

PERSULFATE ACTIVATION BY MAJOR SOIL MINERALS

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ABSTRACT

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Oxidant interaction with subsurface materials is a major factor influencing the effective application of in situ chemical oxidation (ISCO) for contaminant destruction. The newest and least explored ISCO oxidant source is persulfate. Persulfate interaction with subsurface minerals was investigated as a basis for understanding persulfate activation in the subsurface. The mineral-mediated decomposition of persulfate and generation of oxidants and reductants was investigated with four iron and manganese oxides and two clay minerals at both low pH (<7) and high pH (>12). At both low and high pH, persulfate decomposition was minimal in the presence of all six minerals. The manganese oxide birnessite was the most effective catalyst for degrading the hydroxyl radical probe nitrobenzene, indicating hydroxyl radical generation at both low and high pH regimes. The iron oxide goethite was the most effective catalyst for degrading the reductant probe hexachloroethane. Several fractions of a natural soil were used to confirm the catalytic behavior of synthetic minerals. Natural soil fractions did not effectively catalyze the generation of hydroxyl radicals or reductants. However, soil organic matter was found to promote reductant generation at high pH. The results of this research demonstrate that synthetic iron and manganese oxides can activate persulfate to generate reductants and oxidants, however, iron and manganese oxides

in the natural soil fractions do not show the same reactivity, most likely due to the lower masses of the metal oxides in the soil fractions relative to the masses studied in isolated mineral systems.

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1. Introduction

The unregulated and improper disposal of toxic and biorefractory organic contaminants is the most common cause of subsurface soil and groundwater contamination. Various biological, chemical, and physical methods have been used for contaminated site remediation. One such cleanup method is in situ chemical oxidation (ISCO), in which strong oxidants are injected into the subsurface. Permanganate, catalyzed H_2O_2 propagations (CHP), and ozone are the most commonly used ISCO reagents (Watts and Teel, 2006). Each of the ISCO reagents has its limitations related to reactivity, stability, transport, and availability. CHP has the potential to degrade almost all organic contaminants in all phases including sorbed, aqueous phase, and DNAPLs (Watts and Teel, 2005; 2006; Watts et al., 2007a); however, it is unstable in the subsurface (Chen et al., 2001). In contrast, permanganate is reactive with a narrow range of contaminants (Trantnyek and Waldemer, 2006) but is stable in the subsurface (Watts and Teel, 2006). Low solubility, variable reactivity, and inefficient mass transfer from the gas phase to aqueous phase are some limitations of ozone.

The newest and least explored ISCO reagent is persulfate, which has the potential to have greater stability than CHP and ozone, and wider reactivity than permanganate. As a source of persulfate, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) is commonly used because of its high water solubility (73g/100g water) and stability in the subsurface (Liang et al., 2003). Persulfate dissociates in aqueous solutions to persulfate anion ($\text{S}_2\text{O}_8^{2-}$), which is a strong oxidant (oxidation-reduction potential, $E^\circ \sim 2.01 \text{ V}$). Persulfate decomposition can be initiated by heat, uv light, high pH, or transition metals to form sulfate radical, which has even a greater E° (2.6 V) (Kolthoff, 1951; House, 1962; Berlin, 1986). Sulfate radical can

react with water or hydroxide to generate hydroxyl radical (House, 1962; Berlin, 1986; Peyton, 1993). In CHP reactions, hydroxyl radical can initiate a series of propagation reactions that generate perhydroxyl radical (a weak oxidant), superoxide radical anion (a reductant and nucleophile), and hydroperoxide anion (a strong nucleophile) (Watts and Teel, 2005). The generation of similar reactive species by hydroxyl radical is possible in aqueous persulfate systems. Although the presence of soluble iron or manganese was found to accelerate the decomposition of persulfate to sulfate radical (House, 1962; Peyton, 1993; Kislenko et al. 1997), the initiation of persulfate decomposition by iron or manganese oxide minerals to generate reactive chemical species has not been investigated to date.

The objectives of this study were to (i) examine the activation of persulfate by major soil-minerals, (ii) identify the reactive species generated by using reaction specific probe compounds during persulfate activation, and (iii) confirm persulfate activation in natural soils.

2. Materials and methods

2.1. Chemicals

Sodium persulfate ($\geq 98\%$), sodium citrate (99%), and hexachloroethane were purchased from Sigma Aldrich (St. Louis, MO). Sodium hydroxide (98.6%), sodium bicarbonate, potato starch, nitrobenzene, and hexanes were obtained from J.T. Baker Inc. (Phillipsburg, NJ). Sodium thiosulfate (99%), potassium iodide and n-hexane were purchased from Fisher Scientific (Fair Lawn, NJ). Hydrogen peroxide was provided by Great Western Chemical Co. (Richmond, CA). Sodium dithionate (87%) was purchased from EMD Chemicals Inc (Darmstadt, Germany). Hydroxylamine hydrochloride (96%) was

purchased from VWR international (West Chester, PA). A Barnstead NANOpure II Ultrapure system was used to obtain double-deionized water ($>16 \text{ M}\Omega\cdot\text{cm}$).

2.2. Minerals

Six minerals were used to investigate their potential to activate persulfate: goethite $[\text{FeOOH}]$, hematite $[\text{Fe}_2\text{O}_3]$, ferrihydrite $[\text{Fe}_5\text{HO}_8\cdot 4\text{H}_2\text{O}]$, birnessite $[\delta\text{-MnO}_2]$, kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ and montmorillonite $[(\text{Na},\text{Ca})(\text{Al},\text{Mg})_6(\text{Si}_4\text{O}_{10})_3(\text{OH})_6\cdot n\text{H}_2\text{O}]$. Goethite and hematite were purchased from Strem Chemicals (Newburyport, MA) and J.T. Baker (Phillipsburg, NJ) respectively, ferrihydrite was purchased from Mach I Inc. (PA), and montmorillonite and kaolinite were provided by the Clay Minerals Society (West Lafayette, IN). Birnessite was prepared by the dropwise addition of concentrated hydrochloric acid (2M) to a boiling solution of potassium permanganate (1M) with vigorous stirring (Mckenzie, 1971). Examination of the X-ray diffraction pattern confirmed the minerals were the desired iron and manganese oxides. Minerals surface areas were determined by Brunauer, Emmett, and Teller (BET) analysis under liquid nitrogen on a Coulter SA 3100 (Carter et al. 1989).

2.3. Soils

Four fractions of a surface soil were used in this study. The natural soil, which is termed *total soil* in this study, was collected from the Palouse region of Washington State. The *total soil* was air dried and ground to pass through a $300\mu\text{m}$ sieve. Soil organic matter (SOM) was removed by heating in the presence of 30% hydrogen peroxide (Robinson, 1927). After SOM removal, the soil was dried at 55°C . The dried soil was ground to pass

through a 300 μ m sieve. The SOM-free soil was labeled the *total-mineral fraction*. From the *total-mineral fraction*, manganese oxides were removed by extracting with hydroxylamine hydrochloride (NH₂OH.HCl) (Chao, 1972). The manganese oxide free soil that still contained iron oxides was called the *iron-mineral fraction*. Iron oxides were then removed from the *iron-mineral fraction* by citrate-dithionate extraction (Holmgren, 1967). After the iron oxides were removed, the soil was labeled the *no-mineral fraction*. The soil was washed with deionized water (25ml/g) to remove the residual extractant after each treatment. The soil was dried at 55 °C, and ground to pass through a 300 μ m sieve. Characteristics of the soil fractions at different removal stages are summarized in Table 1.

2.4. Probe compounds

Nitrobenzene (NB) ($k_{OH\cdot} = 3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_{SO_4^{\cdot-}} \leq 10^6 \text{ M}^{-1}\text{s}^{-1}$) was used as a hydroxyl radical probe because of its high reactivity with hydroxyl radical but negligible reactivity with sulfate radicals (Buxton et al., 1988; Neta et al., 1977). Hexachloroethane (HCA) was used as a reductant probe because it is readily degraded by superoxide in the presence of cosolvents and is reduced by alkyl radicals, but is not oxidized by hydroxyl radicals ($k_{OH\cdot} \leq 10^6 \text{ M}^{-1}\text{s}^{-1}$).

2.5. Experimental procedure

All reactions were conducted in 20 ml borosilicate volatile organic analysis (VOA) vials capped with polytetrafluoroethylene (PTFE) lined septa. Reactions were conducted with 2 g mineral and 5 ml reactant solution at 20 ± 2 °C. However, the bulk density of birnessite and ferrihydrite was significantly lower than the other minerals and they were not

covered completely with 5 ml of reactant solution. Therefore, 1 g of birnessite and 0.5 g of ferrihydrite were used instead of 2 g. For the natural soil, 5 gm of the soil and 10 ml of reactant solution were used. For high pH systems, 0.5 M persulfate and 1 M NaOH were used, and 0.5 M persulfate alone was used for the low pH systems. Triplicate sets of vials were extracted with 5 ml hexane at selected time points over the course of the reactions. Control experiments using DI water and the probe compounds, and positive control experiments using the probe compounds and 0.5 M persulfate or 0.5 M persulfate + 1 M NaOH were performed in parallel. No minerals or soils were used in the control or positive control systems.

