

REMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBONS POLLUTED SOIL USING FENTON'S REAGENT

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Abstract: The feasibility of Fenton's reagent to remediate Polycyclic Aromatic Hydrocarbons (PAHs) in spiked soil was investigated. PAHs were spiked into soil to simulate contaminated soil. Fenton's reagent and surfactant were very efficient in destruction of PAHs including naphthalene, anthracene, fluoranthene, pyrene, and benzo(a)pyrene from spiked soil. In fact, PAHs were degraded of more than 96% in the solution and the spiked soil.

Keywords: Fenton's reagent, polycyclic aromatic hydrocarbons, spiked soil

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are one class of environmental pollutants that have accumulated due to a variety of anthropogenic activities. They associated with sediments that may become buried and persist until degraded, re-suspended, bio-accumulated, or removed by dredging. PAHs are formed naturally during thermal geologic production and during burning of vegetation in forest and bushfires [1]. However, anthropogenic sources, particularly from fuel combustion, pyrolytic processes and spillage of petroleum products are significant sources of PAHs in the environment. Industrial activities, such as processing, combustion and disposal of fossil fuels, are usually associated with the presence of PAHs at highly contaminated sites.

Currently, a number of physical and chemical approaches have been used for the remediation of contaminated soil [1-2]. Soil washing and soil flushing may be used as an *ex situ* process for the removal of organic, inorganic and radioactive contaminants from soil. Unfortunately, the above approaches are often expensive, inefficient, and may lead to additional problems such as the collection of concentrated organic waste after solvent extraction or air borne pollution after incineration. The limitation of the above process is that it does not collect the

organic contaminants which often are bound to the soil particles. This is where “surfactant-enhancement” is important.

In situ chemical oxidation is an effective way to remediate soil and groundwater contaminated with organic compounds such as polycyclic aromatic hydrocarbons. *In situ* chemical oxidation can be applied using different types of oxidizers such as ozone, Fenton's reagent (hydrogen peroxide and iron salts), potassium permanganate and sodium permanganate [3]. Extreme caution has to be used when performing an *in situ* chemical oxidation with Fenton's reagent and whenever handling a peroxide solution. Therefore Fenton's reagent can mineralize organic contaminants, or weather partially oxidized organic compounds, which pose fewer hazards than the parent compounds, but little evidence is available regarding this matter [4]. In this study, we wished to confirm the observation of Nadarajah *et al.* [5], that the use of surfactants in the Fenton's oxidation improved the removal of anthracene and benzopyrene in simulated contaminated soils. The aim of this study was to use the anionic sulfonate surfactant, Dowfax, and was expected to be more resistant to oxidation under the reaction conditions.

MATERIALS AND METHODS

Chemicals

Standard solution, naphthalene, phenanthrene and anthracene were purchased from Supelco (Sigma Aldrich, Castle Hill, NSW, Australia). Fluoranthene was obtained from Koch-Light (Colnbrook, Bucks, England). Pyrene was purchased from Sigma Chemical Company (St. Louis, MO, USA). Benzo(a)pyrene was purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Ferrous sulfate, hydrogen peroxide, and Dowfax (alkyldiphenyloxide disulfonates) were reagent grade.

Instrumentation

Ultrasonic extractions were performed using a 300 watt Fisher Sonic Dismembrator Model 300 with a 1 inch diameter titanium tip at maximum power. A Buchi R 110 rotavapor was used for reduction of organic solvent volumes. Gas Chromatography/Mass Spectrometer was performed on a Varian Saturn 4D equipped with an on-column injector, a flame ionisation detector, and a model 3390A integrator.

GC-MS analysis of PAHs

Analytical gas chromatography was conducted on a Varian Saturn 4D GC-MS. The GC conditions were an initial temperature 150°C for 2 minutes, and then a temperature ramp from 150°C to 300°C at a rate of 30°C min⁻¹, and then kept at 300°C for a further 7 minutes in order to burn off any involatile organic compounds remaining. The quantification of the PAHs was achieved by comparison with tetradecane as an internal standard. The area of the standard peak and that of the PAHs were determined and their ratio was then used to quantify the concentration of PAHs.

