

APPLICATION OF FENTON'S REAGENT ON REMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SPIKED SOIL

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ABSTRACT

Problem associated with Polycyclic Aromatic Hydrocarbons (PAHs) contaminated site in environmental media have received increasing attention. To resolve such problems, innovative in situ methods are urgently required. This work investigated the feasibility of using Fenton's Reagent to remediate PAHs in spiked soil. PAHs were spiked into soil to simulate contaminated soil. Fenton's Reagent ($H_2O_2 + Fe^{2+}$) and surfactant were very efficient in destruction of PAHs including naphthalene, anthracene, fluoranthene, pyrene, and benzo(a)pyrene from spiked soil. It was indicated by the fact that more than 96% of PAHs were degraded in the solution and the spiked soil.

Keywords: Environmental, Fenton's Reagent, Polycyclic Aromatic Hydrocarbons, and Spiked soil.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are one class of environmental pollutants that have accumulated due to a variety of anthropogenic activities. The term PAH generally refers to hydrocarbons containing three or more fused benzene rings in linear, angular or cluster arrangements [1]. The stability of PAHs is related to the arrangement of the benzene rings in the structure. PAHs with an angular arrangement tend to be more stable than PAHs with a linear arrangement [2]. PAHs are hydrophobic compounds and their persistence in the environment is due to their low water solubility [3]. They thus rapidly become associated with sediments, and may become buried and persist until degraded, re-suspended, bio-accumulated, or removed by dredging. Generally, PAH solubility decreases with an increase in number of fused benzene rings. Volatility also decreases with an increase in the number of fused rings [4].

PAHs are ubiquitous environmental contaminants which have been detected in a wide variety of environmental samples, including air, soil, sediments, water, oils, tars and foodstuffs. The major source of PAHs is from the combustion of organic material. PAHs are formed naturally during thermal geologic production and during burning of vegetation in forest and bushfires [2]. PAHs and their alkyl homologues may also be derived from biogenetic precursors during early diagenesis [5].

However, anthropogenic sources, particularly from fuel combustion, pyrolytic processes and spillage of petroleum products [6], 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. For example, at an oil refinery, PAH concentrations may range up to 1.79×10^6 ng PAH/g of

soil. PAHs also represent approximately 85-90% of creosote constituents.

Currently, a number of physical and chemical approaches have been used for the remediation of contaminated soil. Soil washing and soil flushing may be used as an *ex situ* process for the removal of organic, inorganic and radioactive contaminants from soil. In addition, solvent and chemical extractions may be used to remove contaminants from soil, sediment or water. These methods are based on equilibrium separation techniques and are commonly used in the chemical industry. A number of thermal techniques have been developed for treating contaminated soil, which can involve either desorbing the contaminant from a matrix or thermally destroying organic compounds. Chemical treatments include technologies that use reagents to destroy or chemically modify contaminants by other than pyrolysis or combustion. Some of the physical and chemical processes may be used as stand-alone techniques or in combination for cleaning up contaminated soils. 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. Chang *et al* investigated the possibility of using surfactants to extract phenanthrene on spiked sand in a batch system [7]. They used six surfactants which were both non-ionic and ionic surfactants. This study demonstrated that the surfactants allowed the efficient extraction of phenanthrene under optimum conditions at 30 minutes, 125 rpm, and surfactant concentrations of 4%, and the ionic surfactant resulted in similar effects to the non ionic ones under the same operating parameters. In

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2002, An *et al* used perfluorinated surfactant (PFS) for solubilization of PAHs because of their chemical and thermal stability [8]. This study focused on PAH and PFS interactions, particularly for the solubilization of PAHs by PFS micelles. The results showed that solubilities of molecular oxygen and PAHs in the micellar solutions depended linearly on the surfactant concentration, and the surfactant solubilized significant amounts of PAHs. Other researchers studied the solubilization of the PAHs in solutions of nonionic surfactants, Tween 20, Tween 80, Triton X 100, Brij 35 and Brij 58 in considerable detail [9]. Based on these studies, both PAH-PAH interactions and micelle-PAH interactions should be taken into account when predicting the concentrations of PAH mixtures in micellar surfactant solutions. This should be done because PAH-PAH interactions can influence aqueous solubility, while micelle-PAH interactions can affect the distribution of PAHs in the micellar phase, which may change as the mixture composition changes. Yeom *et al* studied the effect of nonionic polyoxyethylene (POE) surfactants on the solubilization rate of individual PAHs from a weathered, coal tar-contaminated soil obtained from a manufactured gas plant (MGP) site [10].

