

Destruction of PCB 44 in Spiked Subsurface Soils Using Activated Persulfate Oxidation

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Abstract The effectiveness of persulfate oxidation for the destruction of tetrachlorobiphenyl a representative polychlorobiphenyl (PCB), in spiked subsurface soils was evaluated in this study. Kaolin and glacial till soils were selected as representative low permeability soils; both soils were spiked with 50 mg PCB per dry kilogram of soil. Activation of persulfate oxidation was necessary to achieve effective destruction of PCBs in soils. As persulfate oxidation activators, temperature and high pH were used in order to maximize PCB destruction. In addition, the effect of oxidant dose and reaction time was investigated. The optimal dose for persulfate was found to be 30% for maximum oxidation. The persulfate activation with temperature of 45°C was superior to persulfate activation with high pH (pH 12), where higher PCB destructions were observed for

kaolin and glacial till soils. PCB destruction increased with reaction time, where maximum degradation was achieved after 7 days. The highest PCB destruction was achieved with temperature activation at 45°C using a dosage of 30% persulfate at pH 12 for kaolin and glacial till soils after 7 days.

Keywords PCBs · Persulfate oxidation · Remediation · Soils

1 Introduction

Contamination of soils and groundwater is of environmental concern due to the toxicity exhibited by compounds such as polychlorobiphenyls (PCBs). PCBs were referred to by the trade names Aroclor, Phenoclor, and Kanechlor, and they encompass a class of chlorinated compounds that includes up to 209 variations, or congeners, with different physical and chemical characteristics (USEPA 1987). PCBs were used as dielectric fluids in electrical transformers and capacitors, as plasticizers in paint, and as dye carriers in carbonless copy paper. From 1929 to 1980, the cumulative world production of PCBs was approximately 2.4 billion pounds (Dávila et al. 1993). PCBs have not been manufactured in the USA since 1977. Due to their widespread use, large amounts of PCBs have been released into the environment. Furthermore, exposure still occurs due to their presence in old transformers and capacitors.

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United States Environmental Protection Agency (USEPA) has determined that PCBs may cause adverse reproductive effects, developmental toxicity, and cancer and thus are dangerous to human health and wildlife. PCBs tend to persist in the environment and to occur in natural media, such as soil, sediments, and water, in particular, due to their hydrophobic nature and low water solubility; they can become rapidly associated soils. According to the USEPA for soils, the preliminary remediation goals should generally be 1 ppm in residential areas (USEPA 1990).

PCB remediation techniques include incineration, thermal desorption, chemical dehalogenation, solidification/vitrification, phytoremediation, and bioremediation (Sharma and Reddy 2004). Selecting PCB remedial technologies are dependent on many factors, such as the varied structures and properties of PCBs, site conditions, cost, etc. Although incineration is a widely used technology for treating soils contaminated with PCBs, there is potential danger for release of dioxins via flue gas stream (Dávila et al. 1993). Some of these methods are sensitive to particle size, clay content, soil pH, etc., while some produce other residuals that must be treated and/or disposed of. For that reason, one technology that overcomes these shortcomings is greatly needed. Some of these techniques are unsuccessful at complete remediation of heavily contaminated soils (Ferrarese et al. 2008). For this reason, the chemical oxidation method has gained much importance, since this technique is applicable to a wide range of contaminants, easy to apply, and are rapid and aggressive. The widely used oxidants are Fenton's reagent, hydrogen peroxide, permanganate, and ozone. However, Fenton reagent has some limitations such as fast reaction between oxidant and catalyst, ineffective utilization of quickly generated hydroxyl radicals, and inherent instability of hydrogen peroxide (Watts et al. 2007). Since hydrogen peroxide and ozone have relatively short lifetimes in the subsurface as compared to persulfate, persulfate is an alternate oxidant. More research is greatly needed for the remediation of soils by persulfate oxidation.

In this study, the oxidation of PCB through activation of persulfate with heat and high pH was investigated for contaminated kaolin and glacial till soils. The effects of activators (elevated temperatures and pH), persulfate dosage, and reaction time on the destruction of PCBs in soils were examined through a series of laboratory batch experiments.

