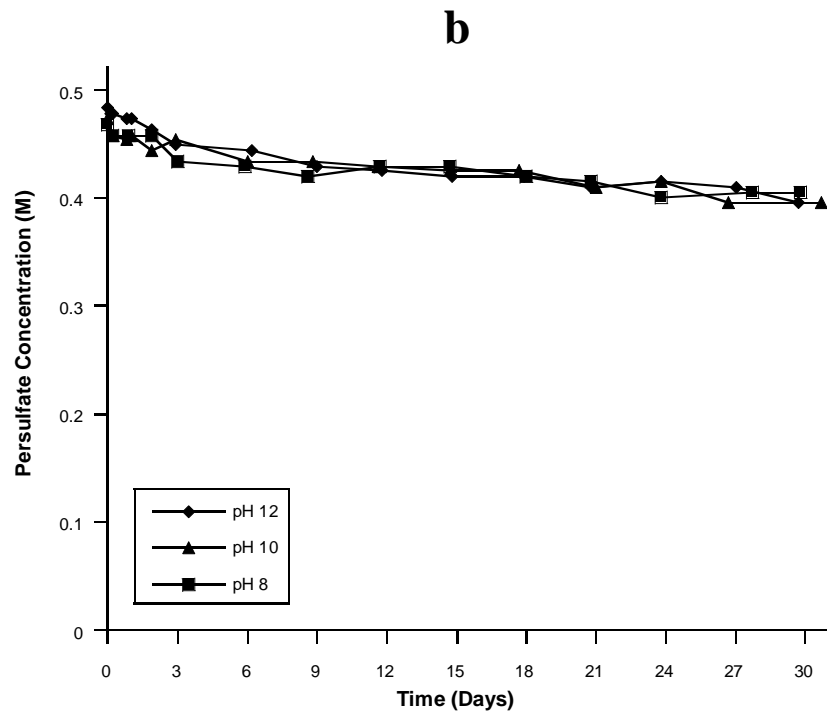
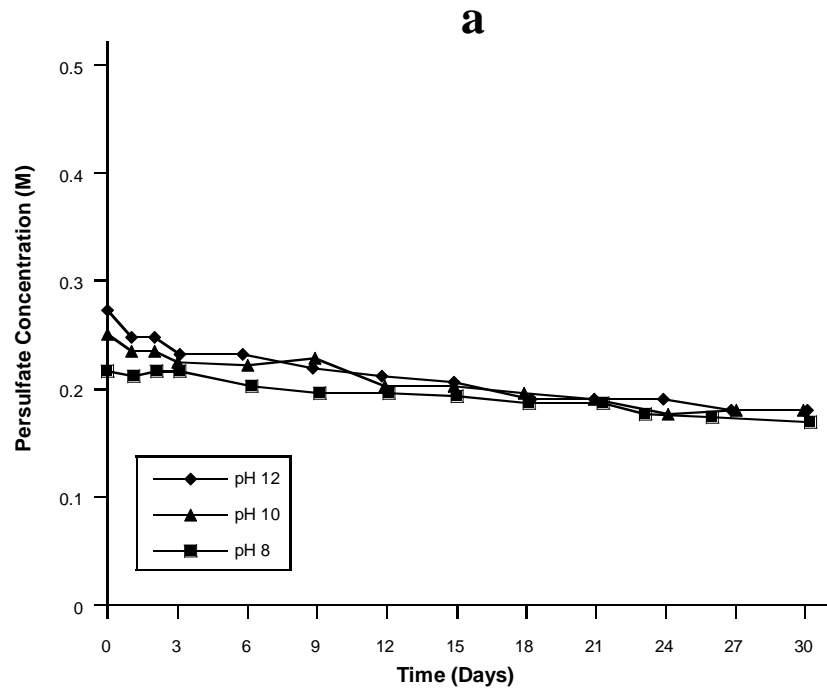


Figure 4. Persulfate concentrations in soil slurries KB1(a) and KB2(b) in conjunction with hydroxyl radical generation experiments.

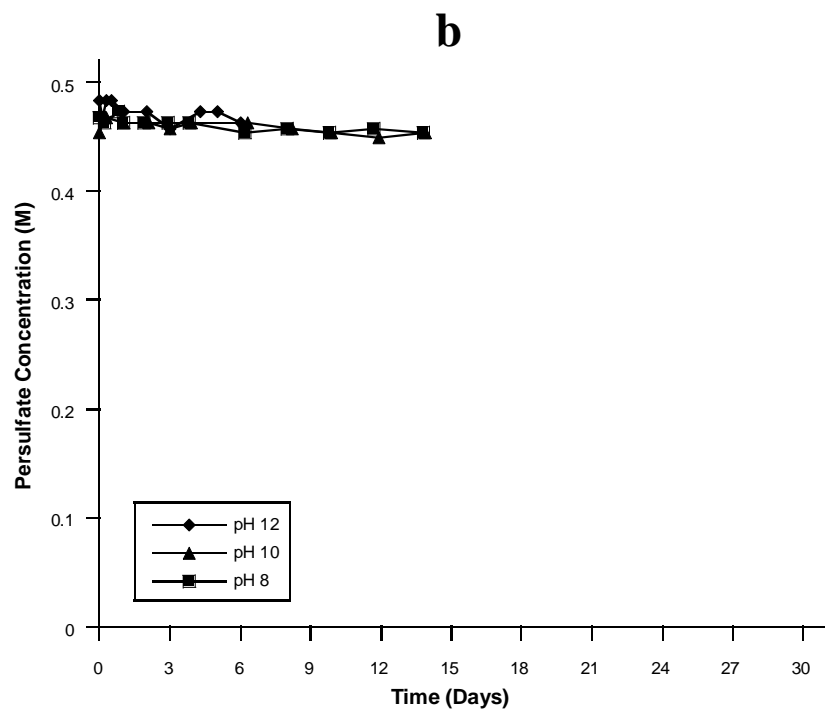
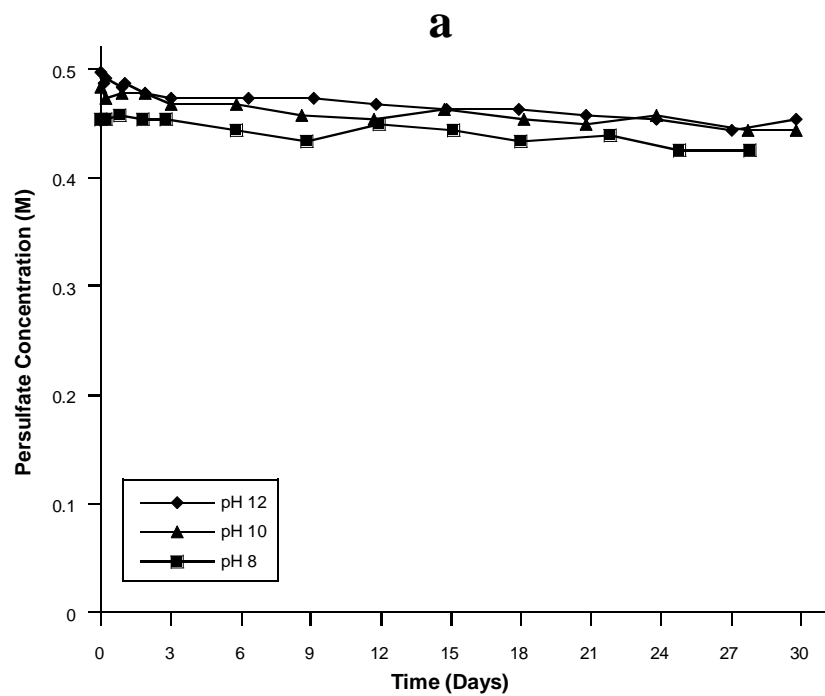


