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THE CHEMICAL PROCESSES OCCURRED IN THE REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) ON THE SOIL BY FENTON'S REAGENT

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ABSTRACT

The chemical processes occurred in the decomposition of polycyclic aromatic hydrocarbons (PAHs) in the soil by Fenton's Reagent have been investigated. The aim of this work was to determine the intermediate products of PAHs oxidation by Fenton's Reagent. The organic material after oxidation was separated into neutral and acidic fraction. Acidic compounds were converted to methyl esters by reaction with diazomethane, and were analysed by using GC/MS. The result showed that a single Fenton's oxidation cycle was clear a reduction occurred, typically mono- and dicarboxylic acids, remain, and would in themselves continue to pose an environmental hazard unless removed by further oxidation. The neutral material contained PAHs as well as oxidized product.

KEYWORDS: PAHs, soil, Fenton's Reagent, and GC/MS



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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are compounds which contain two or more benzene rings in linear, angular or cluster arrangements as an environmental pollutants that have accumulated due to a variety of anthropogenic activities¹. 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 arrangement². PAHs are hydrophobic compounds and their persistence in the environment is due to their low water solubility³. They thus rapidly become associated with sediments, and may become buried and persist until degraded, resuspended, bioaccumulated, or removed by dredging. Many PAHs are carcinogenic and therefore they are of significant concern as environmental contaminant¹. Numerous studies have indicated that one-, two- and three-ring compounds are acutely toxic¹, whereas higher molecular weight PAHs are considered to be genotoxic⁴. Three-ring and higher PAHs can be active as tumour initiators, complete carcinogens or cocarcinogens. Currently, a number of physical and chemical approaches have been used for the remediation of contaminated soil⁵. *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 (H₂O₂) and iron salts (Fe²⁺)], potassium permanganate and sodium permanganate⁵. The addition of Fenton's reagent at low pH to generate hydroxyl radicals (OH•) readily oxidizes contaminants such as fuel oils and PAHs. (H₂O₂ + Fe²⁺ → OH• + OH⁻ + Fe³⁺) The reaction is very fast and much more efficient than H₂O₂ alone⁶. The chemicals used for this technology are inexpensive and abundant, making this approach very popular for remediation.

Many researchers have used Fenton's Reagent (FR) to oxidize PAHs in water and soils. In 1995, Kawahara and coworkers⁶ treated slurries of contaminated soil with Fenton's Reagent and they found that twelve of the

fourteen PAHs showed a consistent increase (13 to 56%) in extractibility from soil after one hour of contact with the reagent. 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 PAHs⁶. 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 and coworkers⁷ 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. 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. The work in this study involved only one oxidation cycle, hence any oxidation products characterised herein would have formed early in the process.

MATERIALS AND METHODS

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 surfactant were reagent grade. 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 3390 integrator. The GC conditions were a temperature 150°C to 300°C for 2 minutes, and then was modified to a temperature ramp from 150°C to 300°C at a ramp 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.

(i) Preparation of diazomethane

a. Precursor of diazomethane nitrosomethylurea

1.5 mole of methylamine hydrochloride and 5 moles of urea were dissolved in 400 mL of water and the solution was boiled under reflux for 3 hr. After the addition of 1.6 mole of sodium nitrite, the solution cooled to -10 °C was run slowly with string into a mixture of 600 g of ice and 110 g of concentrated sulphuric acid cooled with a mixture of ice and salt. The nitroso compound separating out was filtered off and washed with ice-water.

b. Diazomethane ($CH_2=N=N$)

0.1 mole of nitrosomethylurea was added in small portions to layer of 100 mL of ether above 35 mL of cooled 50% potassium hydrochloride in an Erlenmeyer flask. 10 min after the addition of the last portion, the ethereal diazomethane solution was poured off and was dried for 3 hr over a little solid potassium hydrochloride.