Fenton's oxidations in the liquid phase

A mixture of 1 g 30% H₂O₂ was added cautiously to 0.1 g FeSO₄ in 5 mL water (reagent ratio 10:1) at 0°C. The mixture was immediately dripped into a standard solution of PAHs in 10 mL dichloromethane with vigorous stirring. The standard solution comprised 200 mg L⁻¹ each of naphthalene, phenanthrene, anthracene, fluoranthene, pyrene and benzo(a)pyrene. After 24 h stirring, the aqueous and organic layers were separated and the organic layer was analysed by

GC-MS. To enable quantification of the concentrations of PAHs, the internal standard (tetradecane) was added to the organic phase.

Solutions of 1 g 30% H₂O₂ in 5mL water and 0.1 g FeSO₄ in 5mL water were dripped simultaneously into 10 mL of the standard solution with vigorous stirring. The pH was measured as 4.0. The phases were then separated and the organic layer was analysed by GC-MS. The use of surfactant was then studied. The procedure was the same as above, but before the standard solution was treated with the reagents, surfactant was added with prior stirring for 24 h.

Preparation of spiked soil, and Fenton's oxidations

A standard solution, calculated to give 200 mg L⁻¹ each of naphthalene, phenanthrene, anthracene, fluoranthene, pyrene and benzo(a)pyrene in 50 mL dichloromethane was poured onto 50 g uncontaminated sandy soil in a covered glass flask. This soil was left overnight in the fumehood and the solvent was then rotary evaporated. The spiked soil was stored in the refrigerator before use (two weeks). Surfactant was added to the spiked soil, and the mixture was stirred for 24 h. The peroxide and Fe²⁺ solutions were dripped in simultaneously to a 10 g sample of the spiked soil and stirring was continued for 24 h. The phases were separated and the organic layer and water layer were then analysed using GC-MS.

RESULTS AND DISCUSSION

PAH oxidation in solution

In the first investigation, the anionic surfactant Dowfax was added to a standard solution of PAHs in dichloromethane, and after 24 h, solutions of H₂O₂ and FeSO₄ in a molar ratio of 10:1 were then dripped simultaneously into this mixture with vigorous stirring. The low pH established by the excess of ferrous sulfate was close to that recommended by Fenton [6]. After 24 h the organic phase was analysed by GC-MS, using the internal standard tetradecane and pre-established response ratios.

The analyses showed that Fenton's reagent preferentially oxidised higher molecular weight rather than smaller molecular weight PAHs (Table 1). In addition, the chromatogram (Fig. 1) also showed several new peaks which were oxidation products, and were shown to be dibenzofuran from phenanthrene and 9,10-anthracenedione from anthracene, as determined by mass spectral comparisons. Fenton's reagent was clearly very efficient in destruction of PAHs including naphthalene, anthracene, fluoranthene, pyrene and benzo(a)pyrene in the two phase solution.

Table 1: Amounts of PAHs remaining in the solution after treatment with surfactant and Fenton's reagent.

Compounds	% PAHs remaining in the solution
Naphthalene	42
Acenaphthylene	5.9
Acenaphthene	2.8
Fluorene	33
Phenanthrene	72
Anthracene	not detected
Fluoranthene	11
Pyrene	7.7
Benz(a)anthracene	13
Chrysene	5.1
Benz(k)fluoranthene	8.6
Benzo(a)pyrene	not detected

In a preliminary study, the oxidising agents were premixed at low temperature, and then reacted with the PAH solution. While this would be operationally easier on site, it is intrinsically more dangerous as some reaction mixtures boiled, and this procedure was therefore discontinued. Any change brought about by the use of surfactant was then studied. The procedure was the same as above, but before the solution was treated with Fenton's Reagent, surfactant was added to the PAH solution with stirring for 24 h.

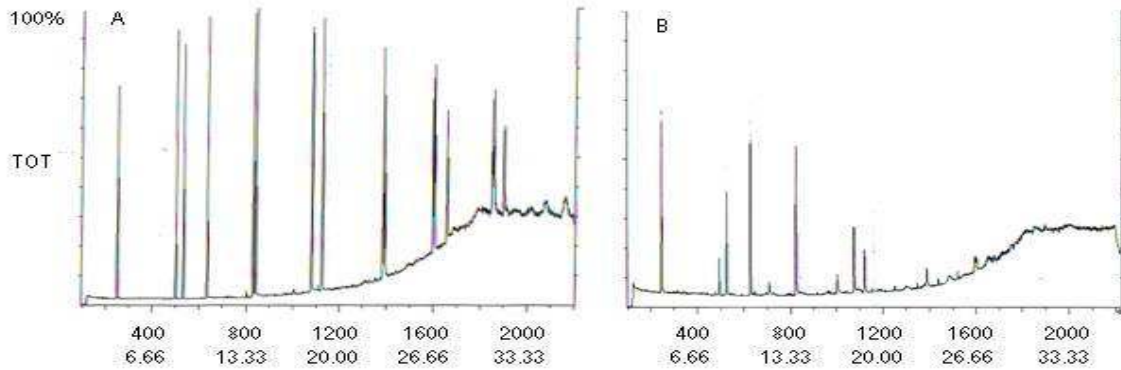


Fig. 1: Chromatogram of standard solution of PAHs before (A) and after (B) oxidation.