Figure 5. Persulfate concentrations in soil slurries KB1-No SOM(a) and KB2-No SOM(b) in conjunction with hydroxyl radical generation experiments.

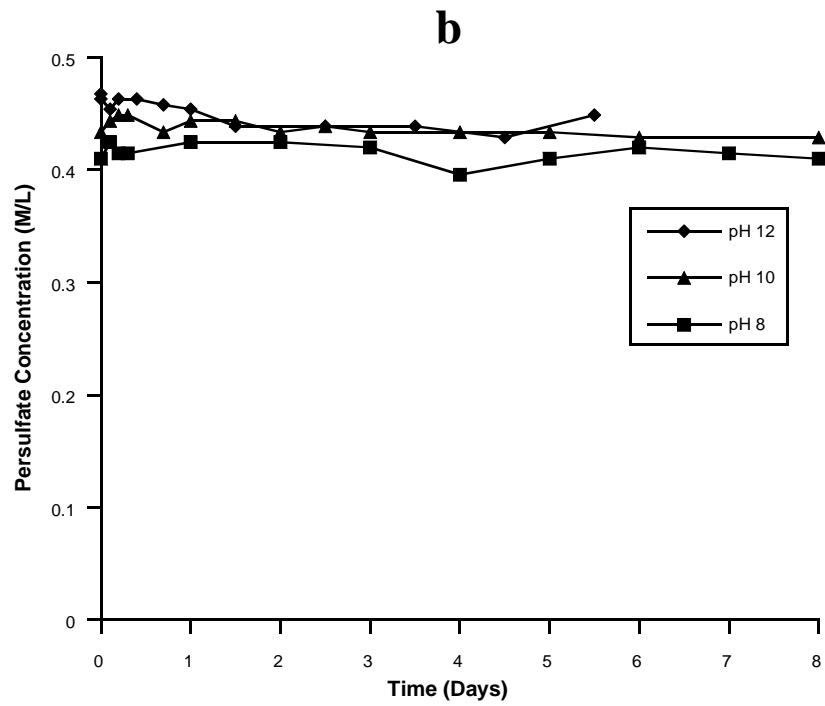
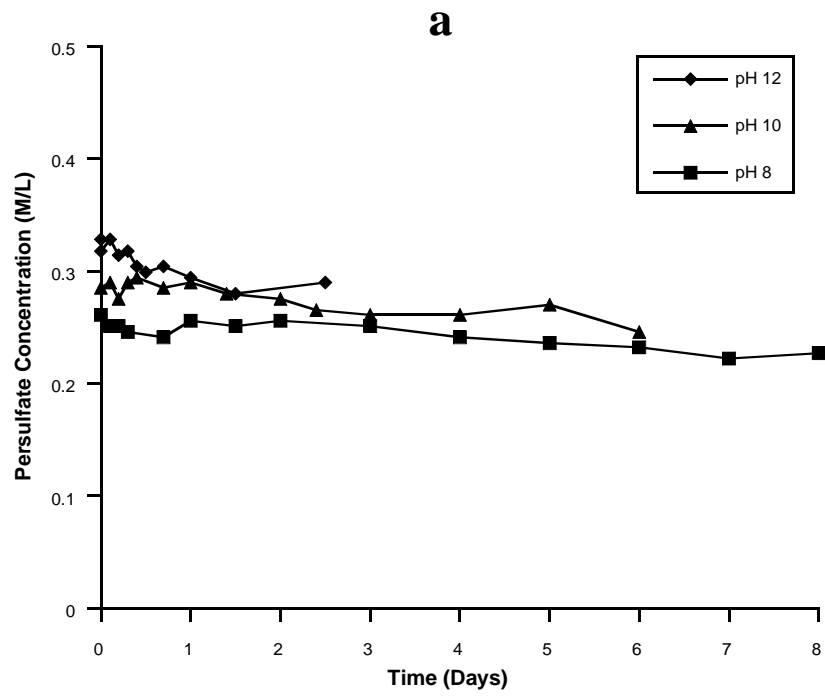


Figure 6. Persulfate concentrations in soil slurries KB1(a) and KB2(b) in conjunction with reductant generation experiments.

