EFFECT OF FENTON'S REAGENT ON DEGRADATION OF ANTHRACENE, FLUORENE,NAPHTHALENE AND PHENANTHRENE MIXTURE IN SOIL

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*ABSTRACT-*A good number of PolycyclicAromatic Hydrocarbons (PAH) have been identified to be carcinogenic in nature and their bioavailability has become a matter of serious concern. Soil is the receptor of large number of aromatic hydrocarbons where from the bioavailable ones enter the living kingdom and continue its bioaccumulation and bio magnifications. It starts its detrimental effects as soon as it crosses the permissible level. Since PAH are of recalcitrant natureand hydrophobic, there is the chance of adsorption of these on soil, sediments etc. in water bodies. As such soil and sediments in river bed are prone to be a storehouse of persistent PAH in areas where river water carries effluents especially from refineries,oilfields, coal fields etc. The biodegradation process is a process of oxidation. In the present experiment, the influence of an eco friendly oxidizing agent Fenton's Reagent (FR) on a mixture of four PAH viz. Anthracene(ANT), Fluorene(FLN), Naphthalene(NPH) and Phenanthrene(PHN)placed in river bed soil is examined in a 60 days experiment. The experimental soil samples are taken from river bed of the river Brahmaputra in the district of Dhubri, Assam, India. A few important physico-chemical parameters of the soil were monitored before placement of measured quantity of PAH. pH is measured at every 20 days of the experimental period.

It has been found that the texture of the experimental soil is Loamy sand; deficient of organic carbon compared to agricultural soil and possesses slightly alkaline soil reaction. Gravimetric determination of the soxhlet extracts shows that the extent of degradation in samples where FR was applied in the reagent ratio of $H_2O_2 : FeSO_4 = 10:1$ is more compared to samples without applied FR. From the GC chromatograms, it has been seen that the mechanism of degradation in presence of FR is quite different from without FR. In a 34 minutes GC analysis, where 50 prominent peaks were recorded in the chromatograms; the samples with FR has only 12,7 and 7 common peaks with the sample without FR in the soxhlet extracts of 0, 20and 40 days respectively.On the other hand, the number of common peaks in the samples without FR is more compared to number of common peaks in samples with FR indicating lower rate of degradation in absence of FR.It has been assumed that concentration of ferrous ions in the 10:1 reagent ratio is not high enough to scavenge hydroxyl radicals which would reduce degradation efficiency of FR.

*KEY WORDS:* **PAH, Fenton's Reagent, Degradation, GC-MS, Loamy Sand.**

INTRODUCTION

Hydrocarbons represent a class of numerous and heterogeneous organic compounds ranging from linear, cyclic and branched; saturated and unsaturated; alkanes to aromatic and polycyclic ones. Each of these species is characterized by a peculiar value of toxicity and, as a consequence, their effect on the human health and environments is strongly different [1].The occurrence and fate of PAHis currently of great concern as it is among the most frequently detected environmental pollutants and a good number of them are persistent. Their persistence in the environment is due to their low water solubility. The term PAH generally refers to hydrocarbons containing three or more fused benzene rings in linear, angular or cluster arrangements. They thus rapidly become associated with sediments, and may become buried and persist until degraded, re-suspended, bio-accumulated, or removed by dredging.Since, PAH are major constituents of coal and crude oil;they are distributed ubiquitously in the environment. PAH produced in the environment are transported over long distances in air before they settle in the atmosphere, on soil surfaces, vegetation, sea and inland waters. Crude oil contains more than 30% PAH. PAH are important environmental contaminants because of their hydrophobic and recalcitrant nature [2]. PAH derivatives are associated with several kinds of human diseases, since many of them are carcinogenic and mutagenic [3,4].Low mol.wt PAHs are highly toxic, having effects on the reproduction and mortality rates of aquatic animals, and most of the high mol.wt PAH (containing 4 or more benzene rings) are mutagenic and carcinogenic [5]. Accidental spillages and improper disposal of petroleum and its fractions have given rise to soil contamination. Contaminated soils are of concern since many PAH are harmful and recalcitrant, resulting in their classification as priority pollutants [6].There is considerable human health concern about the fate of PAH in the environment because many of these compounds are toxic, and some have been shown to be potent and carcinogens [7]. Thus, remediation of PAH contaminated soil is very important.

