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A combined approach to remediate polycyclic aromatic hydrocarbons at a former manufactured gas plant site

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Abstract

A remediation technology consisting of biodegradation and a modified Fenton reaction was developed to degrade mixtures of polycyclic aromatic hydrocarbons (PAHs) at a former manufactured gas plant (MGP) site. The original Fenton reaction (i.e., H_2O_2 + Fe^{2+}) was modified to be biocompatible by using ferric ions and chelating agents such as catechol and gallic acid. The modified reaction was effective in degrading PAHs at near neutral pH and thus was compatible with biodegradation. By the combined treatment of the modified Fenton reaction and biodegradation, more than 98% of 2- or 3-ring hydrocarbons and between 70 and 85% of 4- or 5-ring compounds were degraded in the MGP soil, while maintaining its pH about 6.

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key word: polycyclic aromatic hydrocarbons, manufactured gas plant site, biodegradation, Fenton reaction, chelating agent

1. Introduction

Despite its wide acceptance, bioremediation often has limited applicability when soils are contaminated with complex mixtures of highly hydrophobic aromatic compounds such as occurs with coal tar residues. Therefore, development of new strategies is needed to remediate a wide range of soil contaminants usually found at hazardous waste sites. Hydrogen peroxide, when catalyzed by ferrous ions, generates a strong nonspecific oxidant hydroxyl radical that reacts with most organic compounds at diffusion-controlled rates of 10^7 to 10^{10} $M^{-1}sec^{-1}$. This Fenton reaction has been widely used for the destruction of organic contaminants including (poly)chlorinated aromatic compounds and a variety of herbicides. However, little evidence is available regarding whether the Fenton reaction can completely mineralize organic contaminants in soil, or whether partially oxidized organic compounds are less hazardous than the parent compounds. Therefore, a combined chemical oxidation and biodegradation has a great advantage over either treatment alone in the remediation of organic contaminants in soil. Use of Fenton chemistry in conjunction with biodegradation to destroy PAHs in soil has not been widely studied. Martens and Frankenberg (1) observed an increased mineralization of freshly spiked PAHs after the addition of Fenton's reagent. A recent study, however, reported that the addition of hydrogen peroxide before bioremediation was not effective *in the removal of aged* PAHs *from* a *refinery* soil (2). The present study was thus conducted to test the efficacy and sequence of combined chemical oxidation and biodegradation in the remediation of soils contaminated with mixtures of PAH compounds at a former MGP site.

2. Results and Discussion

2.1. Optimum Condition of Fenton's Reagent. Hydrogen peroxide oxidation was performed in the presence of ferrous sulfate with varying ratios of peroxide to ferrous ions. The greatest degradation of PAHs occurred at the ratio of 10 to 1 (2 g H_2O_2 : 0.2 g $FeSO_4$) in Quakertown silt loam spiked with PAHs (Table 1). At this ratio, more than 90% of initial NAP, FLU, and PHE, and about 85% of PYR were transformed. More importantly, nearly all of the BaP (>96%) was degraded by 24-h Fenton's reagent treatment. However, large amounts of ANT and CHR still remained following the same Fenton reaction. It seems that hydroxyl radical may have substrate specificity although it is known as a nonspecific oxidizer. The amounts of hydrogen peroxide and ferrous ions were also changed, while maintaining the 10:1 ratio, to determine the most efficient condition for the degradation of PAHs. However, no additional benefit was obtained.

Table 1. Effect of hydrogen peroxide oxidation on the degradation of PAHs in the presence of various amounts of ferrous sulfate[a]

PAHs	% Remaining in soil after treatment		
	1:1[b]	5:1	10:1
Naphthalene	35.2	nd[c]	<9.3[d]
Fluorene	76.5	44.5	11.0
Phenanthrene	83.7	48.2	nd
Anthracene	100	75.9	61.9
Pyrene	95.4	51.0	15.5
Chrysene	100	87.0	88.1
Benzo(a)pyrene	84.8	35.3	3.3

[a] Values are the means of five replicate determinations. [b] The ratio of H_2O_2 to Fe^{2+} ;[1:1]=[0.2 g:0.2 g]. [c] Not detected. [d] Detected from only one sample.