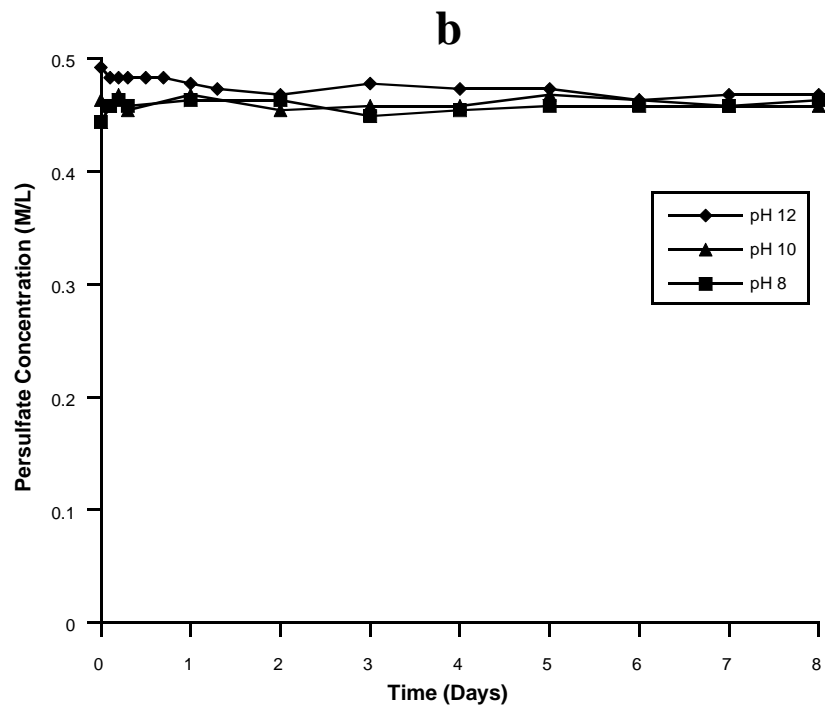
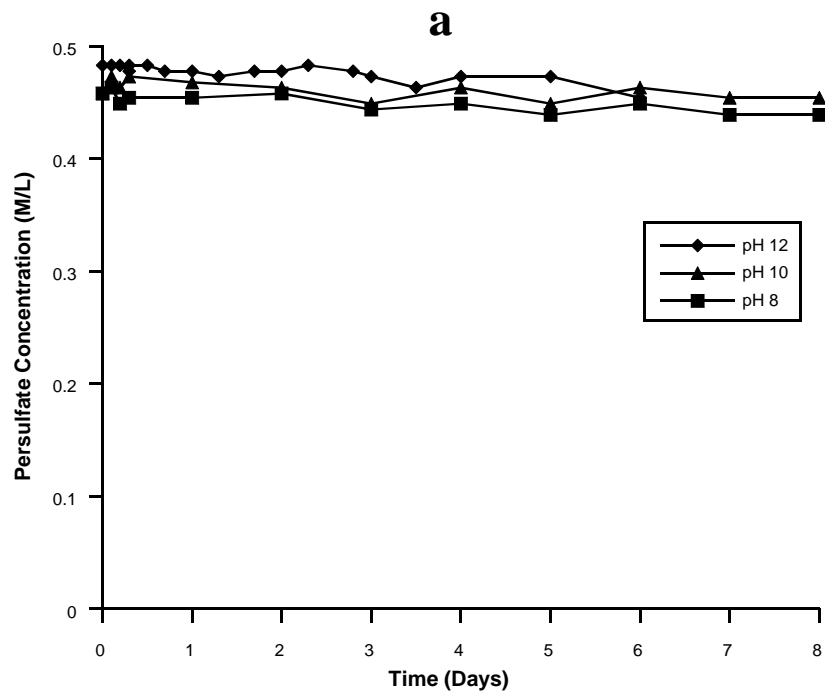


Figure 7. Persulfate concentrations in soil slurries KB1-No SOM(a) and KB2-No SOM(b)) in conjunction with reductant generation experiments.