2 Background

Several remediation techniques have been applied especially for the removal of organic contaminants from contaminated sites. Some of these techniques are unsuccessful at complete remediation of heavily contaminated soils (Ferrarese et al. 2008). For this reason, the chemical oxidation method has gained much importance, since this method is rapid and aggressive. The USEPA identifies in situ chemical oxidation (ISCO) as one of the innovative remediation technologies for Brownfield sites (USEPA 2001). ISCO is a process of injecting chemical oxidants into contaminated soils and groundwater to oxidize the contaminants. It is an emerging technology and is applied at various highly contaminated sites. The effectiveness of the reaction depends on the hydraulic conductivity of the soil as well as the distribution of contaminant mass. Generally, the in situ chemical oxidation technique can be applied for the remediation of contaminated sites with unsaturated halogenated volatile organic compounds (VOCs) such as dichloroethylene, trichloroethylene (TCE), tetrachloroethylene (PCE) and benzene, toluene, ethylbenzene, and xylene (BTEX). It can also be used successfully to remediate pesticides, polycyclic aromatic hydrocarbons (PAHs) and PCBs (Dávila et al. 1993).

Persulfate, widely used in many industrial processes, has been recently used as an oxidant for treating many types of contaminants including TCE (Liang and Bruell 2008, Waldemer et al. 2007), polychloroethylene (Dahmani et al. 2006), PAHs (Rivas 2006; Cuyper et al. 2000; Ferrarese et al. 2008), trichlorobenzene (Barbash et al. 2006), lindane (Cao et al. 2008), MTBE (methyl tert-butyl ether) (Huang et al. 2002), and BTEX (Crimi and Taylor 2007). Huang et al. (2002) used the heat-assisted persulfate oxidation for the remediation of MTBE-contaminated groundwater. They reported the main advantage of using persulfate instead of Fenton's chemistry and ozonation; persulfate is more stable and highly soluble under normal subsurface conditions, and persulfate could more effectively transported to the contaminated zones and react with the contaminants. Studies in the literature show that persulfate oxidation is a very effective remediation method for the removal of PAHs. Isosaari et al. (2007) studied on remediation of creosote-contaminated clay by integration of electrokinetics and chemical oxidation. According to their results,

electrokinetically enhanced oxidation with sodium persulfate resulted in better PAH removal (35%) than either electrokinetics (24%) or persulfate oxidation (12%) alone. Ferrarese et al. (2008) used activated sodium persulfate in order to degrade PAHs in old sediment contamination. The remediation ratio was around 90% with activated persulfate for PAH removal, but when they combined the use of activated persulfate and hydrogen peroxide, it led to a better removal of total PAHs. Huang et al. (2005) used thermally activated persulfate oxidation for the degradation of 59 VOCs. They observed that compounds with carbon-carbon double bonds and with benzene rings bonded to reactive functional groups are easy to degrade in used VOCs. Rastogi et al. (2009) used Fe (II)-mediated activation of persulfate for the remediation PCBs in aqueous and sediment systems. They obtained 54% removal for 2-chlorobiphenyl in sediment-slurry phase.

The reactions of persulfate ions with various organic and inorganic compounds have been studied (Huang et al. 2002; Waldemer et al. 2007; Liang and Bruell 2008). Major advantages of the persulfate oxidation as compared to other oxidant systems are fast kinetics, higher stability, and greater transport in the subsurface. Persulfate has less affinity for natural soil organics than the permanganate ion, is highly reactive, and is able to oxidize a wide range of contaminants. Due to its relatively high stability under normal subsurface conditions, persulfate can effectively transport through the subsurface into the contaminated zone. Persulfate ions in the presence of activators are able to oxidize many organic substances into carbon dioxide.

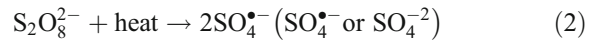
In aqueous solutions, the standard oxidation-reduction potential (E^0) for the reaction



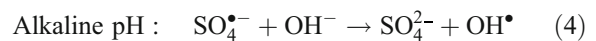
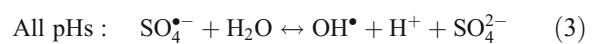
is 2.01 V, which is higher than hydrogen peroxide ($E^0=1.8$ V) and permanganate ($E^0=1.7$ V) but slightly lower than that of ozone at 2.2 V (Block et al. 2004). The resulting strong oxidants can go on to react with contaminants of concern, soil organic matter (SOM), or anions such as chloride or carbonate.