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 (H_2O_2) and iron salts (Fe^{2+})], potassium permanganate and sodium permanganate [11]. The addition of Fenton's reagent at low pH to generate hydroxyl radicals ($OH\bullet$) readily oxidizes contaminants such as fuel oils and PAHs.



The reaction is very fast and much more efficient than H_2O_2 alone [12]. The chemicals used for this technology are inexpensive and abundant, making this approach very popular for remediation. The technology, however, is limited by the interference of subsurface impurities. Soil containing carbonate, bicarbonate and organic matter creates competing reactions that hinder the success of the treatment.

Many researchers have used Fenton's Reagent to oxidize PAHs in water and soils. Kawahara *et al* treated slurries of contaminated soil with Fenton's Reagent and they found that twelve of the fourteen PAHs showed consistent increase (13 to 56%) in extractibility from soil after one hour of contact with the reagent [12]. Only acenaphthylene and acenaphthene showed no increase in extractibility. Electron exchange by structural iron in the clay mineral and the swelling of clay layers is proposed as the release mechanism of tightly held PAHs (Kawahara and coworkers). This study suggested that this treatment would be applicable in soil remediation. In

addition, they found that the analytical method employed for PAHs might provide inaccurate results in some situations. Beltran *et al* studied the oxidation of PAHs by Fenton's reagent in water. This study showed that Fenton's oxidation results in total degradation of PAHs such as fluorene, phenanthrene, and acenaphthene in water in a few minutes provided ferrous ion and hydrogen peroxide are fed to the polluted water at appropriate concentrations [13]. Both reagents play a double role during oxidation since at low concentrations they act as initiators of hydroxyl radicals but at high concentration they slow the oxidation rate. Lindsey and Tarr investigated the formation of hydroxyl radicals in the aqueous iron-hydrogen peroxide reaction [14]. The rate and time dependent concentration of hydroxyl radical formation were determined in pure water, in aqueous fulvic acid (FA) and humic acid (HA) solutions, and in natural surface waters. HA and FA also reduced hydroxyl radical formation under most conditions, although increased radical formation was observed with FA at certain pH values. Lee *et al* predicted Fenton oxidation positions in PAHs according to the corresponding frontier electron density [15]. This study used five recalcitrant PAHs in ethanol and oxidation products were identified by GC-MS and their oxidation positions were compared to those predicted by frontier electron density. Oxidation products were quinones, which were identified for each PAH. All oxidation positions for quinone products of acenaphthylene, anthracene, benz(a)anthracene, and benz(a)pyrene corresponded with predicted positions in which the frontier electron density was high, but fluorene was an exception. The effectiveness of oxidation by Fenton's reagent in removal of PAHs from soil was improved by adding ethanol before Fenton treatment [15].

Fenton's reagent produces an extremely exothermic reaction and, in some cases, can boil water out of the soil. 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.

The extremely low content of plant derived organic material in the target soil would thus facilitate the oxidation of the PAHs present. In addition, we wished to confirm the observation of Nadarajah that the use of surfactants in the Fenton's oxidation improved the removal of anthracene and benzopyrene in simulated contaminated soils [16]. While Reddy has investigated the possibility of utilising the natural iron content of the soil by making it available electrochemically, the size of the ultimate target area precluded such a consideration [17]. Kanel *et al* have

shown, in model systems, that goethite (Fe_2O_3) can be an alternative to ferrous sulfate in such oxidations [18].

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.

EXPERIMENTAL SECTION

Material

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 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.

Procedure

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 to 300 °C at a rate of 30 °C /min, 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 30% H_2O_2 (1 g) and water (5 mL) was added cautiously to a solution of FeSO_4 (0.1 g) in water (5 mL) (reagent ratio 10:1) at 0 °C. The mixture was immediately dripped into a standard solution of PAHs in dichloromethane (10 mL) with vigorous stirring. The standard solution comprised 200 ppm each of naphthalene, phenanthrene, anthracene, fluoranthene and benzo(a)pyrene. After 24 h stirring, the aqueous and organic layers were separated and the organic layer was analysed by GCMS. To enable quantification of the

concentrations of PAHs, the internal standard (tetradecane) was added to the organic phase.

