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## TREATMENT OF CONTAMINATED GROUNDWATER USING CHEMICAL OXIDATION

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### Abstract

Chemical oxidation was evaluated for treatment of a groundwater contaminated with trichloroethylene, acetone, and other organic compounds as measured by the biochemical oxygen demand (BOD) test. Results indicated that maximum contaminant removal was obtained using a combination of hydrogen peroxide, high intensity ultraviolet light, and the addition of tungsten trioxide under acidic conditions.

### Introduction

Chemical oxidation is a promising technology for treatment of groundwater contaminated with low levels of organic compounds. The technology involves the use of powerful chemical oxidizers, such as hydrogen peroxide ( $H_2O_2$ ) and ozone ( $O_3$ ), for destruction of organic contaminants. Typically, ultraviolet (UV) light is added to break down the chemical oxidizers into hydroxyl radicals ( $OH\cdot$ ) which are more powerful oxidizers than the parent oxidizer species (Sundstrum et al. 1989). Jody et al. (1989) concluded that the addition of tungsten trioxide catalyst initiated the degradation of hydrogen peroxide into the hydroxyl radical. Their results indicated that the addition of tungsten trioxide catalyst appreciably increased the removal of hydrazine compounds in an UV/hydrogen peroxide system. The use of hydrogen peroxide rather than ozone has some advantages in that it does not produce a gas stream exiting the reactor and

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introduction into the reactor is simplified because hydrogen peroxide is a relatively stable liquid.

The Lang Superfund Site is located in Pemberton Township, New Jersey. Waste disposal activities at the site have resulted in the contamination of the groundwater with acetone, trichloroethylene (TCE), and other organic compounds as measured by the biochemical oxygen demand (BOD) test. Chemical oxidation using hydrogen peroxide and UV light was evaluated as part of the treatability study phase of the remediation effort. UV light/hydrogen peroxide treatment systems have been successfully used for treatment of groundwaters contaminated with a wide variety of organic compounds (Zappi et al. 1991). Required effluent levels of TCE, acetone, and BOD as set by the regulatory agencies overseeing the cleanup of the site were 2.7 ug/l, 100 ug/l (total ketones), and 3.0 mg/l, respectively.

#### Methods

A composite of groundwater samples from two site observation wells was used as the influent for this study. A photochemical batch reactor with a one liter capacity was used to perform of the UV/chemical oxidation treatability study. An initial hydrogen peroxide concentration of 500 mg/l was used in all of the test runs where UV light was added. The effect of UV light intensity was evaluated by using either a 450 watt medium pressure mercury lamp or a 12 watt low pressure mercury lamp as the UV source. The majority of the spectral output from both of the UV lamps were approximately 254 nm UV wavelengths. Chemical oxidation test runs without UV light addition were performed in one liter volumetric flasks containing an initial hydrogen peroxide concentration of 1,000 mg/l. In some of the runs, tungsten trioxide ( $WO_3$ ) at a concentration of 10 mg/l was used to catalyze the breakdown of hydrogen peroxide into the OH radical (Jody et al. 1989). Catalase was added to each sample to prevent further oxidation from occurring in the sample bottles until chemical analysis could be performed. Acetone and TCE were analyzed using EPA Method SW846-8260 (MS/GC). Standard BOD analytical methods were used for determining reactor influent and effluent BOD. All water sample analyzed in the BOD tests were neutralized to a final pH of 6.5.

### Results

The results of the chemical oxidation runs for acetone, TCE, and BOD are summarized in Tables 1, 2, and 3, respectively. The influent contaminant concentrations varied over the course of the study due to sample instability and variances attributed to sample compositing.

From Table 1, hydrogen peroxide with the addition of the catalyst (Run 1) was not reactive toward the acetone. Runs 2 and 4 indicated that neither the addition of UV light and the catalyst under neutral pH conditions appreciably improve the rate of acetone removal. However, decreasing pH from 6.0 to 2.0 and adding UV and catalyst (Run 3) did result in an 85 percent reduction of acetone. It is suspected that lowering the reaction pH probably increased the solubility of tungsten trioxide which in turn improved catalyst to oxidizer contact frequency in the reactor. All of the UV runs showed an initial increase in acetone after approximately 10 minutes of batch treatment. Run 3 resulted in an approximate fourfold increase in acetone concentrations after 10 minutes. This increase is not surprising because acetone and aldehydes are common intermediates of oxidation reactions involving organic compounds (Li et al. 1985). Run 4 showed a significant build-up of acetone toward the end of the test. This build-up probably occurred due to the formation of acetone during oxidation of the other organic compounds that were present in the groundwater including natural humic and fulvic acids. Run 3 was the most effective of the runs; however, none of the runs were successful in reducing the acetone to within acceptable effluent levels (i.e. 0.1 mg/l total ketones).