In addition to direct oxidation, sodium persulfate can be induced to form sulfate radicals. Persulfate is a strong oxidant; however, its reaction rates are slow for the more recalcitrant contaminants that need to be activated. There are four primary methods for the

activation of persulfate: heat, metal chelates, hydrogen peroxide, or high pH. The activation of persulfate anions ($\text{S}_2\text{O}_8^{2-}$) by these methods produce sulfate free radicals ($\text{SO}_4^{\bullet-}$), which are very powerful oxidants. One of the mechanisms for production of sulfate free radical is thermal activation as follows:



Persulfate is known to be highly reactive under acidic conditions, but it is also highly reactive at pH values greater than 10 (Block et al. 2004). In a persulfate-water system, under alkaline conditions, sulfate-free radicals and hydroxyl radical ($\bullet\text{OH}$) can be formed via following reactions (Liang et al. 2007):



Selecting the suitable activator depends on the site conditions such as lithology (clay, sand, etc.), hydrogeology, structures, and application method.

3 Materials and Methods

In order to determine the ability of persulfate oxidation for the destruction of PCBs in soils, batch tests were performed on kaolin and glacial till soils using various dosages of oxidant, different activators, and reaction times. The experimental program is summarized in Table 1. For quality control, and to ensure the reproducibility of the results, all tests were performed in duplicates.

3.1 Soils

The soils selected for this investigation were kaolin and glacial till. Kaolin has low organic content and consistent and uniform mineralogy with a low cation exchange capacity. For that reason, kaolin is a good control soil for subsurface soils for laboratory tests because soil heterogeneity is minimized. Glacial till is a highly variable soil with a relatively high organic content, complex mineralogy, and particle size distribution; it is more representative of the soil conditions found at field sites. The composition and properties of kaolin and glacial till are summarized in Table 2.

Table 1 Persulfate oxidation of PCB—experimental program

Soil	Contaminant	Equilibration time (days)	Soil/solution (g/mL)	Na-persulfate concentration (%)	pH	Temperature (°C)
Kaolin/Glacial Till	PCB (44)	1	1:25	30	2, 4, 7.2(K) ^a , 7.6(G) ^a , 9, 12	23
		1		20	12	23
		1		40	12	23
		1		30	12.5	23
		1, 2, 4, 7		30	12	23
		1, 2, 4, 7		30	7.2 (K) ^a 7.6 (G) ^a	35
		1, 2, 4, 7		30	7.2 (K) ^a , 7.6 (G) ^a	45
		1, 2, 4, 7		30	12	45
		1, 2, 4, 7		30	12	45

^aNormal pH values for kaolin and glacial till 7.2 and 7.6, respectively, in the presence of 30% Na-persulfate
K kaolin, *G* glacial till

3.2 Polychlorobiphenyl

The neat PCB congener 2,2',3,5' tetrachlorobiphenyl (97+%), also known as PCB 44, was obtained from Ultra Scientific (N. Kingstown, RI). Sodium persulfate (Na₂S₂O₈; >99% purity) was obtained from FMC (Philadelphia, PA). Reagent grade acetone was

obtained from Fisher Scientific (Fair Lawn, NJ). The clean kaolin and glacial till soils were each spiked with the contaminant (PCB 44) at 50 mg/kg dry basis. The PCB–hexane mixture was subsequently combined with the measured amount of soil and with additional hexane so that the soil–PCB–hexane mixture could be easily blended homogeneously. The mixture was stirred