(ii) Oxidation and analysis of soil for oxidation intermediates

Samples of soil (100g), taken from the most contaminated part of the gasworks site, were first homogenised by agitation for 24 h. A portion (10 g) was stirred overnight with Fenton's reagent in the presence of Dowfax surfactant. A second portion (10g) was extracted with dichloromethane by ultrasonication in the usual way⁸. The total dichloromethane extract after oxidation was shaken with 10% aqueous sodium hydroxide (3x10 mL), the organic phase dried over MgSO₄, and evaporated to give the neutral fraction (24 mg). The aqueous extracts were acidified by addition of 5M HCl, and extracted with dichloromethane (3x10 mL). The dried

extracts were evaporated to give the acidic fraction (4 mg). The acidic fraction was dissolved in ether (10 mL) and treated with excess of the standard ethereal diazomethane solution (20 mL) at 0°C for 2h. Excess reagent and solvent were removed by rotary evaporation, and the fraction was analysed by GC/MS.

RESULTS AND DISCUSSIONS

Fenton's reagent (FR) 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. Occurring of decomposition after soil was treated with Fenton's Reagent ultimately leads to the conversion of all organic material to carbon dioxide ("mineralization"). However, it is not known to what extent this process has occurred in this work, which has concentrated on the analysis of the PAHs. The work of Lee⁸ has shown that the primary oxidation products of PAHs are probably quinones, which would undergo subsequent oxidation to dicarboxylic acids. These could be expected to be more water soluble, smaller in size and therefore less toxic than their parents PAHs. La Nafie⁹ also reported the isolation of quinone oxidation intermediate. The work in this section involved only one oxidation cycle, hence any oxidation products characterised herein would have formed early in the process. In order to determine what types of intermediates were formed, the organic material after oxidation was separated into neutral and acidic fractions. Acidic compounds were converted to methyl esters or ethers by reaction with diazomethane, and were analysed by using GC/MS. GC/MS analysis of the methylated acidic fraction showed the presence of methyl esters (Figure 1).

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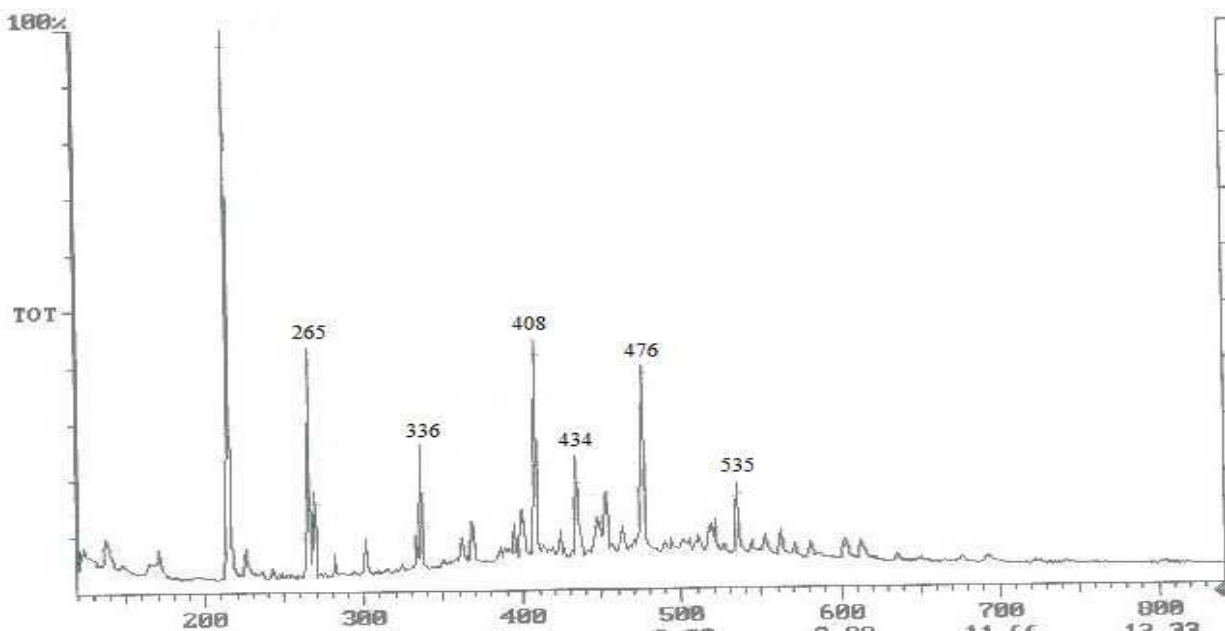
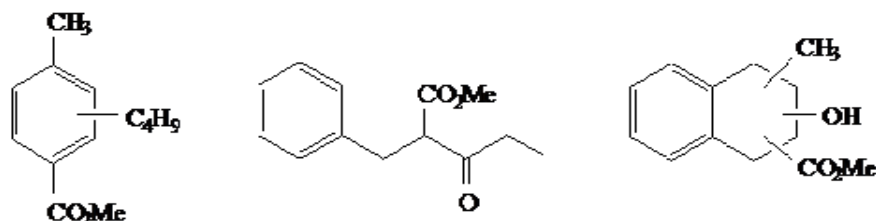
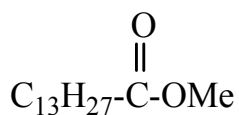