2.6. Extraction and analysis

Extracts containing nitrobenzene were analyzed using a Hewlett Packard 5890 series II gas chromatograph with flame ionization detector (FID) fitted with a 15 m × 0.53 mm SPB-5 capillary column with a 1.0 μm film. For nitrobenzene analysis, the injector and detector port temperatures were 200 °C and 250 °C respectively, the initial oven temperature was 60 °C, the program rate was 30 °C/min, and the final temperature was 180 °C. Extracts containing HCA were analyzed using a Hewlett Packard 5890 series II gas chromatograph with electron capture detector (ECD) fitted with a 30m × 0.53 mm EQUITY-5 capillary column having a 1.5 μm film. The injector temperature was 220 °C, the detector temperature was 270 °C, the oven temperature was 100 °C, the temperature program rate was 30 °C/min, and the final temperature was 240 °C. Persulfate concentrations were measured in triplicate at different time points by iodometric titration using 0.01 N sodium thiosulfate (Kolthoff and Stenger, 1947). pH was measured using a Fisher Accument AB15 pH meter.

Particle size distribution of the natural soil was measured by pipette method (Gee and Bauder, 1986). Acid ammonium oxalate in darkness (AOD) method (McKeague and Day, 1966) was used to extract amorphous iron oxides and manganese oxides. Total iron oxides and manganese oxides were extracted using the citrate-bicarbonate-dithionite (CBD) method (Jackson et al., 1986), and then analyzed by inductively coupled plasma-atomic emission spectrometry (ICPAES). Statistical analysis system, SAS 9.1.3 was used to calculate the variances between the experimental data sets and 95% confidence intervals of rate constants.

3. Results and discussion

3.1. Persulfate decomposition in minerals

Three iron oxides, one manganese oxide, and two clay minerals were investigated for their potential to promote persulfate decomposition. Persulfate decomposition in mineral systems at low pH (<7) and at high pH (>12) over 30 d is shown in Figure 1a-b. In the low pH systems $\leq 15\%$ persulfate decomposition was observed. The highest persulfate decomposition was with birnessite (15%) followed by goethite (13%), while with other minerals (hematite, ferrihydrite, montmorillonite, and kaolinite), persulfate decomposition was $\leq 6\%$. In the high pH systems, persulfate decomposed most rapidly in the presence of ferrihydrite (23%) followed by hematite (18%). In addition, persulfate decomposition in the presence of birnessite, goethite, montmorillonite and kaolinite was not significantly different than in the low pH systems.

With both the low pH and the high pH systems, the highest rate of persulfate decomposition occurred in the presence of iron and manganese oxides, while the lowest

rates were in the presence of the clay minerals. Rates of mineral mediated decomposition in CHP systems were found to be highly dependent on the mineral surface area (Valentine and Wang, 1998; Kwan and Voelker 2003); therefore, to confirm the similarities of mineral mediated persulfate decomposition, the observed persulfate decomposition rates (k_{obs}) were normalized to the surface areas of the iron oxides and manganese oxide minerals (Table 2). In the low pH systems, the surface area normalized rate of persulfate decomposition ($k_{(\text{S.A.})(\text{mass})}$) in the presence of goethite was greater than hematite. However, in the high pH systems, $k_{(\text{S.A.})(\text{mass})}$ in the presence of goethite was smaller than hematite. These results are in agreement with the findings of Watts et al. (2007), who found that iron oxides catalyzed the decomposition of hydrogen peroxide and that the decomposition rate with goethite was greater than with hematite at lower pH, but smaller than with hematite at higher pH. Although the surface area of ferrihydrite was the highest among the minerals studied, relative persulfate decomposition was lower, which may be due to surface scavenging of reactive intermediates resulting in the generation of oxygen on the surface of ferrihydrite. Huang et al. (2001) and Miller and Valentine (1995, 1999) found that during hydrogen peroxide decomposition, the surface scavenging rate was larger than the hydrogen peroxide decomposition rate. Therefore, a large amount of oxygen formed initially left limited surface area for further hydrogen peroxide decomposition. A similar mechanism may be occurring in the ferrihydrite-mediated decomposition of persulfate.

3.2. Hydroxyl radical generation in mineral-mediated reactions

Nitrobenzene was used as a hydroxyl radical probe to investigate the potential of iron and manganese oxides to promote the generation of hydroxyl radical in the low pH and in

the high pH systems. Relative rates of hydroxyl radical generation, measured by the oxidation of nitrobenzene, in the low pH system in the presence of minerals over 144 h is shown in Figure 2a. No loss of nitrobenzene was observed in parallel control systems containing no persulfate over the entire reaction time. With birnessite, > 99% degradation of the nitrobenzene was achieved in 120 h, while nitrobenzene degradation mediated by all of the other minerals was < 40%, which was slower than the degradation achieved in the positive control systems (i.e., 0.5 M persulfate without minerals). These results demonstrate that the manganese oxide mineral birnessite promotes the generation of hydroxyl radical in low pH persulfate systems while iron oxide minerals do not. Furthermore, some iron oxides may inhibit hydroxyl radical generation and/or scavenge the generated hydroxyl radical. Similar phenomena of quenching of hydroxyl radical by iron oxides in catalyzed hydrogen peroxide systems were observed by Miller and Valentine (1995, 1995a).

Relative rates of hydroxyl radical generation, measured through the oxidation of nitrobenzene, over 72 h in high pH systems in the presence of minerals is shown in Figure 2b. The highest relative rates of hydroxyl radical generation were found in birnessite systems (> 92%) followed by goethite systems (> 55%). However, relative hydroxyl radical generation was slower in the other mineral systems than in the positive control. In both the low pH and the high pH systems, the manganese oxide mineral birnessite promoted the generation of hydroxyl radical significantly faster than the iron oxide minerals. The potential cause of this may be the higher redox potential of manganese compared to iron (McBride, 1994), which has the potential to more rapidly decompose peroxygens.

3.3. Reductant generation in mineral-mediated reactions

Hexachloroethane was used as a probe compound to investigate the potential of iron and manganese oxides to promote the generation of reductants, such as superoxide radicals and alkyl radicals, in the low pH systems and high pH systems. The degradation of hexachloroethane over 36 h in the low pH systems with minerals is shown in Figure 3a. The highest relative rates of reductant generation were in the goethite system (>50% loss of the probe relative to the control containing no persulfate) and the hematite system (45% probe loss). Hexachloroethane degradation in the ferrihydrite and birnessite systems was similar to that of the positive control, approximately 30%. In the control system, 10% of the hexachloroethane was lost, likely due to volatilization. The degradation of hexachloroethane in high pH systems over 36 h is shown in Figure 3b. With goethite, 80% of hexachloroethane was degraded in the first 5 h; thereafter, hexachloroethane degradation slowed drastically, so that after 36 h > 90% degradation of hexachloroethane was observed. With hematite, ferrihydrite, and the positive control, degradation of hexachloroethane was 40 % to 50%.

The orders of superoxide radical anion generation in low pH systems and in high pH systems were the same: Goethite > hematite > ferrihydrite > birnessite. The data in Figure 3a-b indicate that the iron-based mineral goethite may catalyze the generation of superoxide radical, while hematite and ferrihydrite have minimal influence in the high pH systems. In addition, hexachloroethane degradation in the presence of the manganese oxide mineral birnessite was the lowest among all minerals. These results suggest that birnessite may inhibit superoxide radical anion generation; alternatively, it may scavenge the generated reductants. Furthermore, the lack of superoxide generation in the manganese oxide

catalyzed persulfate system is very different from the rapid generation of superoxide in manganese oxide catalyzed hydrogen peroxide systems documented by Hasan et al. (1999) and Watts et al. (2005).

3.4. Hydroxyl radical generation in clay mineral-mediated reactions

Nitrobenzene was used as a probe compound to quantify relative rates of hydroxyl radical generation in the low pH and in high pH systems with two clay minerals: montmorillonite and kaolinite. Relative hydroxyl radical generation, quantified by degradation of nitrobenzene, over 108 h in the low pH systems is shown in Figure 4a-b. In the low pH kaolinite system nitrobenzene degradation was approximately 45%, which was the same as the positive control, while nitrobenzene degradation in the montmorillonite system was less, at 36% (Figure 4a). In the high pH systems, nitrobenzene degradation was approximately 92% in the kaolinite systems, which again was the same as the positive control, while the degradation was approximately 82% in the montmorillonite systems. These data show that clay minerals do not promote generation of the hydroxyl radical in both the low pH and the high pH systems; furthermore, montmorillonite may scavenge the hydroxyl radical or inhibit the hydroxyl radical generation.