Advanced Oxidation Processes (AOP) are attractive alternatives to treating wastewater containing toxic and persistent pollutants. Among them, the oxidation using Fenton's Reagent (FR) has proved to be a promising and attractive treatment method for removal of hazardous and organic pollutants. FRprocess is a homogeneous catalytic oxidation process, which uses a mixture of hydrogen peroxide and iron II ions to induce a complex redox for generating hydroxyl radicals [8].. It was shown that the

modification of the FR by using higher concentrations of hydrogen peroxide can enhance contaminant desorption and destruction [9].

AOP are used for removing organic hydrocarbons from soil. In situ chemical oxidation is an effective way to remediate soil contaminated with organic compounds such as PAH. The basis of the Fenton method is the decomposition of H_2O_2 and the production of hydroxyl radicals in the presence of Fe^{3+} ions as a catalyst. Studies have shown that produced hydroxyl radicals are capable of decomposing and degrading organic contaminants such as petroleum hydrocarbons [10].

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\cdot} + OH^{-} + Fe^{3+}$$
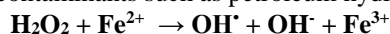
The chemicals used in Fenton's method arenon-toxic, inexpensive, abundant and leaves no harmful residue. It reduces reaction time and energy consumption, and operation and control is simple. The reaction is very fast and much more efficient than H_2O_2alone. The technology, however, is limited by the interference of subsurface impurities and alkalinity of soil. Soil containing carbonate, bicarbonate and organic matter create competing reactions that hinder the success of the treatment.

MATERIALS AND METHODS

ANT, FLN,NPH, PHN, Petroleum Ether, Dichloromethane (DCM) were purchased from sigma Aldrich. Ferrous Sulphate, Hydrogen Peroxide wasof analytical grade.

Soil samples were collected from 20 different locations of each of the five selected areas viz. Ghunimari char, Dhunidanga char, Joruarchar, Birshingchar and Dewaner Alga Char in the bed of river Brahmaputra in Dhubri District(Latitude $26^0 01' 16''$N to $25^0 44' 34''$N: Longitude $89^0 58' 48''$E to $89^0 51' 27''$E) at 0-15 cm depth using hand auger. Samples were air dried. The dried soils were further broken down, pulverized with a pestle and mortar and sieved (1mm pore size) samples were homogenized by quartering process [11]. The amount so collected becomes 1 kg and then stored in polythene bag and labeled.

40 mL of a standard solution of PAH mixture is prepared in solvent DCM (density 1.3266g per mL), by dissolving 0.02g each of NPH, PHN, ANT and FLN. The concentration becomes 1505 ppm with respect to PAH. 20 mL of this solution was poured onto 800 g of the soil in each of two polythene bags.A mixture of 1g of 30% H_2O_2 and 5 mL water was added cautiously to a solution of 0.1 g $FeSO_4$ in 5 mL water at 0^oC to get a reagent ratio of 10:1. The mixture was immediately added into one of the bags containing PAH solution in soil as shown in Table 1.The sample bags were mixed thoroughly and kept open. At an interval of 20 days, the sample bags were agitated after moistening with distilled water.

Table 1- Composition of Samples

Sample No	Composition	Soil taken	PAH added	Total	Conc. of PAH	FR added
		g	g	g	ppm	mL
1	Soil + PAH	799.96	0.04	800	50	0
2	Soil + PAH+FR	799.96	0.04	800	50	10
3	Soil	800	0.00	800	0	0

The selected soil sample is characterized with respect to some important parameters viz. Bulk Density (BD), Electrical Conductivity (EC), Hydraulic Conductivity(HC), Soil Organic Carbon(SOC), pH, Texture and Water Holding Capacity(WHC). The pH was measured using a digital pHmeter at 4.0 buffer solution [12]. PAH were extracted by Soxhlet Extraction method. 20 g of soil were extracted out using petroleum ether solvent at 0, 20, 40 and 60 days in each set. Every time the process was continued for 24 hrs.The recovered material is then extracted into DCM. Column chromatography was used in a column of silica gel (100–200 mesh) using DCM as eluent. Collected fractions were concentrated. It was then subjected to Gas Chromatography-Mass Spectrometry (GCMS) analysis. The quantity of petroleum ether soluble part present in the blank soil is also determined.For gravimetric calculations, the petroleum ether soluble part found in control was subtracted from those with PAH.