Table 2: Amounts of PAHs remaining in solution after treatment with surfactant and Fenton's reagent

Compounds	% PAHs remaining ^a in the solution after		
	Surfactant(S) (B)	Fenton's reagent(FR) (C)	S+FR (D)
Naphthalene	~100	87	8
Anthracene	~96	75	not detected
Fluoranthene	~100	75	not detected
Pyrene	~100	24	not detected
Benzo(a)pyrene	~100	24	not detected

^aall values are average of duplicate analyses, regarded as accurate to +/- 5%.

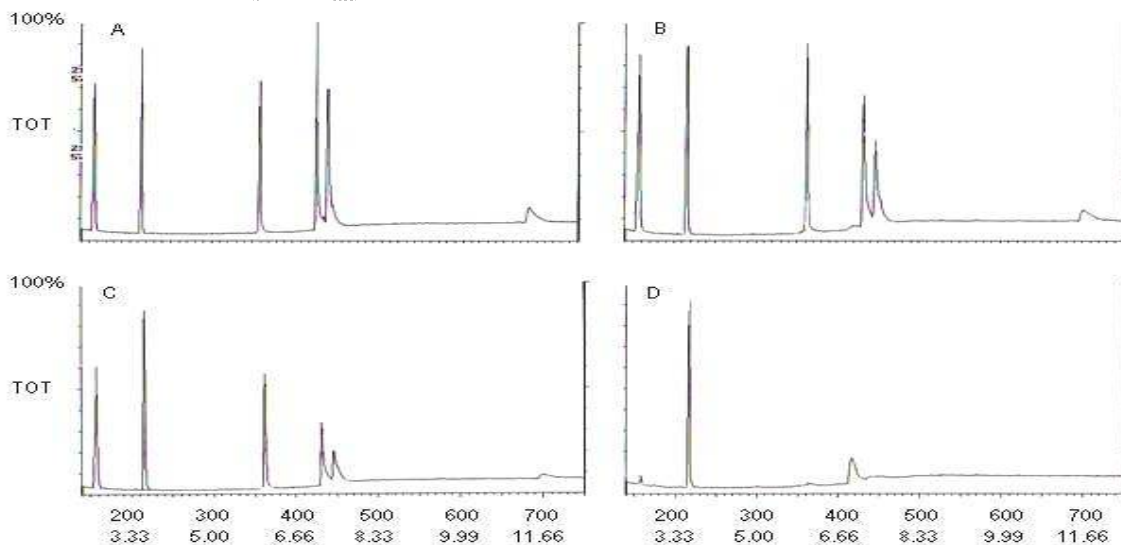


Fig. 2: Chromatogram of standard solution PAHs before treatment (A), after surfactant (B), oxidation (C), surfactant and oxidation treatment (D).

As would be expected, there was no decrease in the PAH level (Table. 2 and Figs. 2A, 2B) on surfactant treatment alone. Oxidation with Fenton's reagent alone was less efficient than in the presence of a surfactant, but was mechanistically informative. In particular, it supports the work of Lee *et al.* [4], who predicted that ease of PAH oxidation would follow the frontier electron densities, which generally are higher for the larger molecules. Their experimental work used a different solvent system, but the results were essentially the same as found here. However, after combination of surfactant and Fenton's agent, all the PAHs had undergone total oxidation (Figs. 2A, 2D), although the smallest hydrocarbon, naphthalene, remained to the extent of 8%. The preferential oxidation of the larger PAHs under these ideal conditions is very important, as our plan to have sequential chemical, then biochemical, oxidation required that the former process reduce the burden of the larger molecules significantly. Fig. 2D showed only one new recognisable peak, identified as an oxidation product of anthracene, 9,10-anthracenedione, which again would be anticipated from the work of Lee *et al.* [4]. It appears that other PAHs have been more extensively oxidised

Fenton's oxidation of PAHs on soil

The next phase of this study attempted to compare the efficiency of oxidation by Fenton's reagent of PAHs adsorbed on soil with that observed above in solution. The "contaminated soil" was obtained by adding a standard solution containing 200 mg L⁻¹ each of naphthalene, phenanthrene, anthracene, fluoranthene, pyrene and benzo(a)pyrene to uncontaminated dry soil at pH 3. This total load (1200 mg L⁻¹), was close to the average level of contamination to be encountered at the gasworks site.