Figure 1
The chromatogram of methyl esters

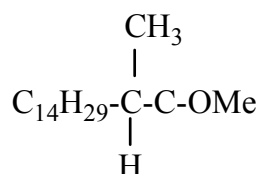
The numbers showed on the peaks in the chromatogram (Figure 1) were the molecular weight of methyl esters which the mass spectra of these compounds showed molecular ion peaks at m/z 265, 336, 408, 434, 476, and 535. Molecular ion peak at $m/z = 265$ corresponded to one of the three methyl esters below, indicating partial oxidation of methylated polycyclic materials,



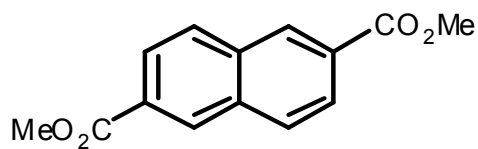
Molecular ion peak at $m/z = 336$ corresponds to the aliphatic ester of tetradecanoic acid. It is possible that this compound is formed by oxidation of petroleum based hydrocarbons, or, less likely, by partial oxidation of the internal standard, tetradecane.



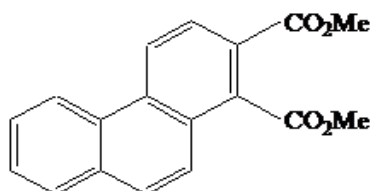
Molecular ion peak at $m/z 408$ is indicative of the presence of aliphatic compounds, and is of the type below, again it is probably oil derived, and suggests that the above compound is likewise.



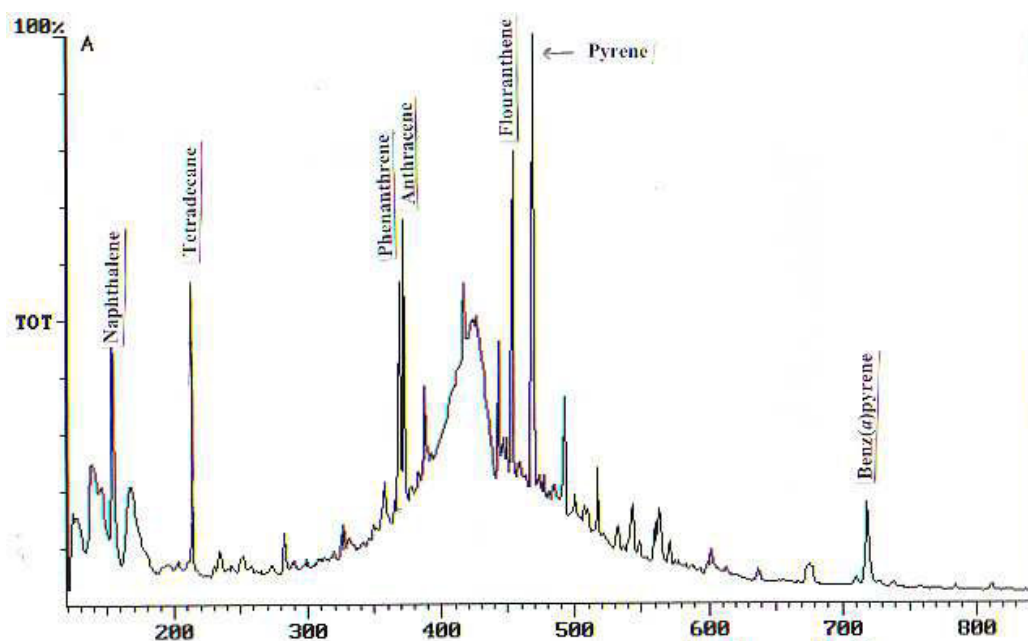
Molecular ion peak at m/z 434 could be the naphthalene diester shown below, suggesting its origin from a tri- or tetracyclic hydrocarbon.