Solutions of 1 g 30 % H_2O_2 / 5 mL water and 0.1 g FeSO_4 / 5 mL water were dripped simultaneously into 10mL of the above standard solution with vigorous stirring. The pH was measured as 4.0. The phases were then separated and the organic layer was analysed by GCMS.

The use of surfactant was then studied. The procedure was the same as in 2 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 ppm naphthalene, 200 ppm phenanthrene, 200 ppm anthracene, 200 ppm fluoranthene, 200 ppm pyrene and 200 ppm benzo(a)pyrene in dichloromethane (50 mL) 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 as in 3 above, and the mixture was stirred for 24 h. The peroxide and Fe^{2+} 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 GCMS.

RESULT AND DISCUSSION

PAH oxidation in solution

In the first investigation, the anionic surfactant Dowfax (alkyldiphenyloxide disulfonates) was added to a standard solution of PAHs in dichloromethane, and after 24 h, solutions of H_2O_2 and FeSO_4 in a molar ratio of 10:1 were then dripped simultaneously into this mixture with vigorous stirring. The low pH established

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

Compounds	% PAHs remaining in the solution on treatment with surfactant and FR
Naphthalene	42
Acenaphthylene	5.9
Acenaphthene	2.8
Fluorene	33
Phenanthrene	72
Anthracene	0 (not detected)
Fluoranthene	11
Pyrene	7.7
Benz(a)anthracene	13
Chrysene	5.1
Benz(k)fluoranthene	8.6
Benzo(a)pyrene	0 (not detected)

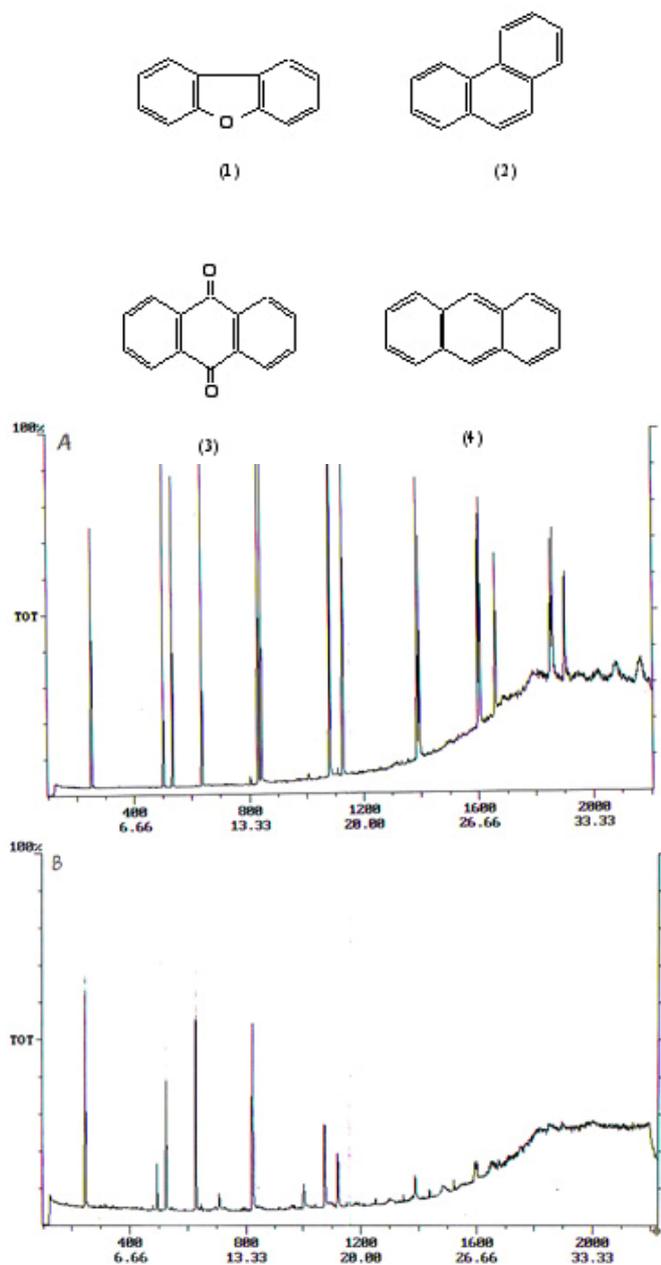


Fig 1. Chromatogram of standard solution of PAHs (a) before and (b) after oxidation

by the excess of ferrous sulfate was close to that recommended by Fenton. After 24 h the organic phase was analysed by GCMS, 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 (1) from phenanthrene (2) and 9,10-anthracenedione (3) from anthracene (4), as determined by mass spectral comparisons.