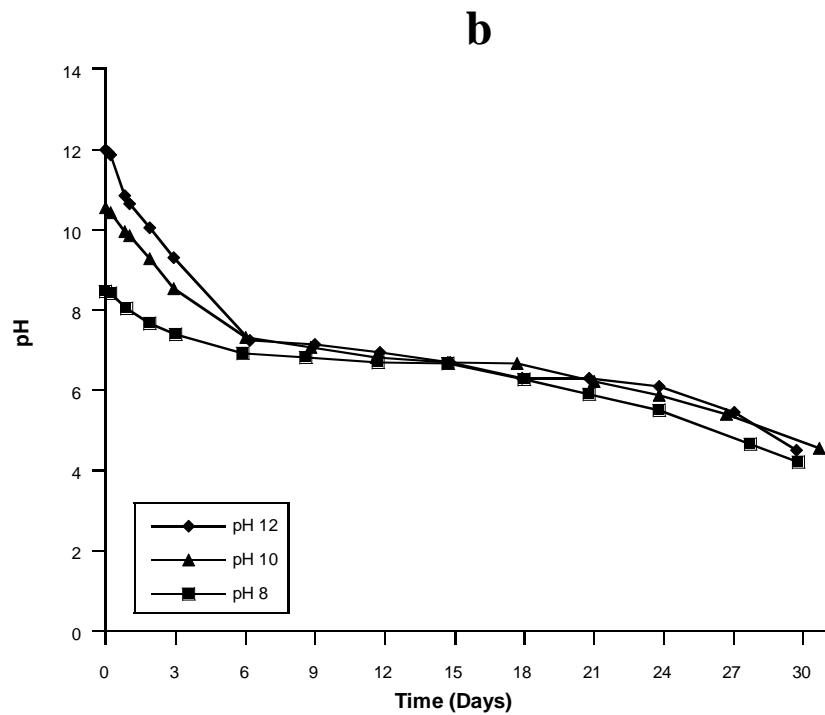
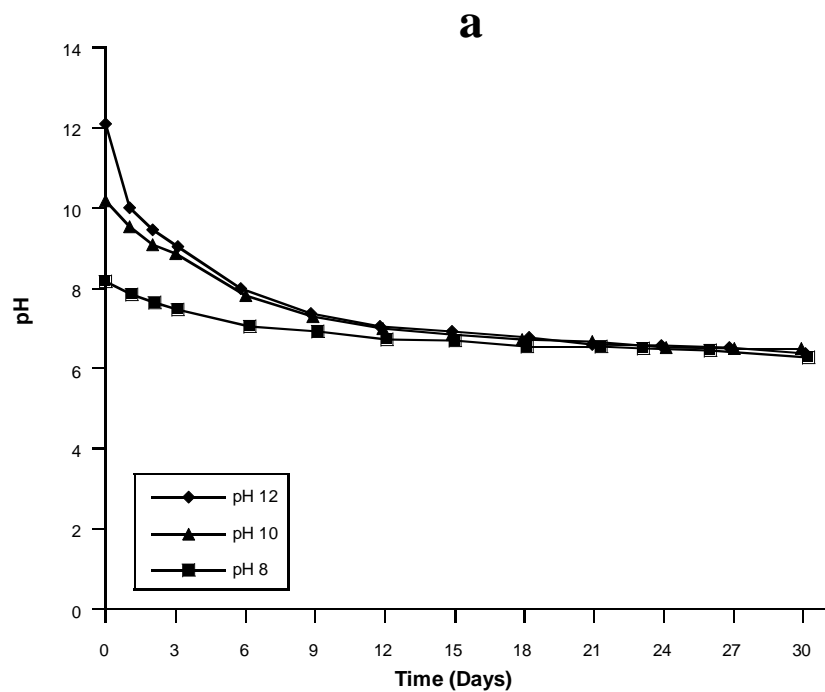


Figure 8. pH profiles for soil slurries KB1(a) and KB2(b) in conjunction with hydroxyl radical generation experiments.

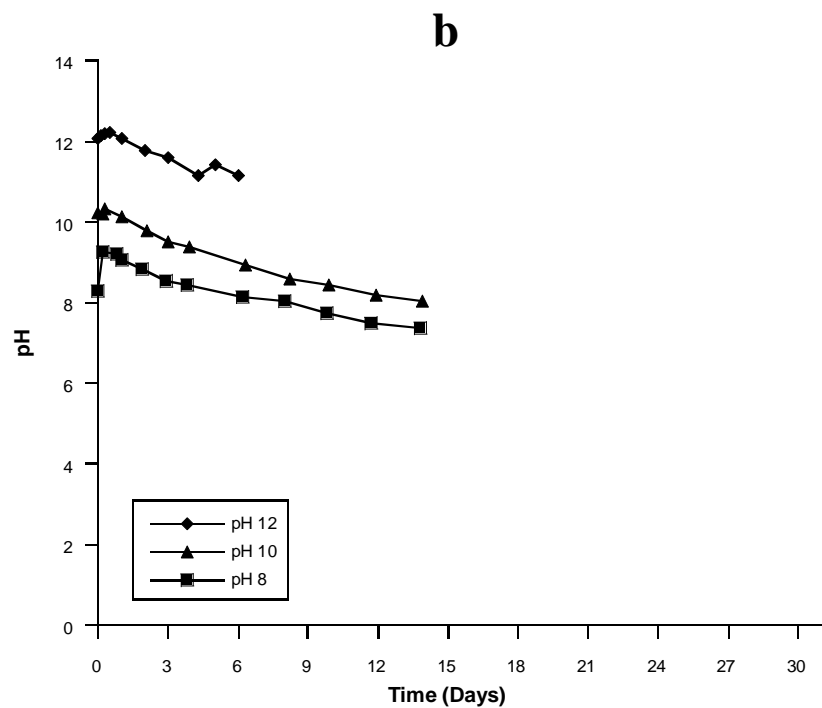
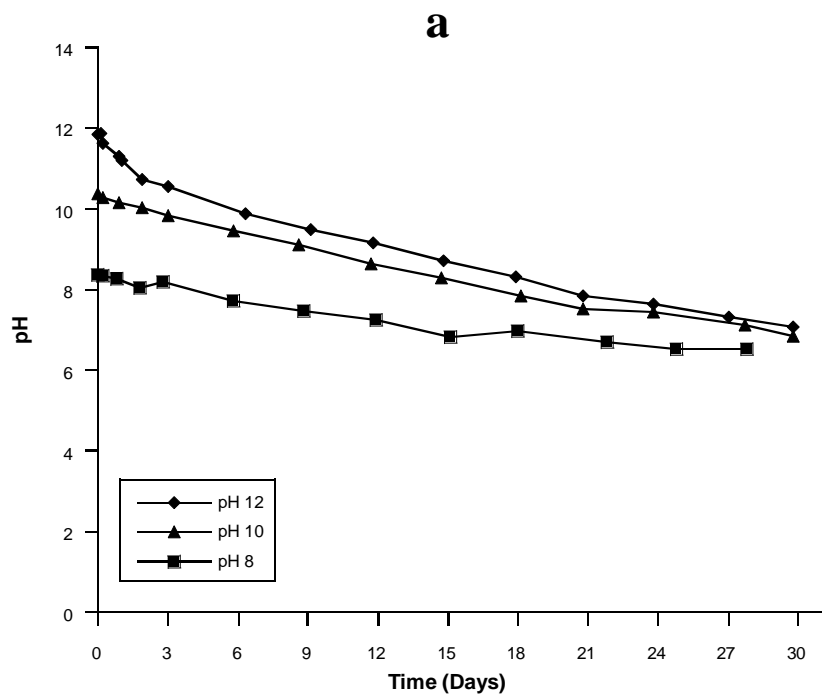


Figure 9. pH profiles for soil slurries KB1-No SOM(a) and KB2-No SOM(b) in conjunction with hydroxyl radical generation experiments.