3.5. Reductant generation in clay mineral-mediated reactions

Hexachloroethane was used as a probe compound to quantify relative generation rates of reductants, such as superoxide radicals and alkyl radicals, in low pH and in high pH systems with the two clay minerals montmorillonite and kaolinite. The degradation of hexachloroethane over 48 h is shown in Figure 5a-b. In the low pH systems < 15% loss of

hexachloroethane was observed. In the high pH systems, hexachloroethane loss was approximately 19% with both kaolinite and montmorillonite. These data show that clay minerals do not promote significant superoxide radical anion generation at either low or high pH regimes.

3.6. Persulfate decomposition in soil fractions

The Palouse soil, the *total-mineral fraction*, the *iron-mineral fraction*, and the *no-mineral fraction* were investigated for their potential to promote persulfate decomposition in low pH and high pH persulfate systems over 7 d (Figure 6a-b). In all of the fractions at low pH, < 15% persulfate decomposition was observed. The highest decomposition was in the *total soil* (15%), while with the modified soil fractions, the persulfate decomposition was < 10%. In the high pH systems, the highest persulfate decomposition was in the presence of *total soil* (85%). However, with all of the modified soils, the persulfate decomposition was <10 %. The noticeable feature of the data shown in Figure 6b is the high rate of persulfate decomposition in the high pH system in the presence of the total Palouse soil. Basic solutions of persulfate in the presence of phenols have been shown to activate persulfate via the Elbs reaction (Elbs, 1893), and this is likely occurring in the presence of soil organic matter.

3.7. Hydroxyl radical generation in soil fractions

Nitrobenzene was used as a probe compound to identify hydroxyl radical generation in low pH and in high pH systems in the presence of *total soil*, *total-mineral fraction*, *iron-mineral fraction*, and *no-mineral fraction*. The degradation of nitrobenzene in the low pH

systems over 168 h is shown in Figure 7a. Nitrobenzene degradation in the positive control, *total soil*, and *no-mineral fraction* did not differ significantly. The highest degradation of nitrobenzene was 64% in the presence of the iron mineral fraction and the lowest was 42% in the presence of the *total-mineral fraction*. Although the *total-mineral fraction* contained manganese oxides, it did not promote the generation of hydroxyl radical, unlike synthetic manganese oxides (birnessite) in the low pH mineral system (Figure 2a). The minimal hydroxyl radical generation was likely due to the much lower mass of manganese oxides relative to the birnessite reaction shown in Figure 2a-b.

Relative hydroxyl radical generation rates, quantified by the degradation of nitrobenzene, in high pH systems over 84 h is shown in Figure 7b. In the high pH systems, nitrobenzene degradation was 92% in the presence of the *no-mineral fraction* and 84% in positive control after 84 h. Moreover, hydroxyl radical generation in the *no-mineral fraction* occurred with a rapid initial rate followed by a much slower rate. With the *total soil*, *iron-mineral fraction*, and *total-mineral fraction*, nitrobenzene degradation was 80%, 68%, and 52% respectively. The degradation of nitrobenzene in the presence of *total soil*, *iron-mineral fraction*, and *total-mineral fraction* was lower than in the positive control, suggesting that soil organic matter, iron oxides, and manganese oxides may be responsible for scavenging hydroxyl radicals.

3.8. Reductant generation in soil fractions

Hexachloroethane was used as a probe compound to identify reductant generation in low pH and in high pH systems with the *total soil*, *total-mineral fraction*, *iron-mineral fraction*, and *no-mineral fraction*. The degradation of hexachloroethane in the low pH

systems over 48 h is shown in Figure 8a. After 48 h, the degradation of hexachloroethane in the *no-mineral fraction*, *total-mineral fraction*, and *total soil* was 82%, 66% and 40%, respectively. In presence of the *iron-mineral fraction*, and in the positive control containing persulfate, hexachloroethane degradation was < 20%. In the high pH systems, hexachloroethane degradation over 48 h is shown in Figure 8b. With the *total soil*, hexachloroethane was rapidly degraded to undetectable concentration in 4 h; in contrast, hexachloroethane loss in the soil fractions and in the positive control was < 32% after 48 h. In the high pH system, fast degradation of the hexachloroethane in the presence of the *total soil* may be the result of reductant generation through reactions of persulfate with the soil organic matter, potentially generating alkyl radicals.

In the high pH systems, the difference between reductant generation in the soil fractions (Figure 8b) and in the synthetic minerals (Figure 3b) was noticeable. The iron minerals in natural soils did not promote reductant generation in reaction with persulfate; however, the synthetic iron-minerals did promote reductant generation. The difference in results between natural soils and mineral systems is likely the higher masses of the iron minerals in the mineral systems relative to much lower masses in the soil fractions.

4. Conclusions

The potential for persulfate activation by iron oxides, manganese oxide, and clay minerals was investigated in high pH (>12) and low pH (<7) systems. In both the high and low pH systems, the manganese oxide mineral birnessite was found to be the most active catalyst for generating oxidants, and the iron oxide mineral goethite was the most active

catalyst for generating reductants. The clay minerals kaolinite and montmorillonite did not show any detectable catalytic activity in the generation either oxidants or reductants.

Various fractions of a natural soil were also studied. The natural soil minerals in each of the soil fraction were not effective in catalyzing persulfate to generate reactive oxygen species. However, soil organic matter was highly active in promoting the generation of reductants in the high pH persulfate system.

Minimal persulfate decomposition was seen in both mineral systems and soil fractions at low pH. However, persulfate decomposition at high pH was approximately 85% in the presence of the *total soil* after 7 d. In the presence of each of the minerals, persulfate decomposition was < 25% after 30 d. At high pH, the surface area normalized rate of persulfate decomposition in the presence of all of the iron and manganese oxides did not vary significantly.

The results of this research demonstrate that although a relatively high mass of birnessite and goethite can activate persulfate to generate reactive oxygen species, the mineral components of the soil evaluated did not promote measurable activation of persulfate. In contrast, high pH persulfate in the presence of soil organic matter promotes significant reductant activity.

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Table 1: Soil characteristics at different removal stages.

	Total Soil	Total-mineral fraction (after SOM removal)	Iron-mineral fraction (After manganese oxides removal)	No-mineral fraction (After manganese oxides and iron oxides removal)
Organic Carbon (%)	1.617	0.083	0.050	0.037
Amorphous oxides				
Fe (mg/kg)	4780	4190	3660	1190
Mn (mg/kg)	610	420	170	30
Crystalline oxides				
Fe (mg/kg)	3900	2700	2700	680
Mn (mg/kg)	260	210	90	10
Cation exchange capacity (cmol(+)/kg)	19	12	9	7
Particle size distribution				
Sand (%)	7.77	9.23	7.83	8.86
Clay (%)	69.15	70.67	76.7	79.46
Silt (%)	23.08	20.10	15.46	11.67
Texture	Silt loam	Silt loam	Silt loam	Silt loam*

*Borderline textural class

Table 2: Persulfate decomposition rate constants in presence of iron and manganese oxides at pH<7 and at pH>12 (95% confidence interval shown).

Mineral type	S.A	(S.A)(mass)	Low pH < 7		High pH >12	
			k_{obs}	$k_{(\text{S.A})(\text{mass})}$	k_{obs}	$k_{(\text{S.A})(\text{mass})}$
Iron oxides						
Ferrihydrite	233	116.5	$(2.1 \pm 0.62) \times 10^{-3}$	$(1.8 \pm 0.53) \times 10^{-5}$	$(8.0 \pm 1.5) \times 10^{-3}$	$(6.9 \pm 1.3) \times 10^{-5}$
Goethite	37	74	$(4.5 \pm 0.82) \times 10^{-3}$	$(6.0 \pm 1.1) \times 10^{-5}$	$(5.0 \pm 0.59) \times 10^{-3}$	$(6.7 \pm 0.80) \times 10^{-5}$
Hematite	28	56	$(1.6 \pm 0.53) \times 10^{-3}$	$(2.9 \pm 0.95) \times 10^{-5}$	$(6.3 \pm 0.25) \times 10^{-3}$	$(1.1 \pm 0.05) \times 10^{-4}$
Manganese oxide						
Birnessite	44	44	$(5.4 \pm 0.65) \times 10^{-3}$	$(1.2 \pm 0.15) \times 10^{-4}$	$(4.8 \pm 0.17) \times 10^{-3}$	$(1.1 \pm 0.04) \times 10^{-4}$

S.A = surface area (m^2/g)

(S.A.)(mass) = surface area in the system, (m^2)

k_{obs} = observe 1st order rate constant (d^{-1}) calculated from the data of Figure 1a-b.