Analytical gas chromatography was conducted on a Perkin Elmer GC/MS. The GC conditions were an initial temperature 100^0C for 2 minutes, and then a temperature ramp from 100 to 350° C at a rate of 10 ^{o} C /min, and then kept at 350 ^{o} C for a further 7 minutes in order to burn off any nonvolatile organic compounds remaining.

RESULTS AND DISCUSSIONS

The characteristics of the soil sample are given in Table 2. The sample contains SOC lower than normal soil. It is advantageous to FR oxidation. The soil is found to be slightly alkaline which is unfavorable for hydrocarbon degradation by FR. The average of the pH values

Table 2-Physico- Chemical Parameters of the Soil

BD	EC	HC	pH	SOC	Texture	WHC
gcm^{-3}	$mScm^{-1}$	$10^{-4} cms^{-1}$		%		%
1.43	0.16	28.58	7.27	0.07	Loamy Sand	41.25

measured during the period of the experiment at an interval of 20 days give 6.3 and 4.0 at sample bags 1 and 2 respectively. However, these parameters are in the range for normal microbial activities [13].Two GC chromatograms,namely for samples 1 at 0day and 2 at 40 days are placed at Figures 1 and 2 in original form for illustration.
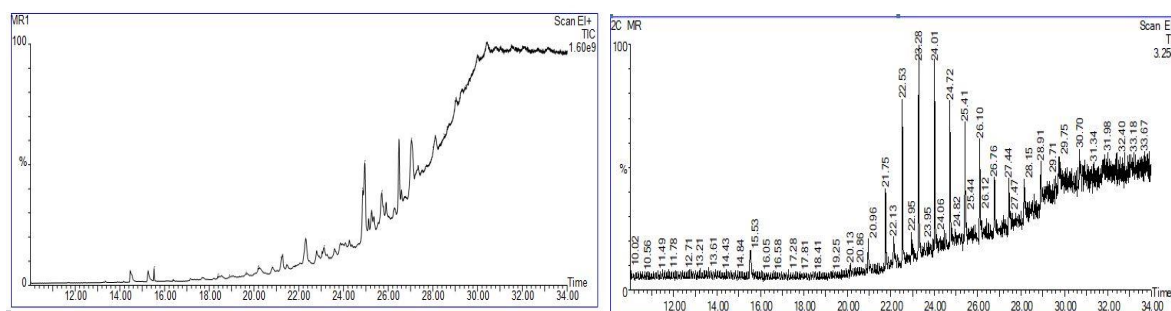
Fig.1:GCChrom.ofsample1at0day**Fig.2:**GCChrom.ofsample2at40 days

On careful examination of the 34 minutes chromatograms, it has been found that on the same span of days of placement of PAH on soil, the number of common components between samples without and with FR is very less; it is only12, 7 and 7 on 0, 20 and 40 days indicating different mechanism of degradation followed (Table-3).

Table 3: Statement of number of similar peaks of sample 1 with those of sample 2 day wise

Days→		0		20		40	
Sample Numbers→		2	1	2		2	1
Number of peaks of sample 2 with similar peaks of sample1→		5 0	1 2	5 0	1	5 0	7

Another significant aspect is that the number of components in FR added sample decreases quickly compared to sample without FR. Out of total 50 peaks in the 0 day extract 19 and 13 components persist till 20 and 40 days respectively in sample without FR. The remaining peaks are due to newer compounds produced as a result of reactions including

Table 4: Statement of number of similar peaks sample wise against days of withdrawal

Sample No.1: Without FR			Sample No.2: With FR		
No. of peaks at 0 day	No. of peaks at 20 days which are similar to peaks at 0 day	No. of peaks at 40 days which are similar to peaks at 0 day	No. of peaks at 0 day	No. of peaks at 20 days which are similar to peaks at 0 day	No. of peaks at 40 days which are similar to peaks at 0 day
50	19	13	50	11	3
	Rest peaks of 20days	No. of peaks at 40 days which are similar to rest peaks of 20 days		Rest peaks of 20days	No. of peaks at 40 days which are similar to rest peaks of 20 days
	31	10		39	4
		Rest peaks at 40 days			Rest peaks at 40 days
		27			43
Total: 50	50	50	Total: 50	50	50

degradation. Corresponding figures stand at 50, 11 and 3 in the sample with FR. Similarly out of the remaining 31 peaks of 20 day extracts of the sample without FR, 10 components retain to 40 days. The corresponding figures in sample with FR are 39 and 4 (Table-4). The gravimetric determination supports the above trend of degradation (Table-5).It has been found that a maximum of 90% degradation occurs in sample with FR after 2 months.