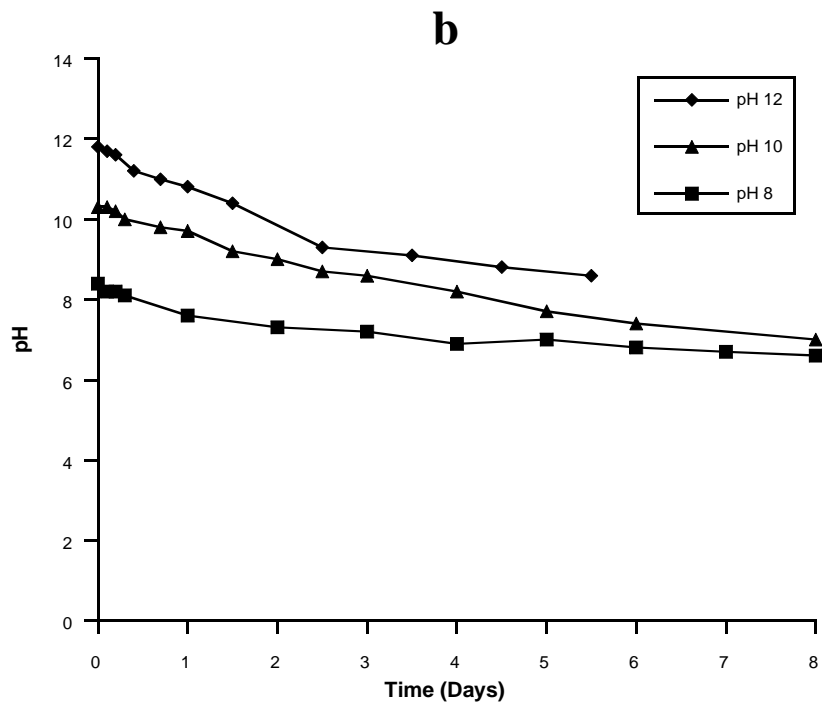
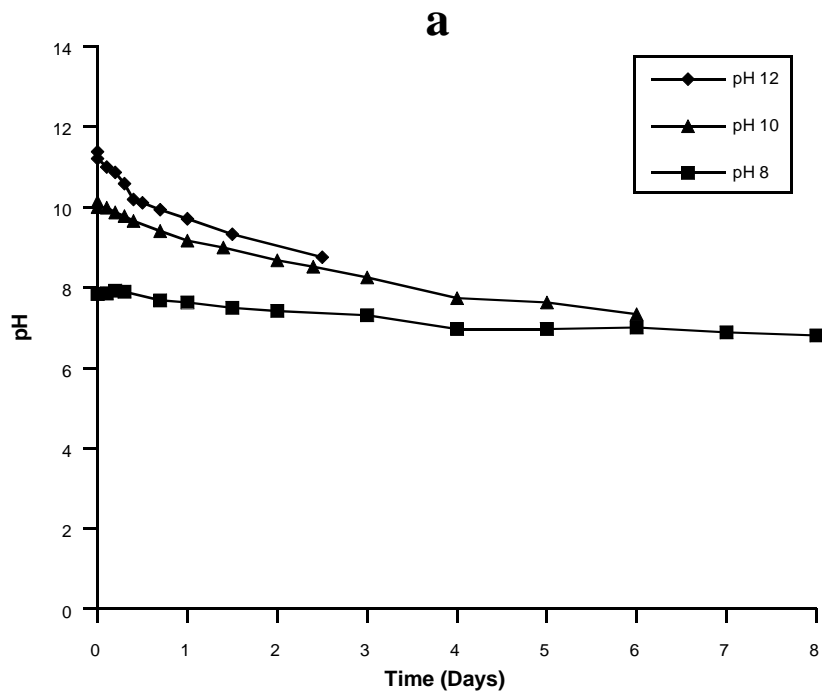


Figure 10. pH profiles for soil slurries KB1(a) and KB2(b) in conjunction with reductant generation experiments.