$k_{(\text{S.A})(\text{mass})} = k_{\text{obs}}/(\text{S.A})(\text{mass})$, (d^{-1}/m^2)

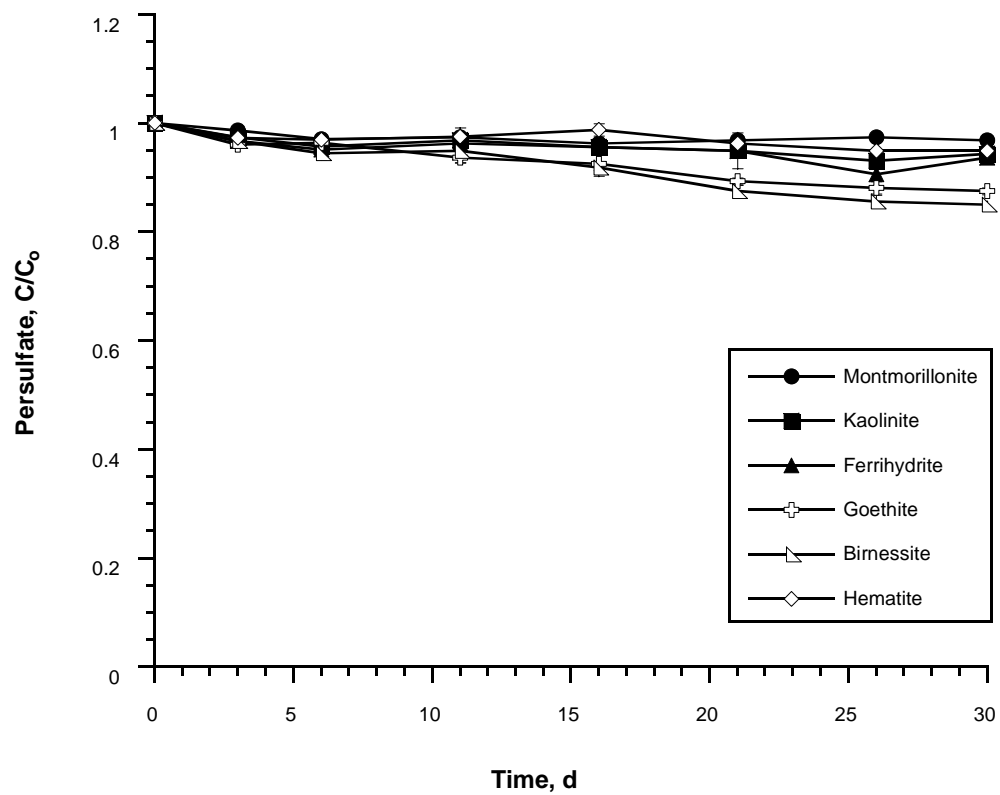


Figure 1a: Mineral-mediated decomposition of the persulfate in low pH systems.

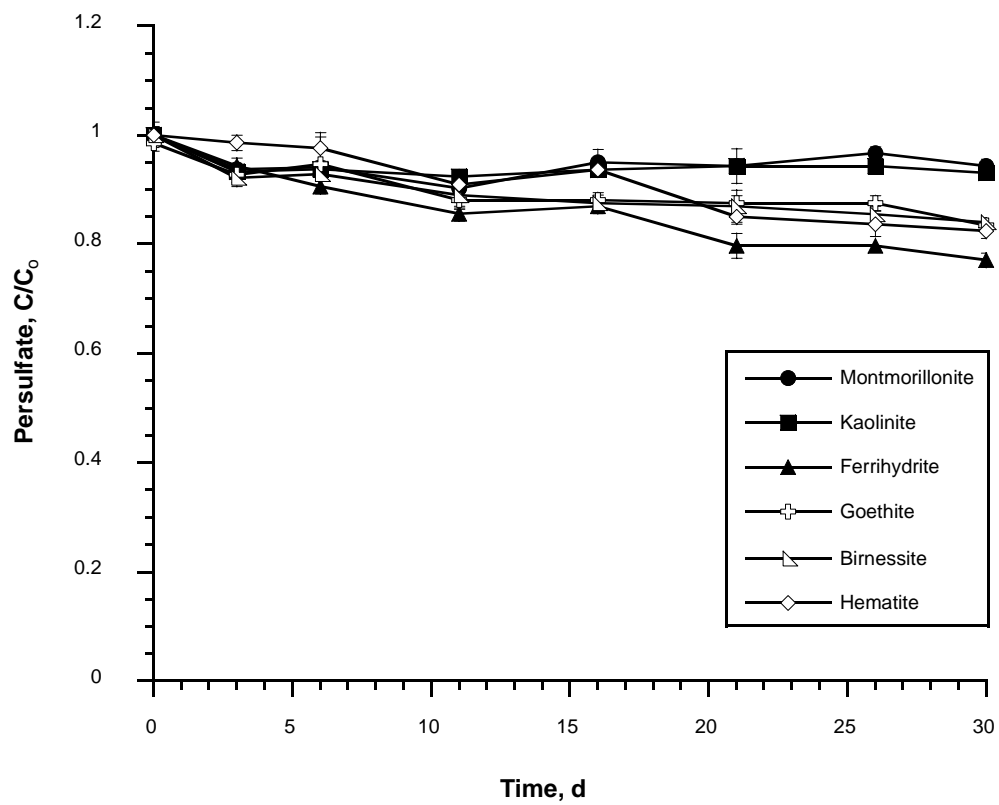


Figure 1b: Mineral-mediated decomposition of the persulfate in high pH systems.

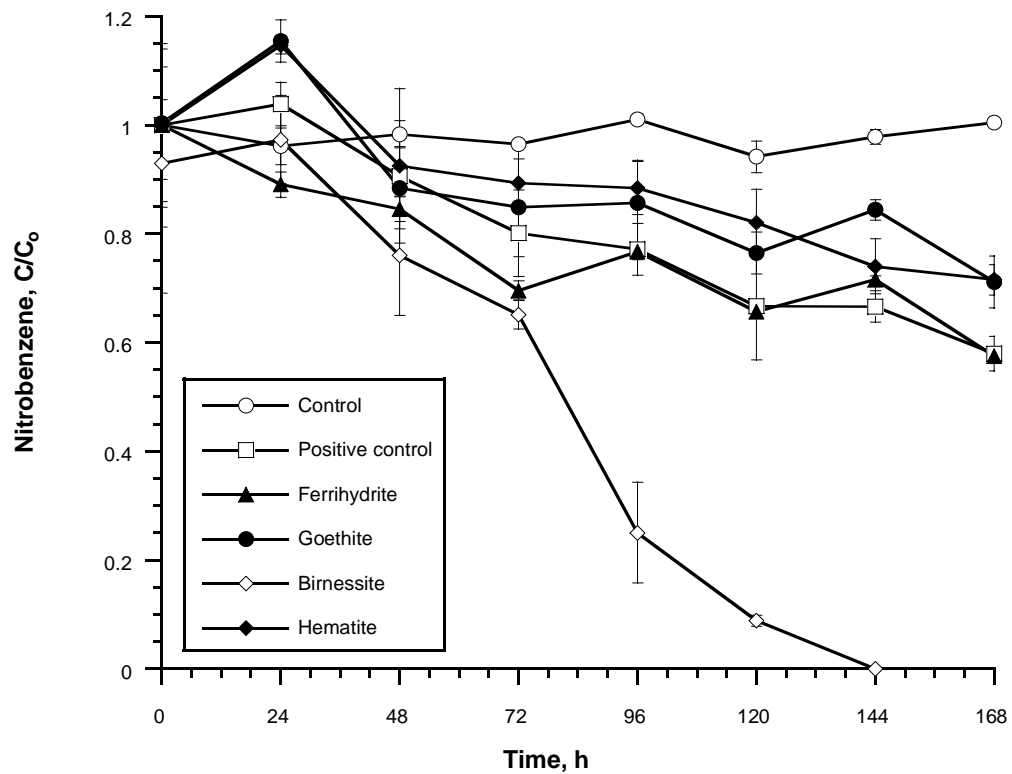


Figure 2a: Degradation of hydroxyl radical probe nitrobenzene in low pH systems with minerals.