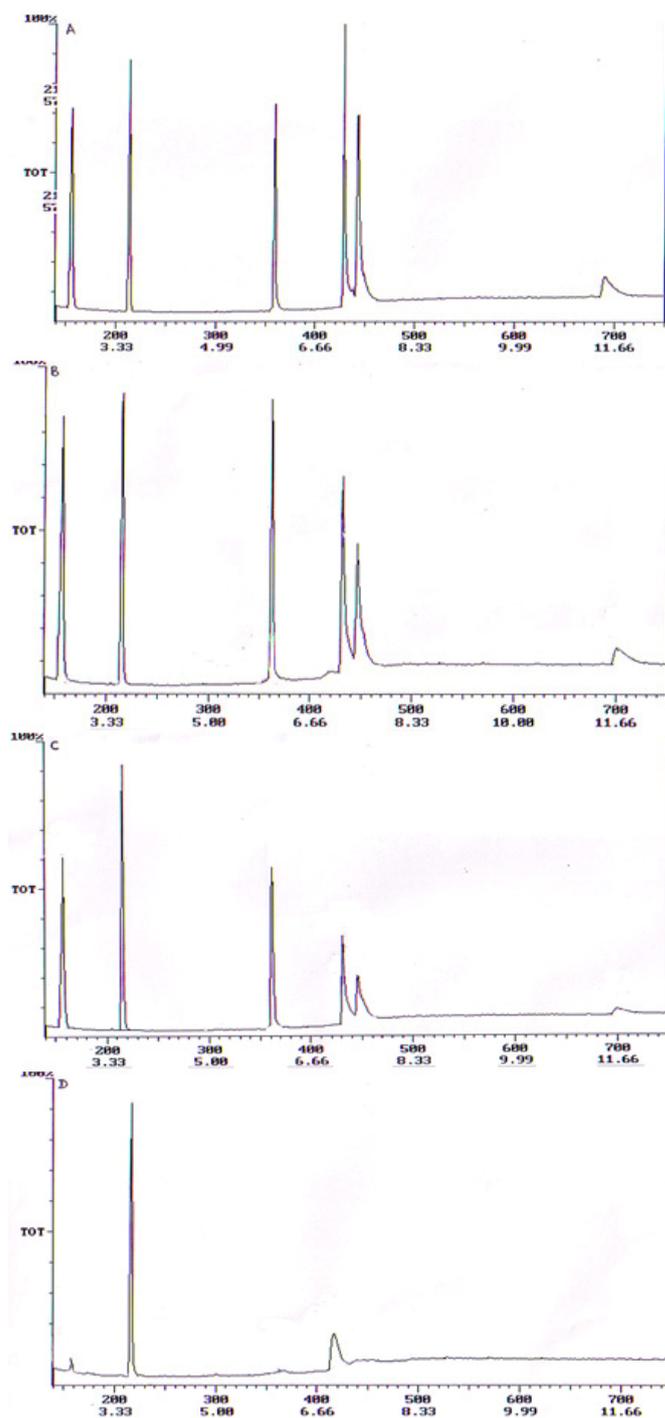


Fig 2. Chromatogram of standard solution PAHs (a) before treatment, (b) after surfactant, (c) oxidation, (d) surfactant and oxidation treatment.

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.