From Table 2, Run 1 demonstrated that hydrogen peroxide oxidation with catalyst addition and no UV light addition was not reactive toward the TCE in the groundwater. Both Runs 3 and 4, which included the addition of UV light and catalyst, removed TCE to levels below the analytical detection limit. Run 2, which included neither pH adjustment nor catalyst addition, removed approximately 98 percent of the TCE; however, residual concentrations (J values) of TCE remained throughout the batch run. All of the runs involving UV addition were successful in meeting the target effluent concentrations within 10 minutes of batch treatment. Run 3 was considered the most effective for oxidation of TCE.

As compared to the individual organic compounds, BOD removal was kinetically slower (Table 3). All of the BOD runs indicated that batch treatment times of at least 60 minutes were required to meet the target effluent BOD concentration of 3.0 mg/l. Run 1 in which the 12 watt lamp was used instead of the 450 watt lamp resulted in only a 40 percent reduction in BOD indicating that UV intensity had an appreciable impact on BOD removal. In the case where the pH was reduced (Run 3), a 100 percent reduction of BOD was achieved after 60 minutes of batch treatment. Runs 2 and 4, which were performed without pH adjustment, resulted in almost identical removal rates. This observation further strengthens the hypothesis that lowering the pH increases the solubility of the catalyst which in turn increases the contact frequency of the catalyst with the hydrogen peroxide.

### Conclusions

In conclusion, chemical oxidation using hydrogen peroxide, tungsten trioxide catalyst, high intensity UV light, and pH adjustment to acidic conditions (pH of two) resulted in significant reductions in groundwater contaminant concentrations. Selected variations of the process proved capable of meeting the established limits for TCE (2.7 ug/l) and BOD (3.0 mg/l). TCE was especially reactive using various combinations of oxidized, UV, pH, and catalyst. Although the process resulted in approximately 85 percent reduction in the acetone concentration, the residual acetone concentration (160 ug/l) was greater than established limit (100 ug/l total ketones).

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Table 1  
Acetone Data

Batch Treatment Time (min.)	RUN 1 No UV WO <sub>3</sub> Added pH = 6.0	RUN 2 450 W UV No WO <sub>3</sub> pH = 6.0	RUN 3 450 W UV WO <sub>3</sub> Added pH = 2.0	RUN 4 450 W UV WO <sub>3</sub> Added pH = 6.0
	Acetone Concentration (mg/l)			
0	0.60	1.30	1.20	1.30
10	0.45	2.80	5.00	1.90
20	0.59	2.40	1.20	0.89
30	0.50	2.00	0.46	0.35
40	0.60	2.10	0.22	1.40
50	0.50	1.80	0.16	2.90
60	0.55	1.60	0.18	1.80

Table 2  
Trichloroethylene (TCE) Data

Batch Treatment Time (min.)	RUN 1 No UV No WO <sub>3</sub> pH = 6.0	RUN 2 450 W UV No WO <sub>3</sub> pH = 6.0	RUN 3 450 W UV WO <sub>3</sub> Added pH = 2.0	RUN 4 450 W UV WO <sub>3</sub> Added pH = 6.0
	TCE Concentration (mg/l)			
0	0.65	0.21	0.56	0.34
10	0.74	0.0046J	<0.025	<0.025
20	0.76	<0.025	<0.025	<0.025
30	0.77	0.0044J	<0.010	<0.010
40	0.84	0.008J	<0.005	<0.005
50	0.88	0.0007J	<0.005	<0.005
60	0.92	0.003J	<0.005	<0.005

J: Denotes that the results shown were below the certified analytical QA/QC quantitative limits

Table 3  
Biochemical Oxygen Demand (BOD) Data

Batch Treatment Time (min.)	RUN 1 12 W UV WO <sub>3</sub> Added pH = 6.0	RUN 2 450 W UV No WO <sub>3</sub> pH = 6.0	RUN 3 450 W UV WO <sub>3</sub> Added pH = 2.0	RUN 4 450 W UV WO <sub>3</sub> Added pH = 6.0
	BOD Concentration (mg/l)			
0	140	126	143	143
30	99	43	49	46
60	92	36	0	37

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