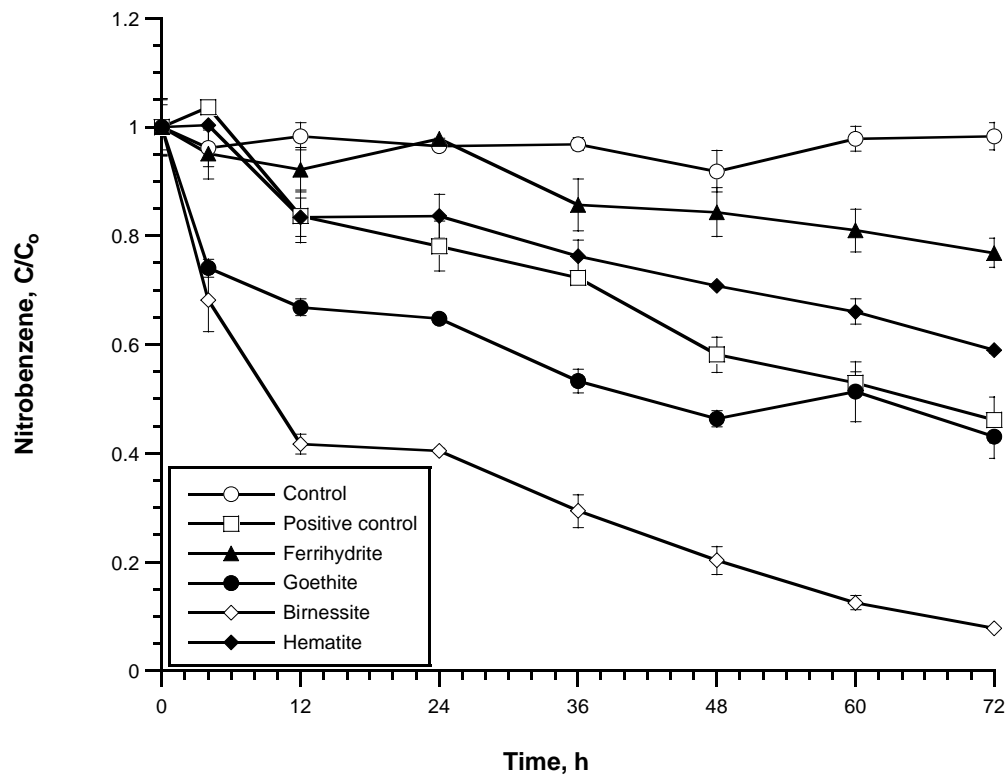


Figure 2b: Degradation of hydroxyl radical probe nitrobenzene in high pH systems with minerals.

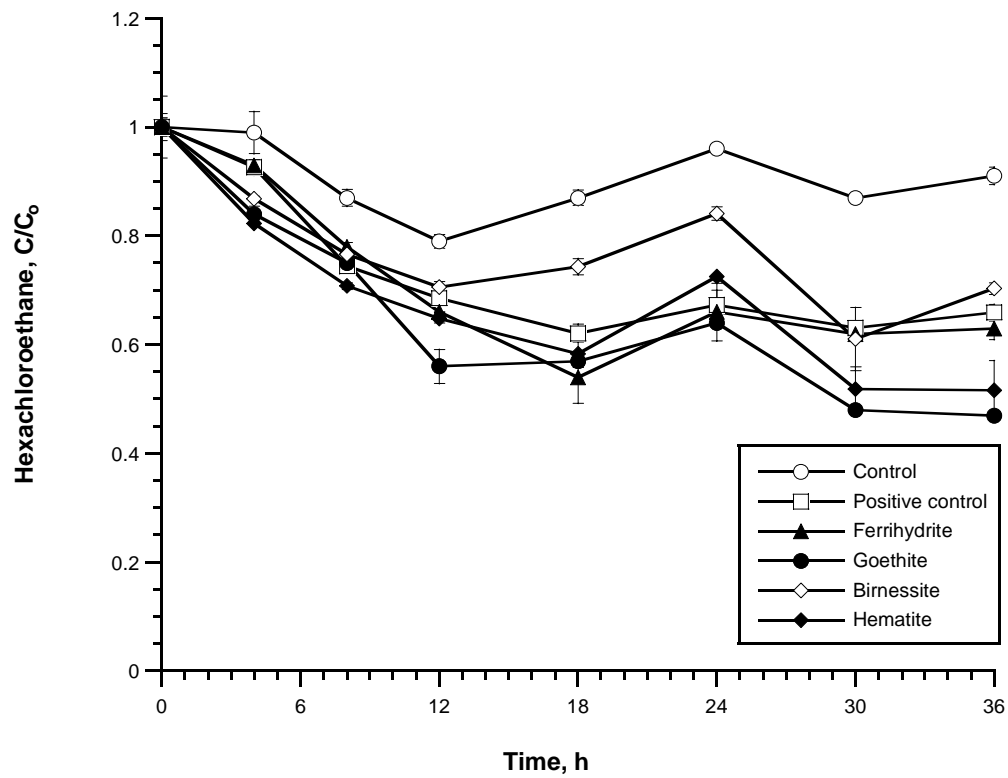


Figure 3a: Degradation of superoxide radical probe hexachloroethane in low pH systems with minerals.

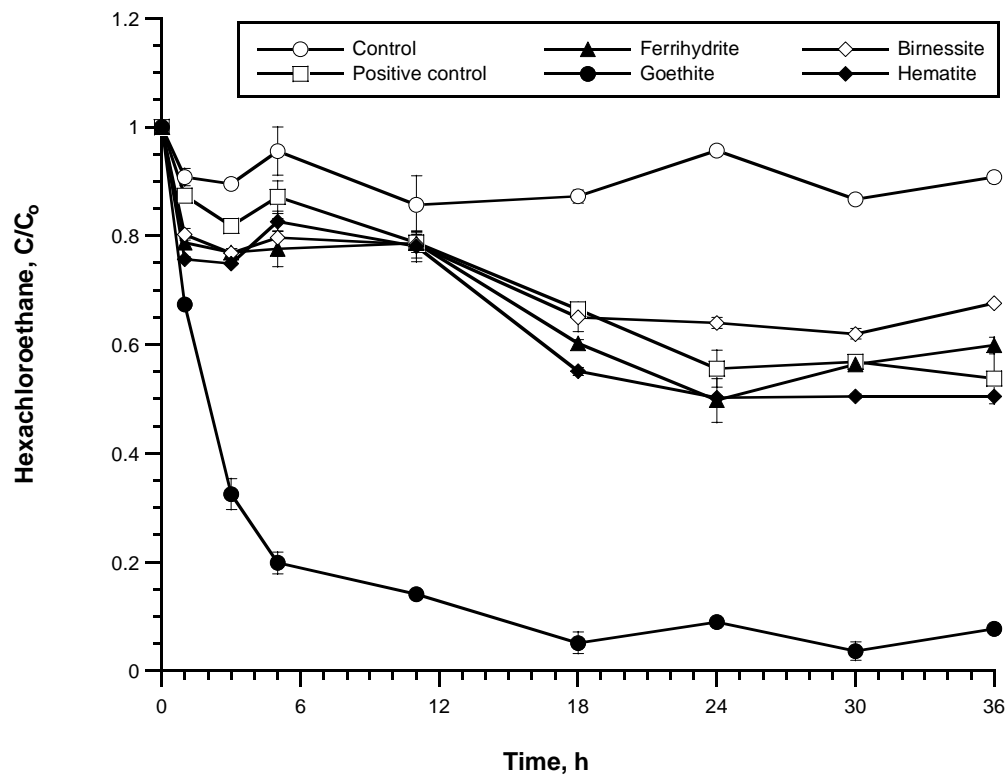


Figure 3b: Degradation of superoxide radical probe hexachloroethane in high pH systems with minerals.