Table 2 Properties of kaolin and glacial till soils used in this study

Property	Kaolin	Glacial till
Mineralogy	Kaolinite: 100% Muscovite: trace Illite: trace	Quartz: 31% Feldspar: 13% Carbonate: 35% Illite: 15% Chlorite: 4-6% Vermiculite: 0.5% Smectite: trace
Particle size distribution (ASTM D422)		
Gravel	0%	0%
Sand	4%	20%
Silt	18%	44%
Clay	78%	36%
Atterberg limits (ASTM D2487)		
Liquid limit	50%	21.7%
Plastic limit	27.4%	11.7%
Plasticity index	22.6%	10.0%
Specific gravity (ASTM D854)	2.6	2.71
Hydraulic conductivity (cm/s) (ASTM D5084)	1.0 × 10 ⁻⁸	4.1 × 10 ⁻⁸
pH (ASTM D4972)	4.9	8.2
Cation exchange capacity (meq/100 g) (ASTM D9081)	1–1.6	13–18
Organic content (ASTM D2974)	~0	2.8%
USCS classification (ASTM D2487)	CL	CL

with stainless steel spoons in glass beakers to ensure uniform distribution of PCB in the soil. The soil–PCB–hexane mixture was then placed in a ventilation hood for nearly 10 days until the hexane evaporated completely and the contaminated soil was dry. The initial concentration of the PCB 44 in soil samples was determined before starting the experiments.

3.3 Batch Experiments

A series of batch experiments was conducted to determine the ability of persulfate oxidation for destruction of PCB 44 in soil. For each test, 1 g of dry contaminated soil was taken in a 50-mL centrifuge tube. About 10 mL of persulfate solution was added to the tube to produce a soil to solution mixing ratio of 1 g/10 mL. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was used in various concentrations of 10%, 20%, 30%, and 40%. Sulfuric acid was used for pH adjustment. Once the soil sample and persulfate solution were added, they were placed in a mechanical shaker for various reaction time periods (1, 2, 4, and 7 days). At the end of reaction time period, the soil and solution were separated by centrifugation at 6,400 rpm for about 10 min. The soil was then solvent-extracted with acetone for 24 h to determine the residual PCB concentration in soil after the persulfate oxidation. Several solvent extraction ratios (1 g/10 mL, 1 g/20 mL, and 1 g/25 mL) were tried, and the results show that the 1 g:25 mL soil/solvent extraction ratio was the most effective extraction ratio for both kaolin and glacial till soils. The spiked soils were solvent-extracted after the spiking period, and the initial levels of PCB contamination were determined for both soils. In addition, for every batch of tests, the initial PCB concentration was routinely determined using solvent extraction. For kaolin, the initial concentration of PCB in soil was close to the extracted value determined after the spiking period. The soil extracts were analyzed for PCB 44 using gas chromatography (GC) according to US EPA Method 8082. The GC used was an Agilent model 6890 GC (Wilmington, DE) equipped with a microelectron capture detector. All tests were performed in duplicates.

4 Results and Discussion

The degradation of PCB 44 was investigated with persulfate oxidation under high pH, high temperature,

and different reaction times. The PCB degradation means the disappearance and breakdown of PCB 44. The strong oxidant will break up the biphenyl ring and cleave the aromatic ring, resulting in smaller (and non-toxic) organic fragments after oxidation. Complete oxidation will result in the formation of CO_2 , H_2O , and Cl^- (mineralization). The degradation of PCBs using persulfate is primarily a soil phase interaction. PCB 44 (2,2',3,3'-tetrachlorobiphenyl) is a hydrophobic organic compound with a $\log K_{ow}$ of 5.7 and an aqueous solubility of less than 0.1 mg/L. For glacial till that has appreciable soil organic matter (SOM), sorption will result in strong binding of PCB 44 onto glacial till primarily through sorption in the organic matter matrix in addition to adsorption onto soil mineral surface. For kaolin that has no organic matter, adsorption of PCB 44 onto soil occurs through adsorption onto the surface sorption sites of kaolin. Both glacial till and kaolin have large soil surface areas (kaolin has the larger surface) due to the large clay content of both soils. The interaction between the chemical oxidant and the PCB occurs at the soil–water interface, i.e., at the soil surface (true for both kaolin and glacial till). The chemical oxidant also interacts with the SOM of glacial till where most of the PCB 44 is bound in glacial till. For aged soils, the PCB may penetrate the micropores of the porous SOM further than for freshly spiked soils, making it more challenging for the oxidant to destroy the strongly bound PCB. However, even in a freshly spiked soil, a hydrophobic compound such as PCB 44 adsorbs strongly onto the surface of SOM (without extensive penetration and binding of PCB onto SOM, which transpires with the aging of the soil).