Table 5- Amounts of PAH (%) remaining in the soil against number of days.

Sample No. 1(soil without FR)			Sample No. 2(soil with FR)		
20 days	40 days	60 days	20 days	40days	60 days
50 %	39 %	20 %	30 %	22 %	10 %

The efficiency of the Fenton process is dependent on the utilization of free radicals. Excess $FeSO_4$ would produce too many ferrous ions, which would scavenge hydroxyl radicals resulting in reduced degradation efficiency. In the present experiment, 10:1 ratio of H_2O_2 :Fe^{2+}has given a good result. pH is one of the important aspects on the oxidation potential in the Fenton process. It was established that Fenton oxidations are efficient in the acidic range by directly increasing the availability of •OH radicals for the desired reaction of oxidation of PAH.Oxidation lowers the pH due to formation of acidic oxygenated derivatives. The study clearly showed that the use of Fenton's reagent to oxidize PAH in solution and soil is far superior. It is indicated by the fact that 90% of PAHs were degraded in a period of 60 days in the soil.

REFERENCES

[1] Clerici L, Mongini E, Robles P, Dellavedova P, and De Gregorio M A, 2015. GC/MS: A Valid Tool for Soil Gas Hydrocarbons Speciation, International Journal of Analytical Mass Spectrometry and Chromatography, 3, 54-62.

[2] Toledo F L, Calvo C, Rodelas B and lez-Lopez G J, 2006. Selection and identification of bacteria isolated from waste crude oil with polycyclic aromatic hydrocarbons removal capacities, SystApplMicrobiol, 29, 244-252.

[3] Enell A., Reichenberg. F., Ewald, G., et al. 2005. Desorption kinetics studies on PAH-contaminated soil under varying temperatures. Chemosphere, 61, 1529–38.

[4] Lewis, C., Guitart, Z., Pook, C., et al. 2010. Integrated assessment of oil pollution using biological monitoring and chemical fingerprinting, Environmental Toxicology and Chemistry, 29, 1358–1366.

[5] Patowary K, Kalita M C and Deka S, 2015. Degradation of PAH employing biosurfactant producing Pseudomonas aeruginosa KS3, Indian Journal of Biotechnology. 14, 208-15.

[6] Wilson, S.C. and Jones K.C. 1993. Bioremediation of soil contaminated with PAH Environ. Pollut.81, 229-49.

[7] Dean A. Martens, William T, Frankenberger J. 2016. Enhanced degradation of Polycyclic Aromatic Hydrocarbons in Soil, treated with an Oxidative Process─ Fenton Reagent.

[8] Haddad E M, Regti A, Laamari M R, Mamouni R, and Saffaj N. 2014,Use of FR as advanced oxidative process for removing textile dyes from aqueous solutions,J. Mater. Environ. Sci. 5 (3), 667-674.

[9] GoiA and Trapido M. 2004. Degradation of PAH in soil: the FR versus ozonation, Environmental Technology, 25. 155-164.

[10] Farzadkia M, DehghaniM and Moafian M. 2014. The effects of Fenton's process on the removal of petroleum hydrocarbons from oily sludge in Shiraz oil refinery, Iran; Journal of Environmental Health Science & Engineering, 12:31.

[11] Singh D, Chhonkar R K, and Pandey R N, 2000-Soil, Plant Water Analysis- a Method Manual Indian Council of Agricultural Research, New Delhi, pp-2-35.

[12] Nafie N L, 2007, Application of FR on Remediation of PAH in spiked soil, Indo. J. Chem, 7 (2), 208-213.

[13] Khan Z, and Anjaneyulu Y, 2005. Review on Application of Bioremediation Methods for Decontamination of Soils, *Res. J.Chem. Environ*. 9(2), 75-79.