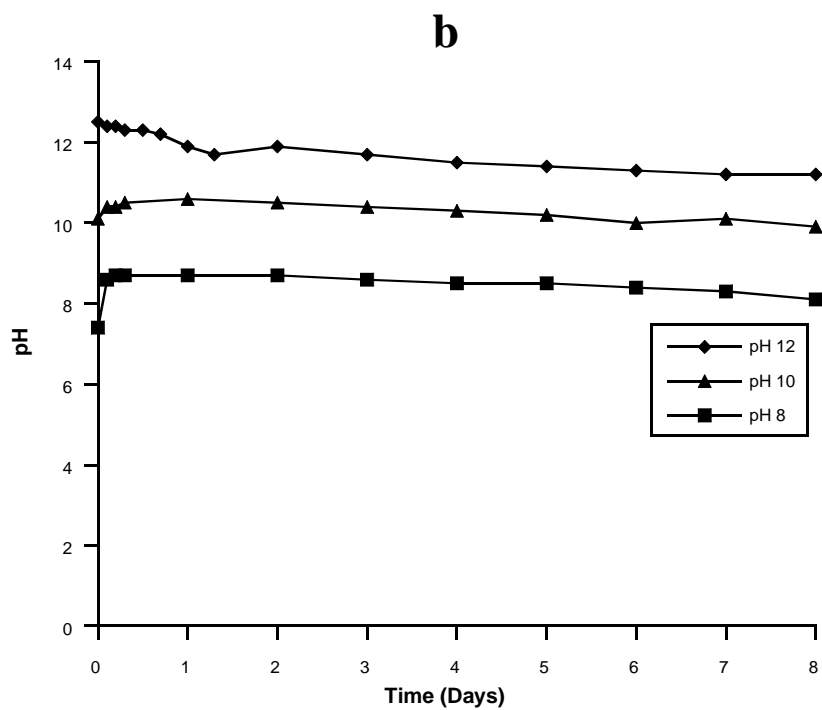
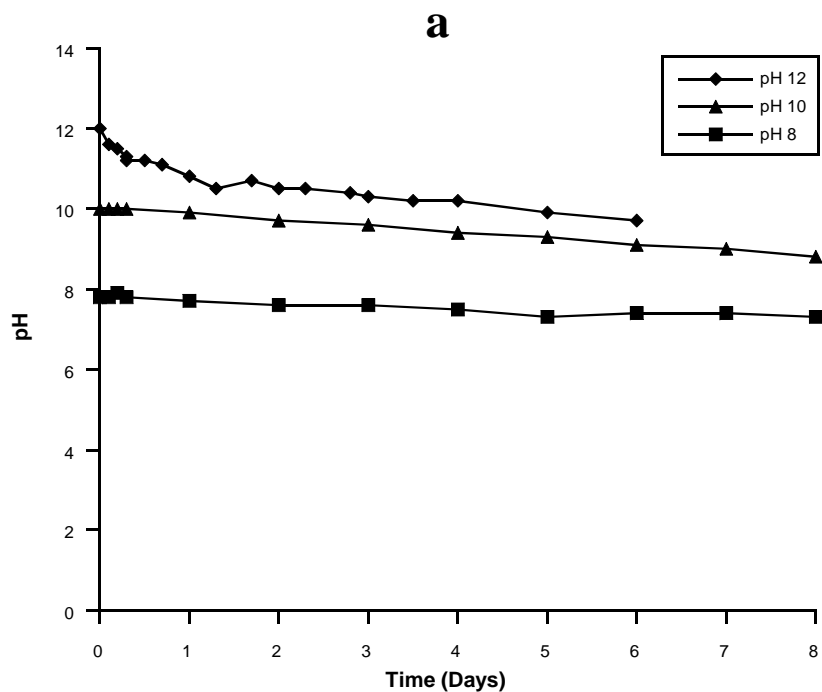


Figure 11. pH profiles for soil slurries KB1-No SOM(a) and KB2-No SOM(b) in conjunction with reductant generation experiments.

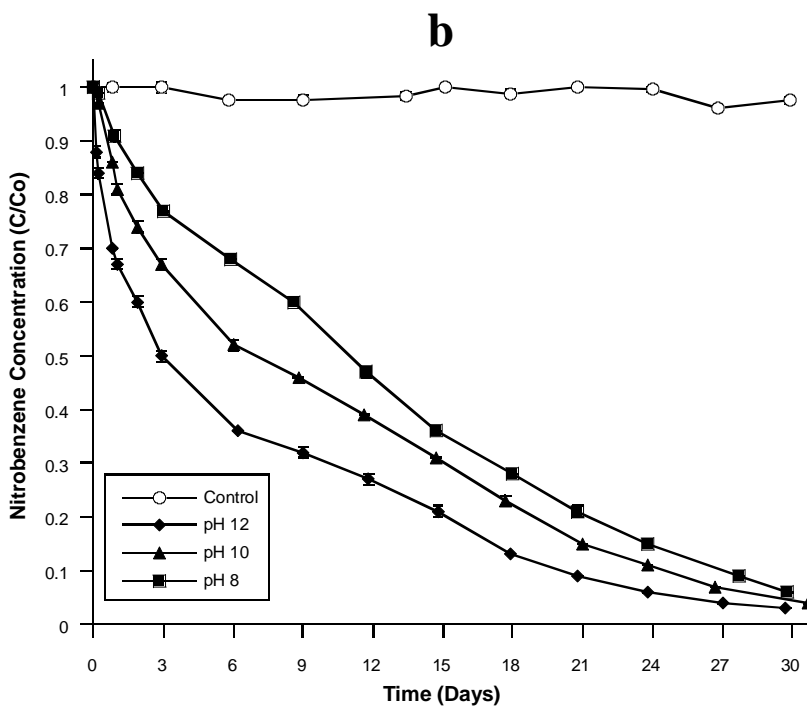
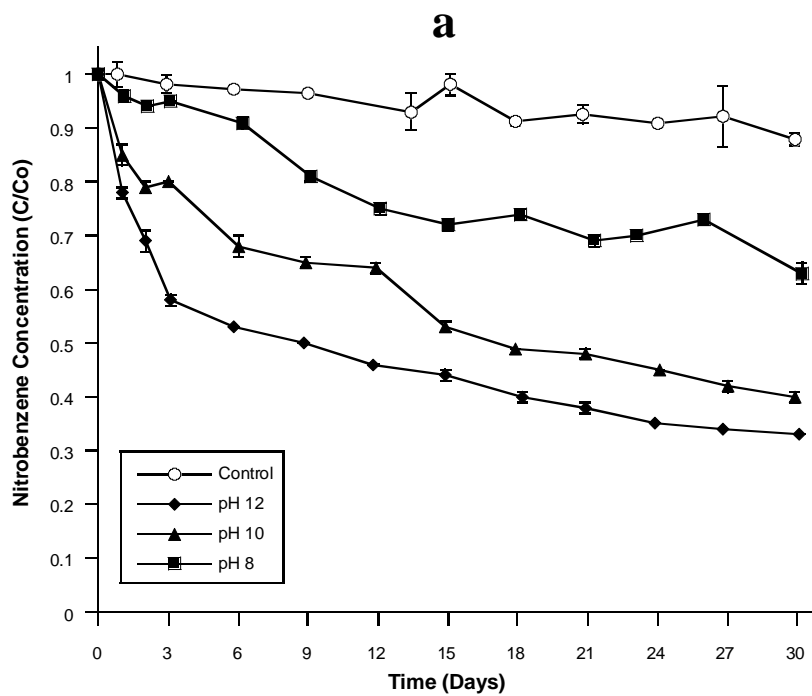


Figure 12. Hydroxyl radical generation quantified through nitrobenzene degradation in soil slurries KB1(a) and KB2(b).