4.1 Optimal Persulfate Dosage

The effect of persulfate dosage on PCB degradation was evaluated at pH 12 and room temperature (23°C). As shown in Fig. 1, PCB degradation increased with increasing concentration of persulfate in solution, with the highest PCB degradation obtained for 30% persulfate dosage. When the persulfate dosage increased from 30% to 40%, the PCB degradation decreased. Therefore, the 30% persulfate dosage was selected as the optimum persulfate dosage for the other tests in this study. With temperature activation at 45°C using a dosage of 30% persulfate at pH 12, the PCB degradation was 42% and 34.3% for kaolin and glacial till soils, respectively. For 40% persulfate, the PCB degradation

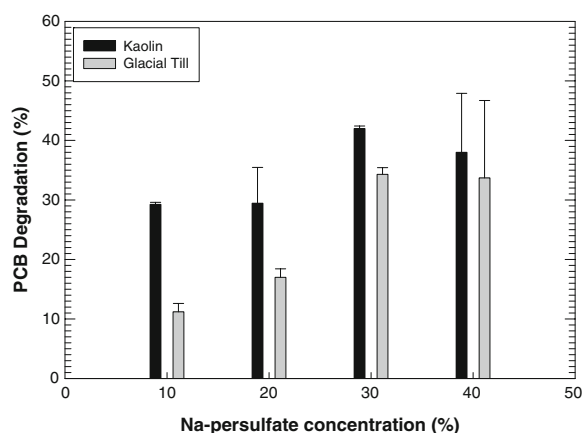


Fig. 1 The effect of persulfate dosage on the degradation of PCB 44

decreased to 38% and 33.7% for kaolin and glacial till, respectively. The lesser PCB degradation obtained with 40% persulfate shows that the reactant cannot effectively oxidize the PCB contaminant in soil without adequate dosage of oxidant, while also too high of an oxidant dose can result in a decrease in oxidant efficiency (Ferrarese et al. 2008).

4.2 Temperature Activation

The effect of temperature on activation of persulfate on PCB oxidation was evaluated by performing tests at room temperature (23°C) and two elevated temperatures (35°C and 45°C). All tests were performed for 24 h using a dosage of 30% sodium persulfate. The initial solution pH was the natural pH of the system with no pH adjustment. The initial pH values were 7.2 and 7.6 for kaolinite and for glacial till soils, respectively. A comparison of the PCB degradation data at 23°C, 35°C, and 45°C is presented in Fig. 2. The data from Fig. 2 show that PCB degradation increased with increasing temperature and that temperature was a strong activator of the persulfate. The highest PCB degradation was obtained at 45°C after 24 h for both soils. The highest PCB degradation was 92.6% and 62.3% for kaolin and glacial till, respectively. As temperature increased from 23°C to 45°C, the PCB degradation increased from 22.5% to 92.6% and from 10% to 62.3% for kaolin and glacial till, respectively. The PCB degradation was lower for glacial till than for kaolin primarily due to the binding of PCB in the organic matter matrix of glacial till. In addition, the more complex mineralogy of the glacial till may have rendered the oxidant less effective

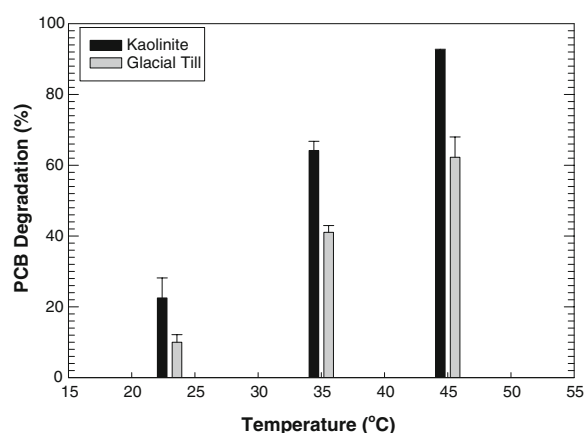


Fig. 2 The effect of temperature activation on persulfate oxidation of PCB 44

for the oxidation of PCB due to reactions with the various surface minerals (which may have altered the oxidation chemistry at the soil–solution interface).