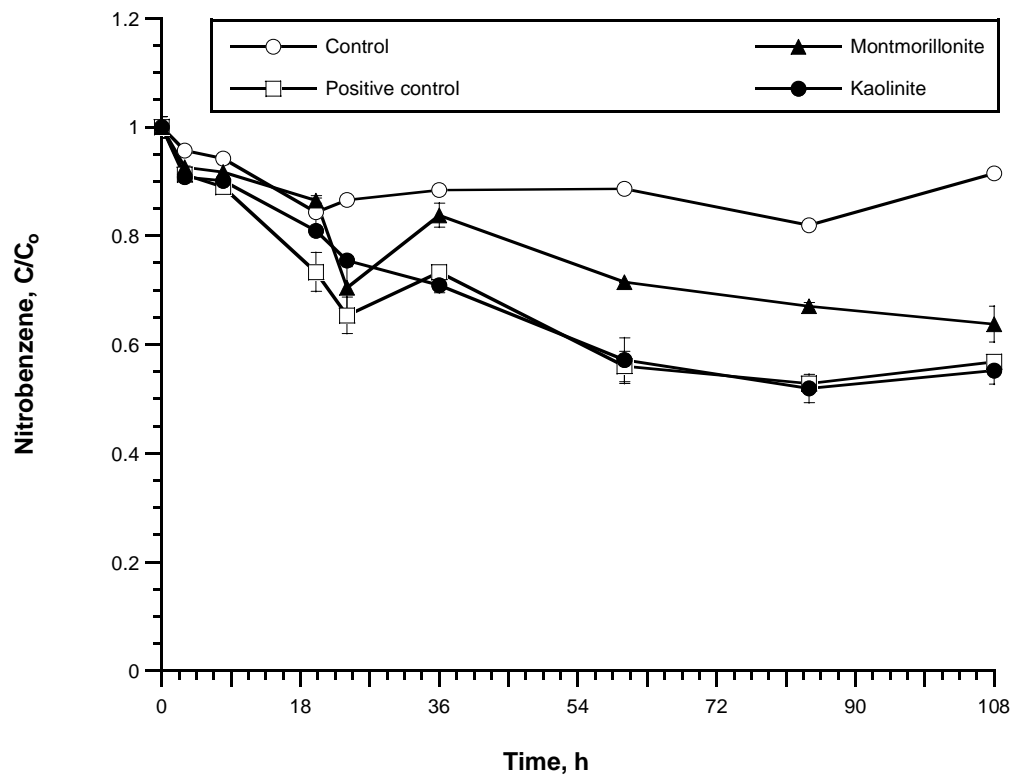


Figure 4a: Degradation of hydroxyl radical probe nitrobenzene in low pH systems with clay minerals.

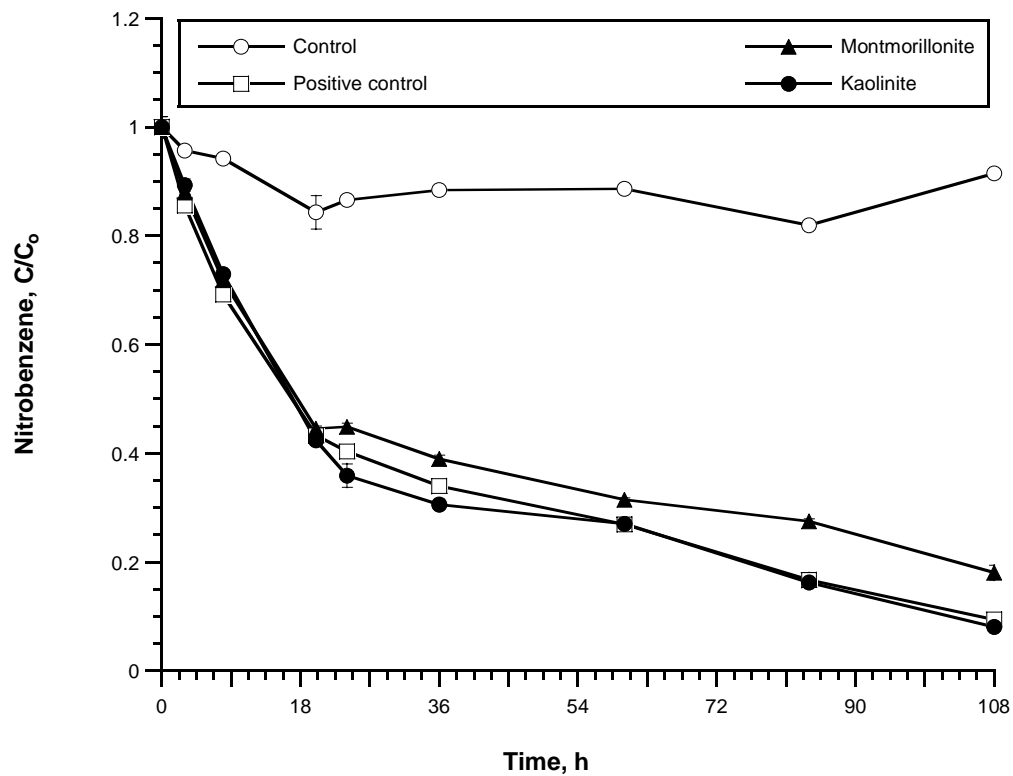


Figure 4b: Degradation of hydroxyl radical probe nitrobenzene in high pH systems with clay minerals.

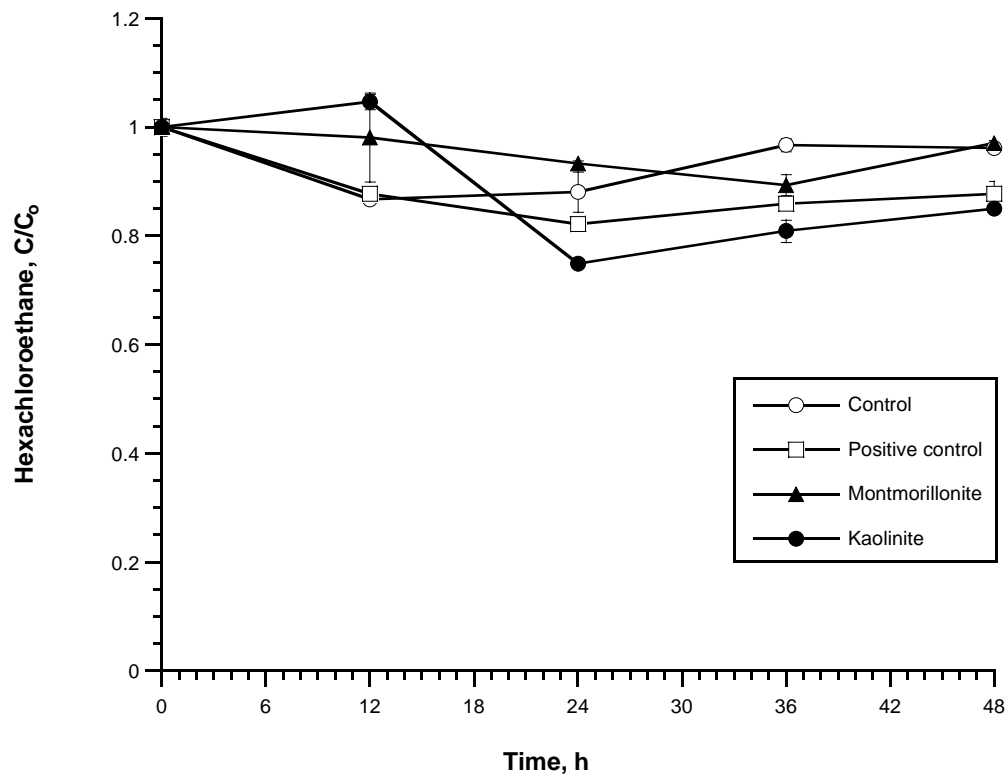


Figure 5a: Degradation of superoxide radical probe hexachloroethane in low pH systems with clay minerals.

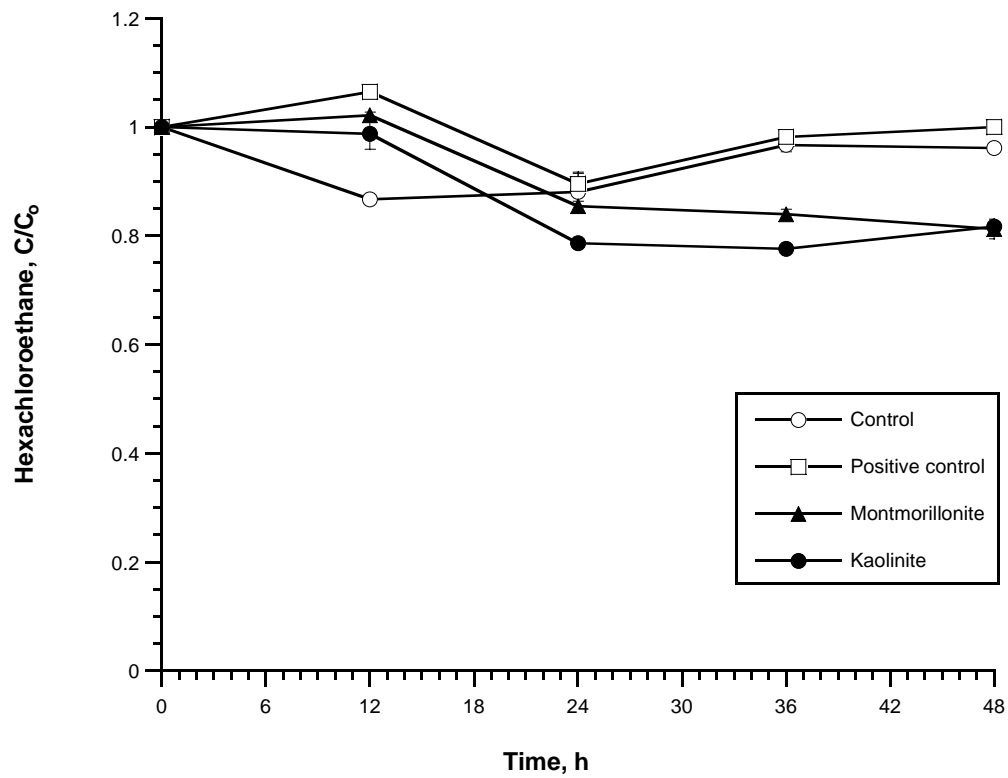


Figure 5b: Degradation of superoxide radical probe hexachloroethane in high pH systems with clay minerals.