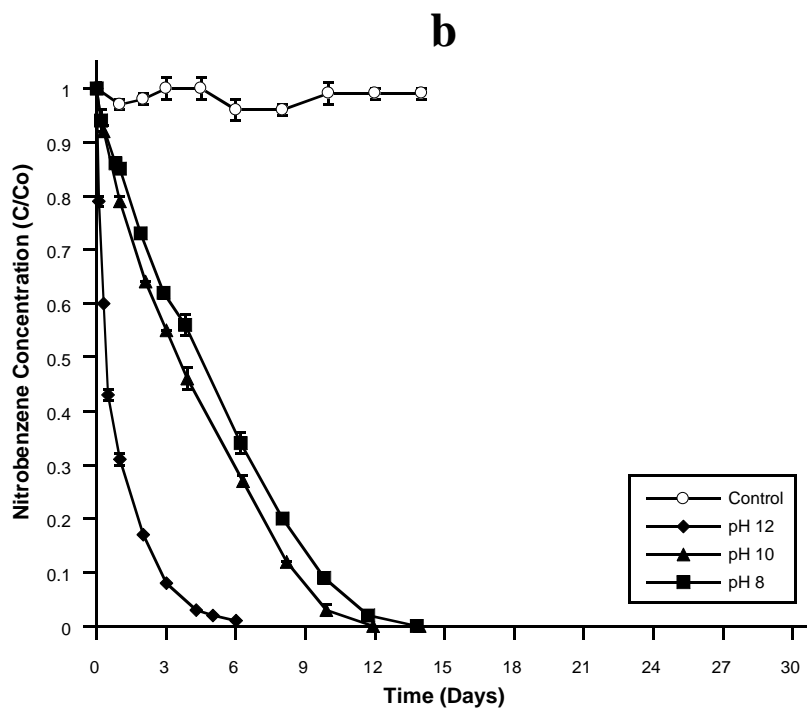
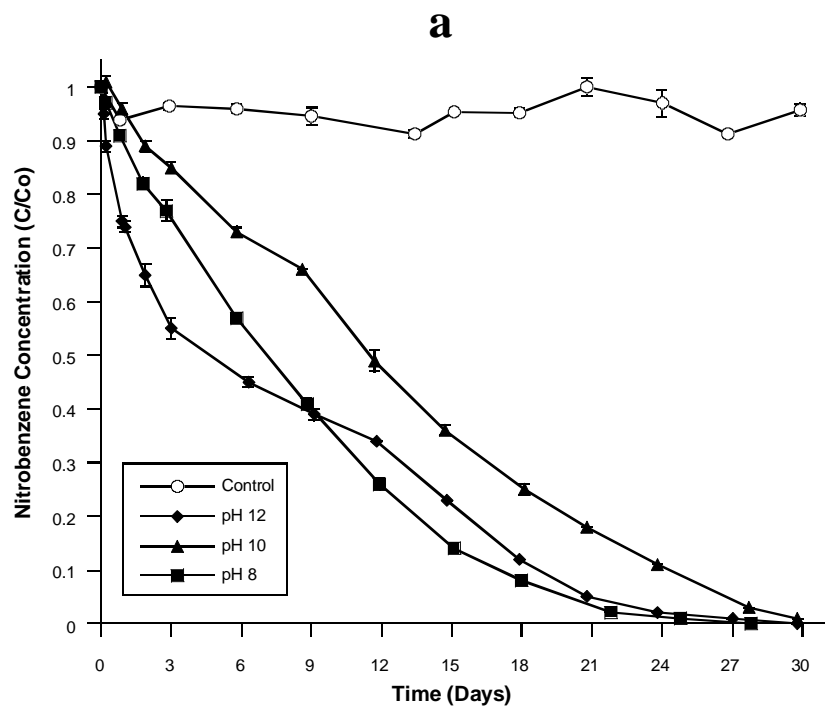


Figure 13. Hydroxyl radical generation quantified through nitrobenzene degradation in soil slurries KB1-No SOM(a) and KB2-No SOM(b).

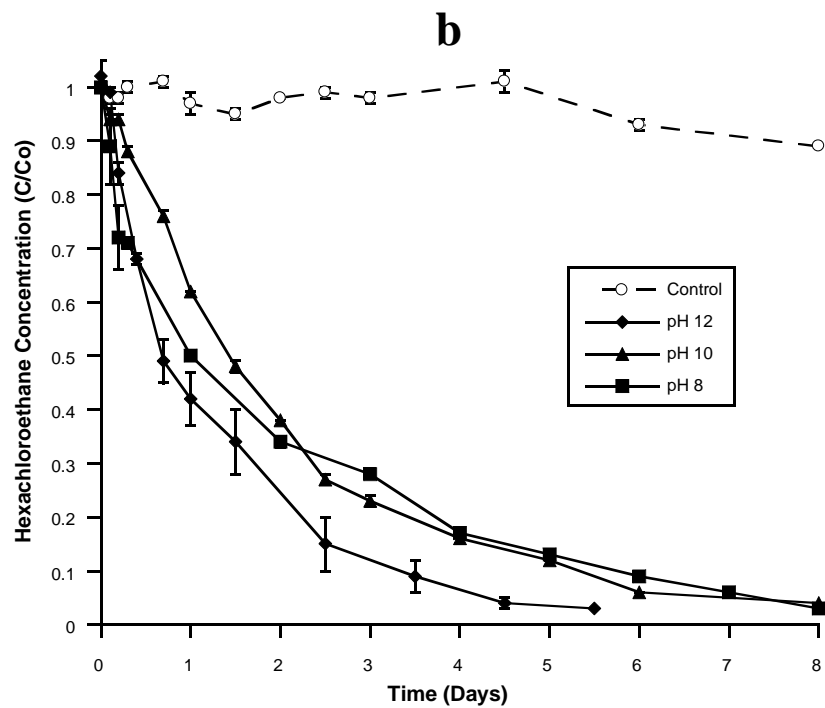
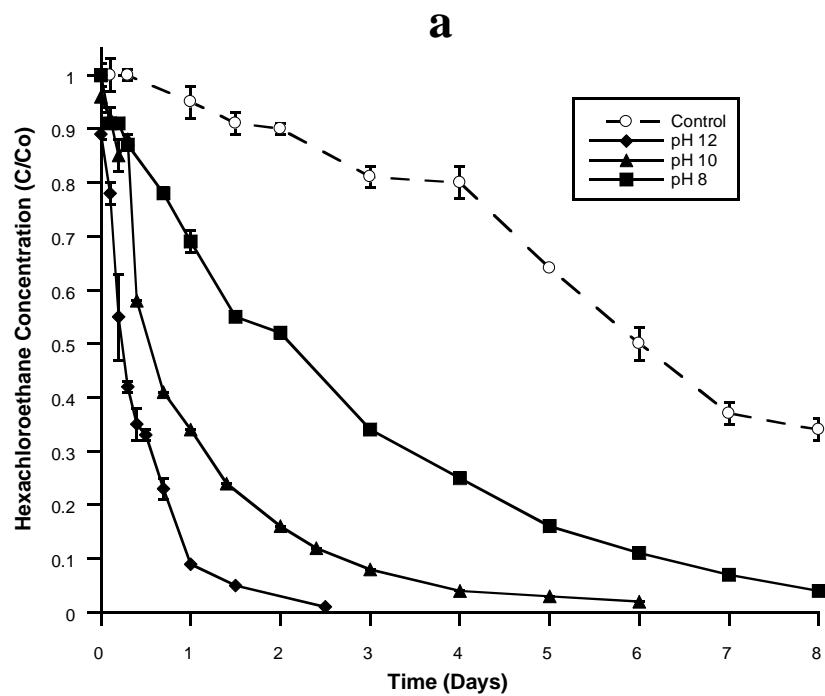