Furthermore, increasing temperature from 35°C to 45°C increased PCB degradation by 28.4% and 21.2% for kaolin and glacial till, respectively. Temperatures greater than 45°C were not considered for this study because the relatively short lifetime of the persulfate at elevated temperatures (e.g., >50°C) will limit the delivery time in contaminated soils in the field (Johnson et al. 2008).

4.3 pH Activation

Persulfate is known to be highly reactive at low pH (<3) and at pHs higher than 10 (Block et al. 2004). Under these pH values, $\text{SO}_4^{\bullet-}$ can react with H_2O or

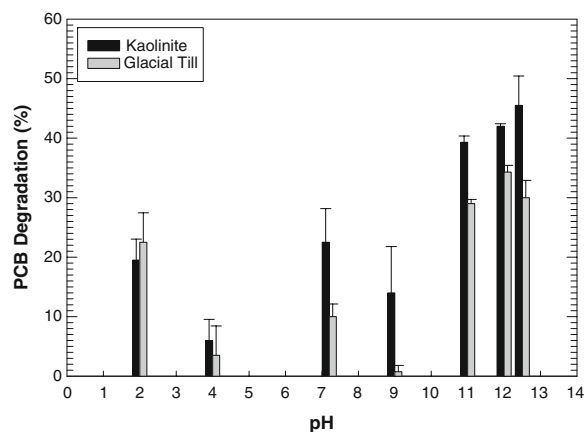


Fig. 3 The effect of pH activation on persulfate oxidation of PCB 44

with OH^- to generate $\cdot\text{OH}$. In this study, low pH (2) and high pH (>10) values were used in order to activate persulfate. The effect of pH activation on the persulfate oxidation of PCB 44 is shown in Fig. 3. All tests were done using 30% persulfate for 24 h. PCB degradation was greater for pH 2 than for pH 4, 7, and 9 because persulfate was active at pH values less than 3. PCB degradation was significantly greater for pH higher than 10. The highest PCB degradation of 45.5% and 34.3% was obtained for kaolin and glacial till, respectively. PCB degradation for pH-activated persulfate oxidation was significantly lower as compared to PCB degradation with temperature activated persulfate oxidation, indicating that activation of persulfate oxidation with higher temperatures (heat) was more effectively than activation with high pH.

Table 3 shows pH changes at the end of the persulfate oxidation process. When the temperature was 23°C, the final pH values were very close to the adjusted initial pH values. However, when the temperature was 45°C, the final pH values decreased significantly for both soils, with final pH values less than 1.0 for kaolin. The results show that, as the persulfate reaction proceeded, the pH of the solution decreased. However, the final pH values were higher for glacial till than kaolin due to the buffering capacity of glacial till. The pH decreased from 12.0 to 4.0 for glacial till at the end of the reaction period.

Table 3 pH changes of the soil after persulfate oxidation testing

Sample	Na-persulfate concentration (%)	Temperature (°C)	Time (day)	Initial pH	Adjusted pH	Final pH
Kaolin	30	23	1	7.19	1.93	1.94
Kaolin	30	23	1	7.06	4.01	2.62
Kaolin	30	23	1	7.07	–	3.11
Kaolin	30	23	1	6.76	8.96	5.80
Kaolin	30	23	1	6.64	12.03	11.76
Kaolin	30	45	1	6.80	–	0.63
Kaolin	30	45	1	6.76	12.06	0.84
Glacial till	30	23	1	7.73	1.94	2.40
Glacial till	30	23	1	7.12	4.33	5.51
Glacial till	30	23	1	7.60	–	6.74
Glacial till	30	23	1	7.19	9.07	6.75
Glacial till	30	23	1	7.21	12.04	6.91
Glacial till	30	45	1	7.16	–	4.02
Glacial till	30	45	1	7.12	12.07	3.42