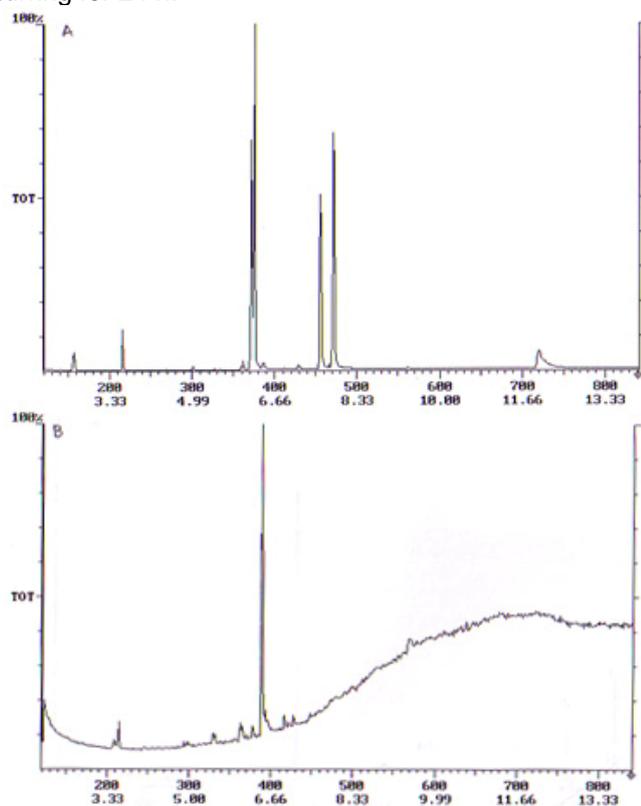
Table 2. Amounts of PAHs remaining in solution after treatment with surfactant and Fenton's Reagent.

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	nd
Fluoranthene	~100	75	nd
Pyrene	~100	24	nd
Benzo(a)pyrene	~100	24	nd

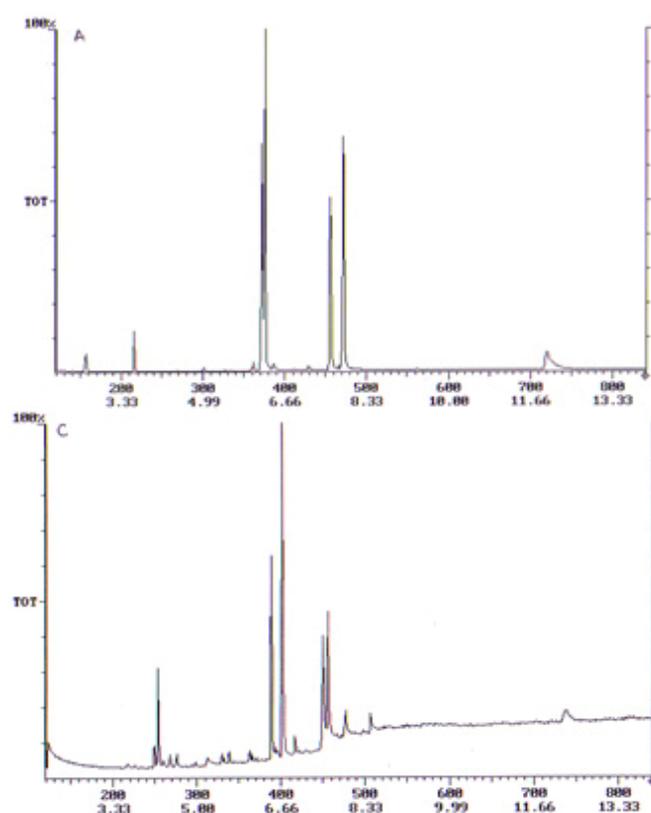
^a all values are average of duplicate analyses, regarded as accurate to +/- 5%; nd not detected

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 3.** The chromatograph of GC-MS (a) before and (b) after Fenton's treatment of PAHs- contaminated soil (organic layer).

As would be expected, there was no decrease in the PAH level (Table 2, Fig. 2(a) and (b)) 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 [19], 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 (Fig 2(a) and (d)), 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 2(d) showed only one new recognisable peak, identified as an oxidation product of anthracene, 9,10-anthracenedione (3), which again would be anticipated from the work of Lee [19]. It appears that other PAHs have been more extensively oxidised

**Fig 4.** The chromatograph of GC-MS (a) before and (b) after Fenton's treatment of PAHs-contaminated soil (aqueous phase).

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 ppm naphthalene, 200 ppm phenanthrene, 200 ppm anthracene, 200 ppm fluoranthene, 200 ppm pyrene and 200 ppm benzo(a)pyrene to uncontaminated dry soil at pH 3. This total load (1200 ppm), was close to the average level of contamination to be encountered at the gasworks site. 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 4(a) and (c)). It is believed that PAHs were not totally sorbed to the soil because only 2 weeks contact with the soil had been possible.

CONCLUSION

In 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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