Molecular ion peak at m/z 476 is further evidence for the presence of aliphatic compounds and corresponds to $C_{14}H_{29}-C-OOCH_3$. Molecular ion peak at m/z 535 corresponds to the structure shown below, and again is consistent with oxidation of a quinone precursor.



The above compounds show that oxidation of the most highly contaminated site with Fenton's reagent is not complete after the first cycle. The neutral material contained PAHs as well as oxidized products. The chemical make up of the neutral organic load is shown below (Figure 2).



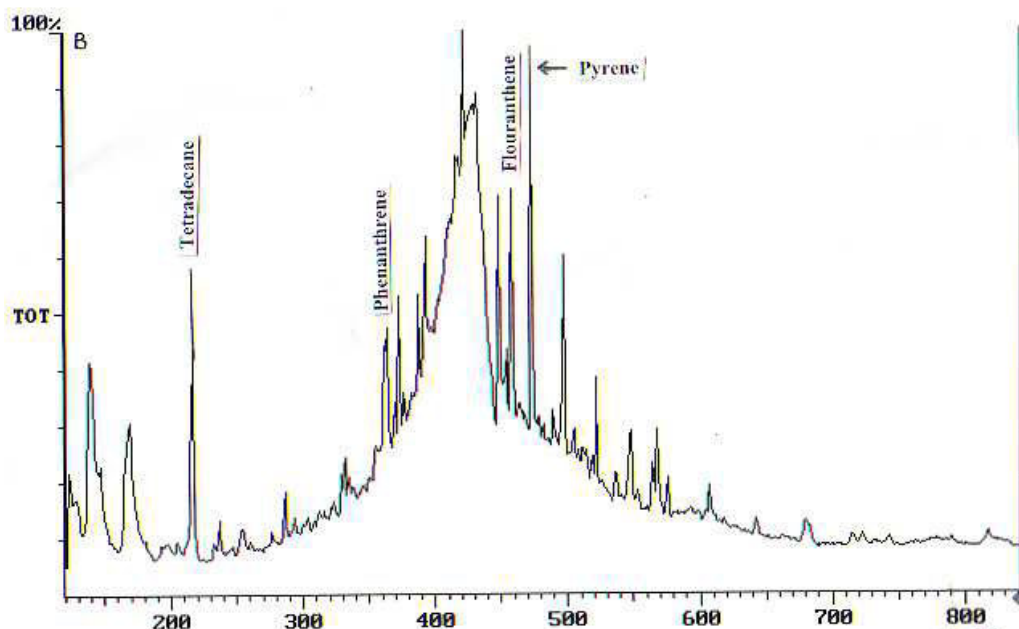


Figure 2

The chromatogram of PAHs in soil before Fenton Reagent (FR) (A), after FR (B) treatment.

The nature of the product isolated is consistent with the mechanism of oxidation discussed above, namely initial hydroxylation at the sites of highest electron density.

Figure 2 indicated that the total load of PAHs (naphthalene, phenanthrene, anthracene, flouanthene, pyrene, and benzo(a)pyrene) in the soil decreased after a single of the Fenton's oxidation.

CONCLUSION

From the above results, determined after a single Fenton's oxidation cycle, it is clear that although a considerable reduction in the total hydrocarbon content has occurred, oxidation products, typically mono- and dicarboxylic acids, remain, and would in themselves continue to pose an environmental hazard unless removed by further oxidation.

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