Figure 14. Reductant generation quantified through hexachloroethane degradation in soil slurries KB1(a) and KB2 (b).

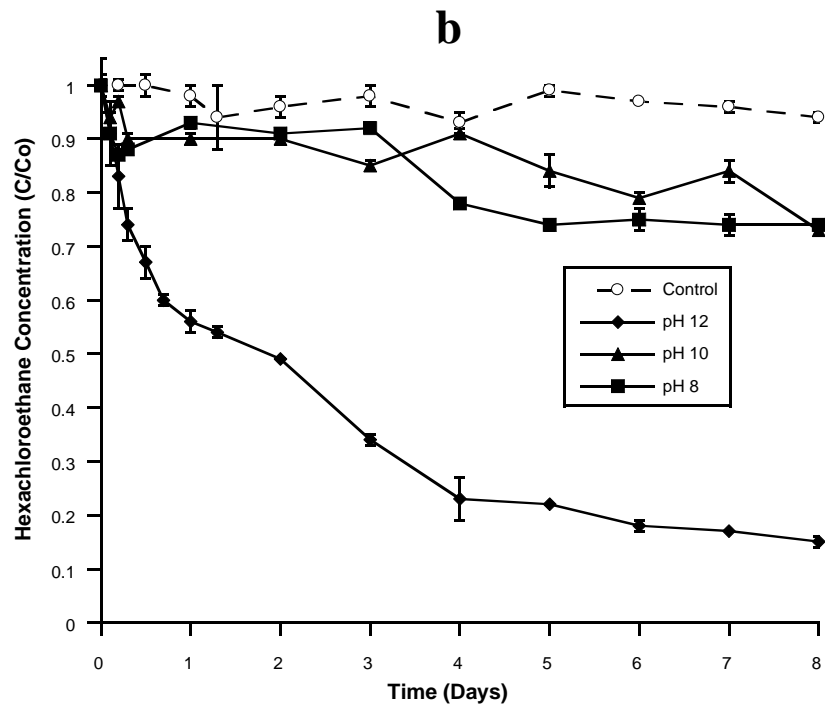
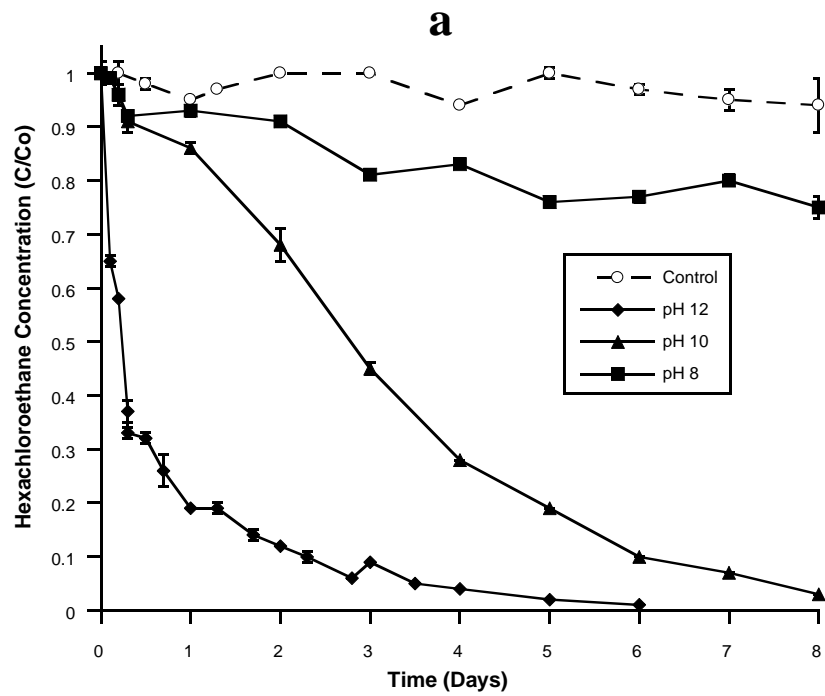


Figure 15. Reductant generation quantified through hexachloroethane degradation in soil slurries KB1-No SOM(a) and KB2-No SOM(b).