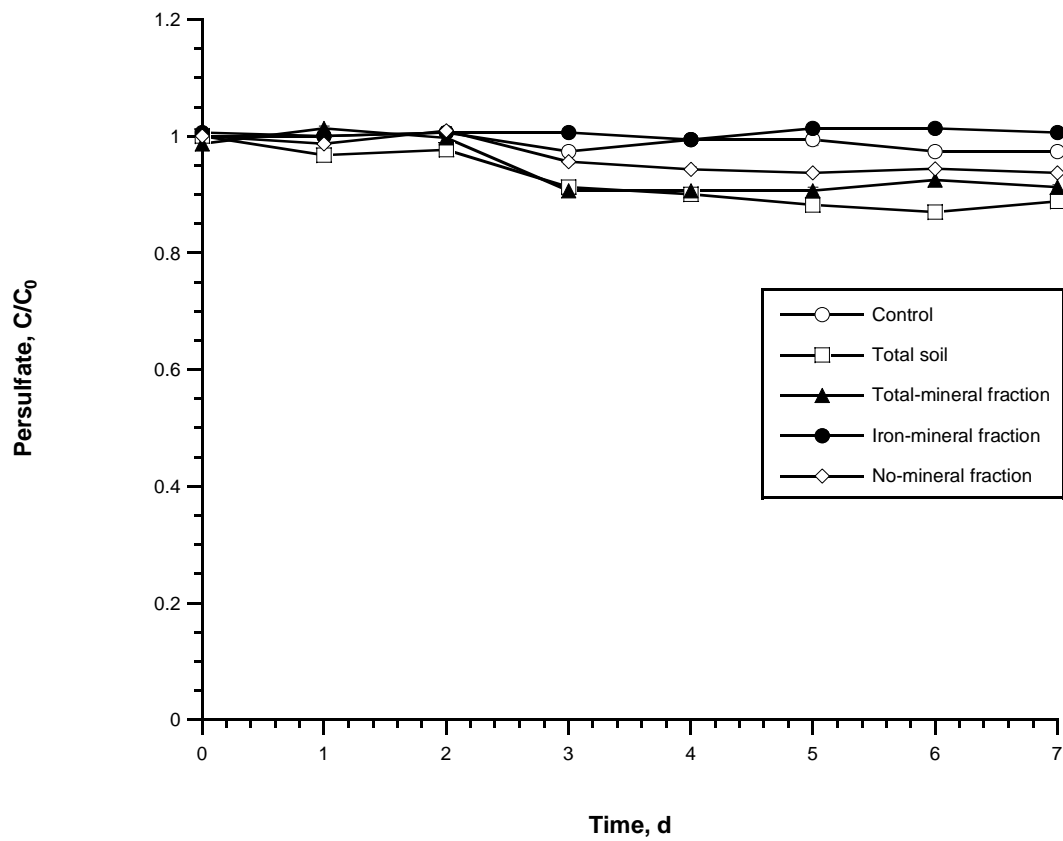


Figure 6a: Persulfate decomposition in low pH systems with soil fractions.

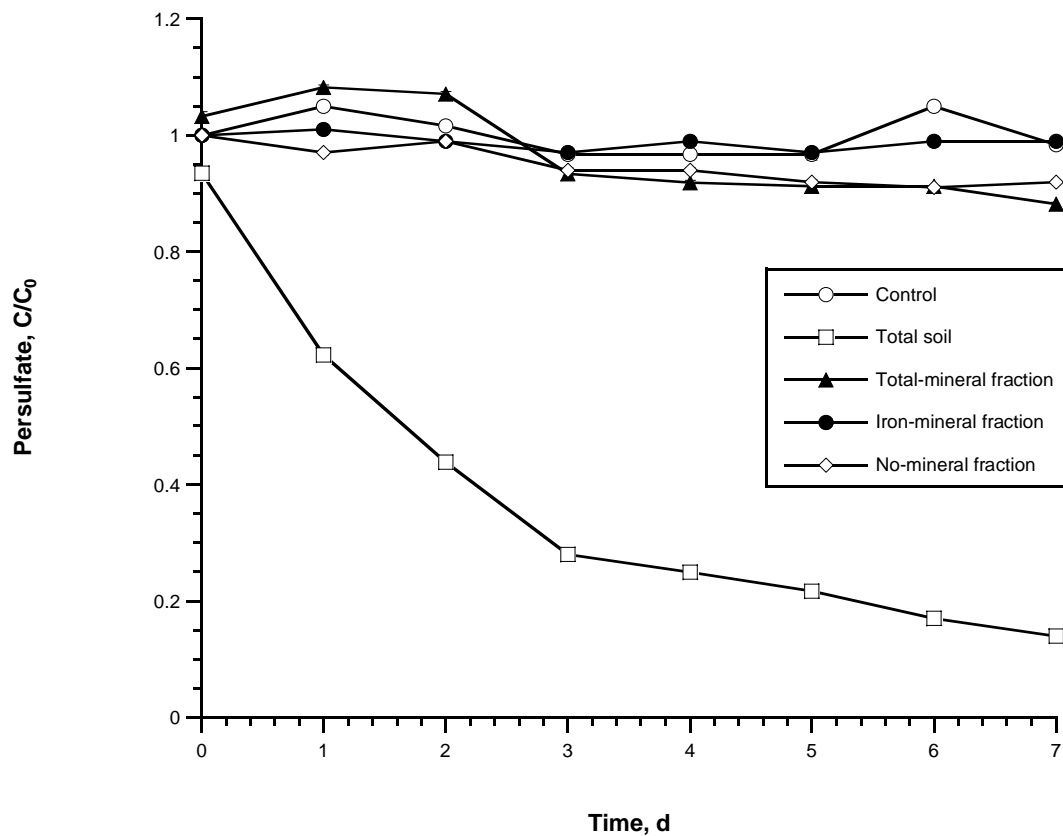


Figure 6b: Persulfate decomposition in high pH systems with soil fractions.

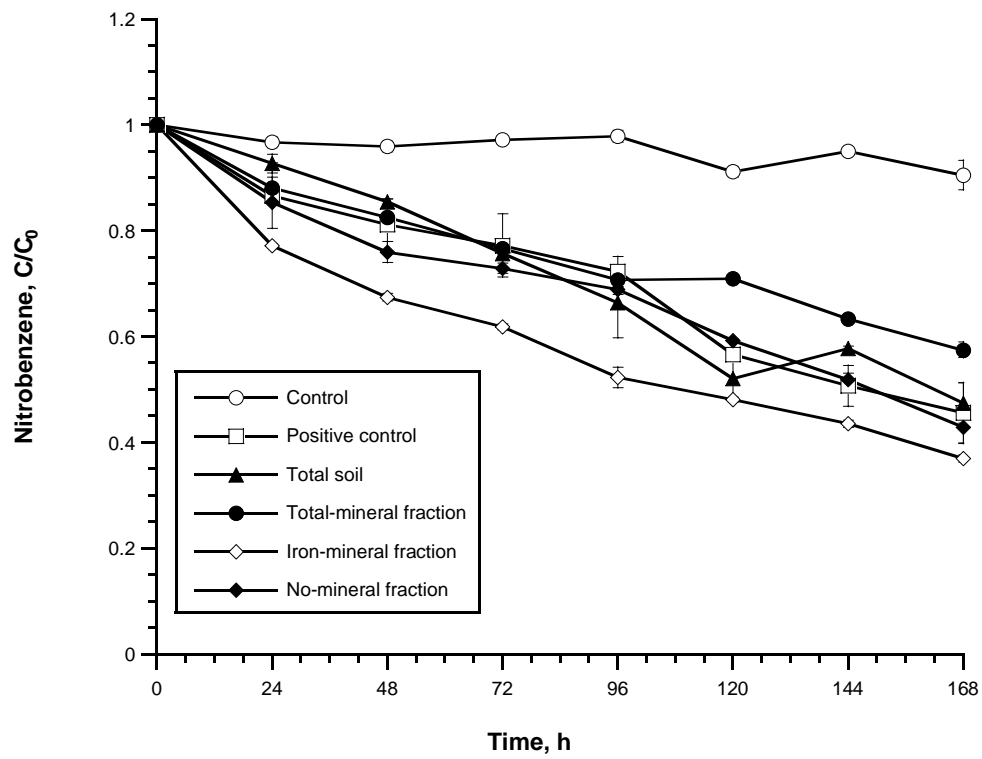


Figure 7a: Nitrobenzene degradation with soil fractions in low pH systems.