2.2. Modified Fenton's Reagent. Although Fenton's reagent was very efficient in removing spiked PAHs from the model soil the same treatment did not degrade high molecular weight PAHs satisfactorily in MGP soil. For NAP, FLU, and PHE, more than 80% removal was attained, but for PYR, CHR, and BaP only 20 to 40% of the initial amounts were degraded. There are two possible explanations for these results: i) PAHs in MGP soil have been aged for over 100 years whereas PAHs in the model soil were freshly added, ii) the amount of total organic carbon is much higher in MGP soil than in the model soil. In an attempt to remove more PAHs from the MGP soil biodegradation in conjunction with Fenton-type oxidation would appear to be a viable option. However, the extremely low pH requirement (optimum pH 2) for Fenton oxidation makes the process incompatible with biological treatment. In addition, this low pH may increase mobilization of heavy metal co-contaminants, and would devastate the soil ecosystem where the reagent is used. In order to overcome these limitations, two approaches were used. In the first approach, the pH of the system was adjusted to approximately 6 by addition of alkali or buffer solutions. However, this approach failed to produce the desired result. Either the pH of the system dropped to pH 2 or the efficiency of the reaction decreased greatly. As a second approach, the Fenton reaction was modified by use of chelating agents (i.e., catechol or gallic acid) and ferric ions instead of ferrous ions. Use of this modified Fenton's reagent allowed for destruction of PAHs (Table 2). The modified Fenton's reagent resulted in a decline in overall performance relative to the original Fenton's reagent, but the pH was maintained at about 6.2.

TABLE 2. Amounts of PAHs remaining in Quakertown silt loam following modified Fenton's reagent treatment

PAHs	% Remaining in soil after treatment[a]	
	+ Catechol	+ Gallic acid
Naphthalene	15.3	11.1
Fluorene	67.2	63.8
Phenanthrene	68.3	70.1
Anthracene	70.8	66.8
Pyrene	58.3	58.9
Chrysene	100	91.1
Benzo(a)pyrene	54.8	49.6

[a] Values are the means of five replicate determinations.

2.3. Combined Chemical Oxidation and Biodegradation. The primary objective in modifying Fenton's reagent was to make the process compatible with biodegradation. The modified Fenton's reagent has been tested in combination with biological treatment using a PAH-degrading bacterial consortium isolated from the same site. Two possible treatment sequences were tested: modified Fenton's reagent followed by biodegradation and biodegradation followed by modified Fenton's treatment. The results in Table 3 show that the sequence in which the combined treatment was carried out had a pronounced effect on the outcome. Biodegradation followed by modified Fenton's treatment was superior to the reverse-order sequence in the degradation of PAHs in MGP soil. Catechol was a slightly better chelator than gallic acid. When the combined treatment sequence was used the extent of degradation of PAHs was similar to that obtained from the same sequence using the original Fenton's reagent. The results show that there are distinct advantages to using a modified form of Fenton's reagent in combination with biodegradation for the remediation of PAHs-contaminated soil.

TABLE 3. Combined effect of hydrogen peroxide oxidation and biodegradation on the removal of PAHs in MGP soil

PAHs	% Remaining in soil after treatment[a]				
	mFR[b] → Bio[c]		Bio → mFR		Bio → FR[d]
	Catechol	Gallic acid	Catechol	Gallic acid	
NAP	5.88	5.67	nd[c]	nd	nd
FLU	31.4	34.5	1.37	2.53	nd
PHE	33.1	38.9	1.23	1.29	nd
PYR	62.2	74.8	14.2	24.6	27.4
CHE	85.9	81.7	34.2	48.7	26.2
BaP	74.1	75.5	32.3	44.1	38.8

[a] Values are the means of five replicate determinations. [b] Modified Fenton reaction was performed for 24 h at room temperature. [c] Biodegradation was performed for four weeks at room temperature. [d] Original Fenton's reagent. [c] Not detected.

3. Conclusion

Our data demonstrate that combined biodegradation with a modified Fenton-type reaction is a promising technology to remediate soils heavily contaminated with mixtures of PAHs. In addition, use of chelating agents eliminates the concerns of an acidified soil environment which is associated with the original Fenton reaction. A treatability study is now being conducted in order to ascertain the most cost-effective manner to deploy this technology in the field.

4. References

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