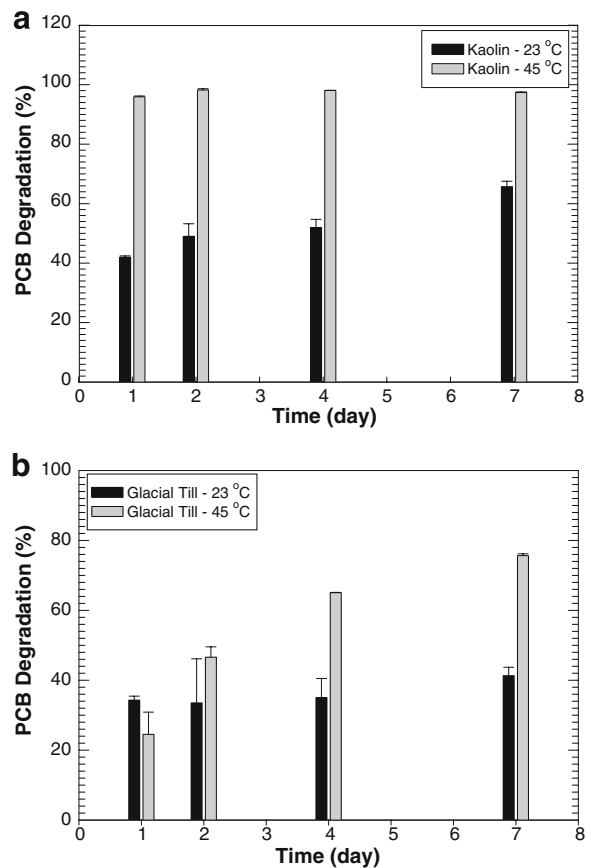


Fig. 4 The effect of reaction time on the degradation of PCB 44: **a** kaolin and **b** glacial till

4.4 Combined Temperature and pH Activation

In order to evaluate maximum removal efficiency, elevated temperature and high pH activators were used together. The tests were done at 45°C and pH 12, with 30% Na-persulfate dosage and reaction time of 1 day. When these two activators were used together, degradation values were 95.9% and 24.5% for kaolin and glacial till, respectively. When these results were compared with only temperature activation results, kaolin had slightly lower (92.6%) and glacial till had higher (62.3%) degradation with elevated temperature activation of persulfate. Furthermore, with only high pH activation (pH 12) and at room temperature (23°C), PCB degraded 42% at kaolin and 34.2% at glacial till. According to these results, the oxidation of PCB can be enhanced by temperature activation effectively.

4.5 Reaction Kinetics

In order to determine the effect of reaction time on the degradation of PCB 44, experiments were conducted with 30% persulfate at pH 12 and at temperatures of 23°C and 45°C for 1, 2, 4, and 7 days (Fig. 4). In addition to these tests, the effect of reaction time was evaluated at natural initial pH at two elevated temperatures of 35°C and 45°C results not shown. As shown in Fig. 4, PCB degradation increased with reaction time, where this increase was more significant for glacial till than for kaolin. The PCB degradation at room temperature (23°C) after 7 days was 65.7% and 41.3% for kaolin and glacial till, respectively. For glacial till, the PCB degradation increased by 51% from days 1 to 7 for glacial till at 45°C. The greatest PCB degradation was obtained after 7 days of oxidation for both soils, where degradation increased to 97.4% and 75.7% for kaolin and glacial till when temperature was increased to 45°C at the end of the 7 days.

5 Conclusions

The optimum persulfate dosage was 30% where the degradation of PCB increased with persulfate dosage up to 30% persulfate, decreasing afterwards with 40% persulfate. The elevated temperature of 45°C was found to be more effective than the high pH of 12 for activation of persulfate oxidation. Temperature activa-

tion was superior to activation at high pH, where the PCB degradation increased from 42% to 92.6% for kaolin and from 34.3% to 62.3% for glacial till. When both activators (temperature and high pH) were used at the same time, the degradation increased only 3.3% for kaolin; however, degradation decreased from 62.3% to 24.5% for glacial till in comparison to only elevated temperature activation after 1 day of reaction. It can be concluded that temperature (45°C) activation alone is adequate to activate persulfate oxidation. The highest PCB degradation was observed at 45°C after 7 days.

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