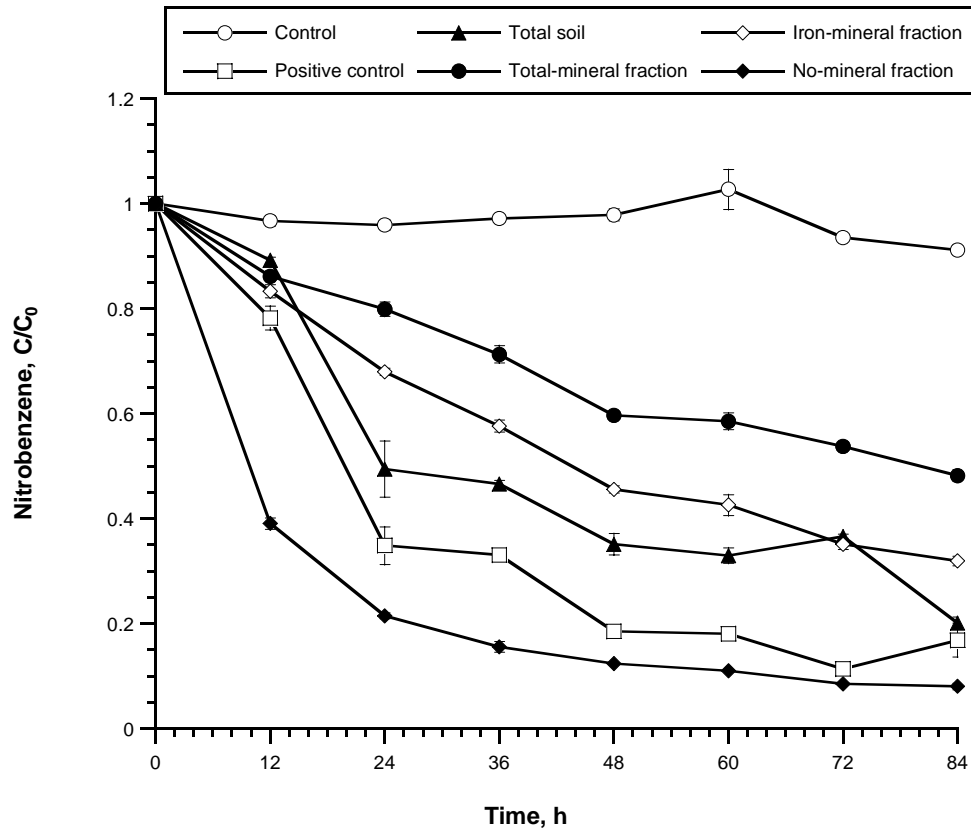


Figure 7b: Nitrobenzene degradation with soil fractions in high pH systems.

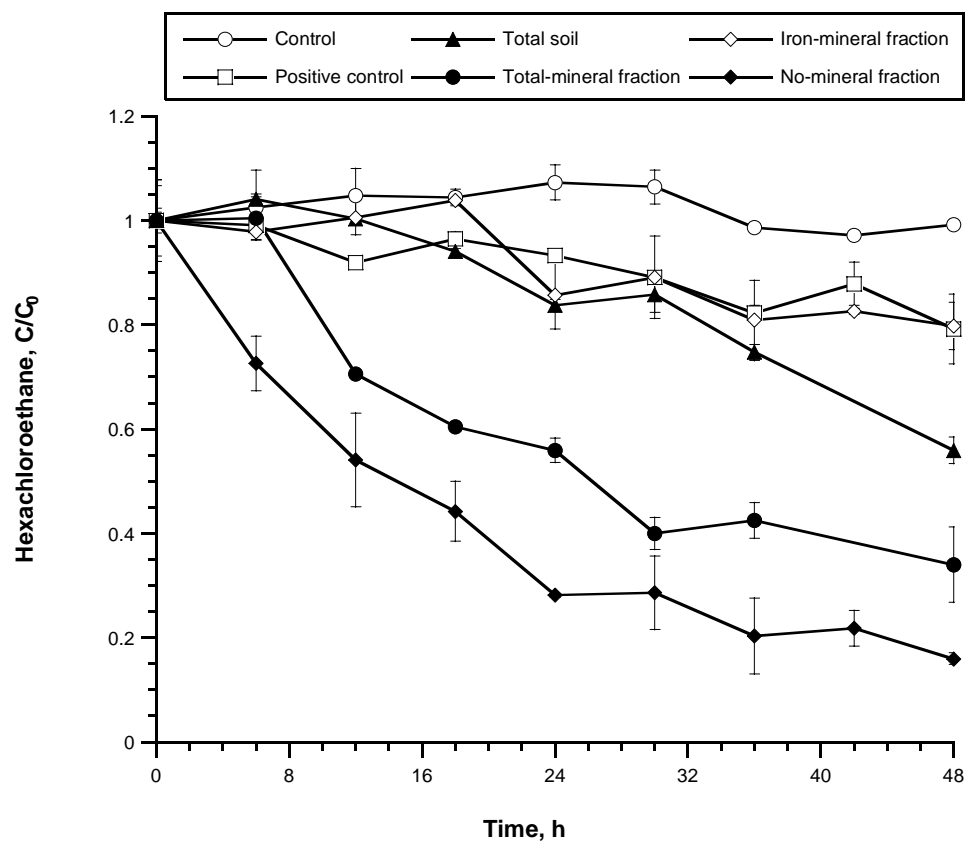


Figure 8a: Hexachloroethane degradation with soil fractions in low pH systems.

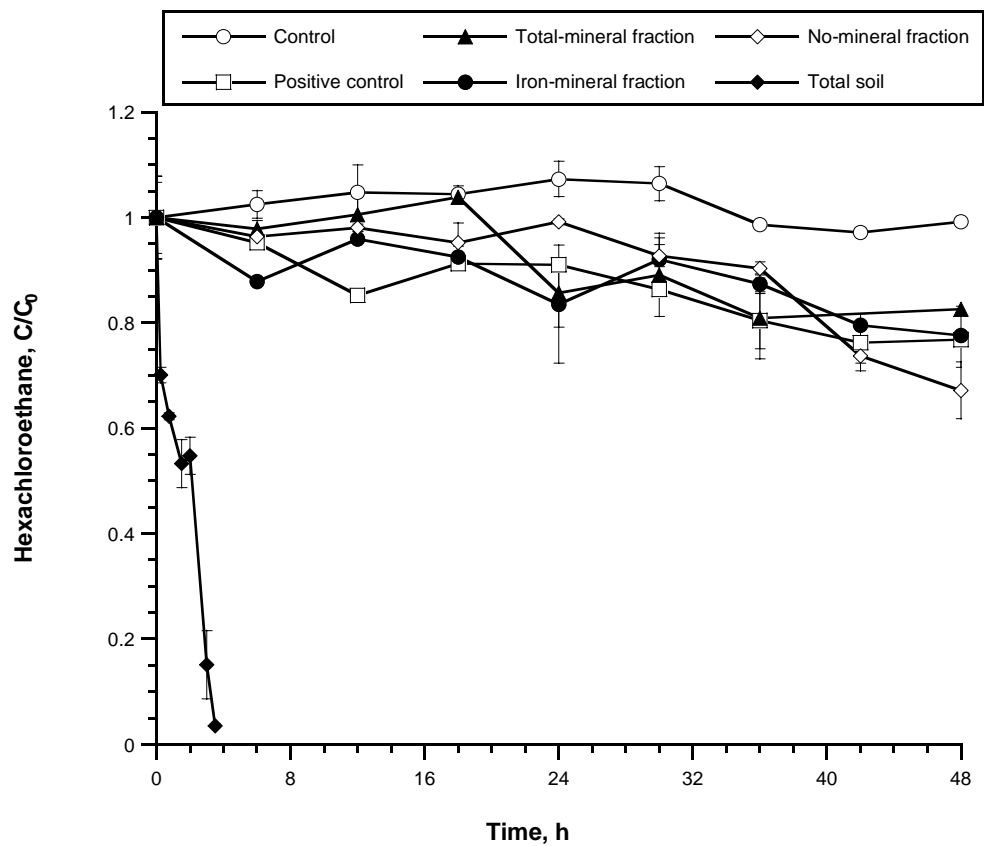


Figure 8b: Hexachloroethane degradation with soil fractions in high pH systems.