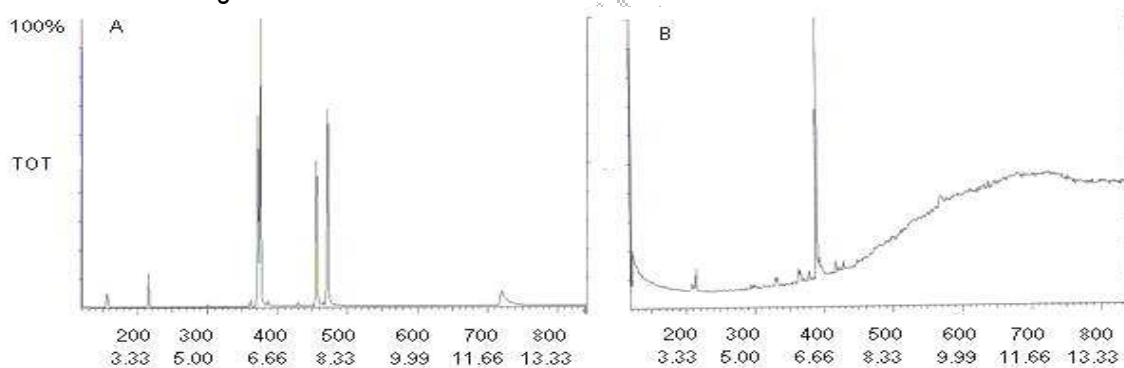


Fig. 3: The chromatograph of GC-MS before (A) and after (B) Fenton's treatment of PAHs-contaminated soil (organic layer).

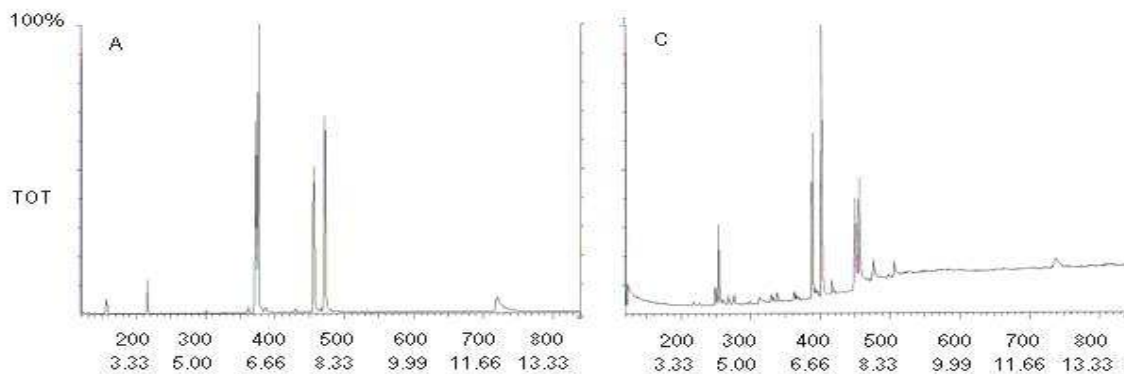


Fig. 4: The chromatograph of GC-MS before (A) and after (C) Fenton's treatment of PAHs-contaminated soil (aqueous phase).

As shown in the chromatograms (Fig. 3), the effectiveness of the Fenton's reagent with the PAH contaminated soil was the same as its effectiveness noted with the standard solution, above. Almost no PAHs remained in the soil after Fenton's reagent treatment: oxidation was extremely effective. However, it was clear that PAH removal in this case was not solely due to oxidation. The aqueous phase after oxidation also contained a considerable concentration of PAHs (Fig. 4A, 4C). It is believed that PAHs were not totally sorbed to the soil because only 2 weeks contact with the soil had been possible.

CONCLUSION

The studies of solution and soil containing PAHs clearly showed that the use of surfactant and Fenton's reagent to oxidize PAHs is far superior. It was indicated by the fact that more than 96% of PAHs were degraded in the solution and in the spiked soil.

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