

# Effect of Bulky Groups of PAH on Organic Hydrocarbon Contamination Detoxification

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**Abstract-** A careful observation of the degradation pattern of PAH with remediation techniques revealed that larger groups pose great resistances to degradations.

The study highlights the photo-Fenton type degradation of polycyclic Aromatic Hydrocarbons (PAHs) using starch stabilized magnetic Nano-particles (SSMNPs) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) in place of iron II in a Fenton reaction (control experiment). The degradation occurred with respect to size of PAH molecules, number of double bonds present in PAH, and type of PAH molecules. The magnetic nanoparticles were synthesized via-co-precipitation reaction of iron III and iron II chlorides with varying weights of starch at 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10g of MNPs and SSMNPs for the zero (0.00g) starch and starch coated samples respectively. A mixture of 2.0ml crude oil, 8.0ml H<sub>2</sub>O<sub>2</sub>, 10.0ml H<sub>2</sub>O and 0.5g of each of the samples were exposed to sun light for fifty hours. Two other samples of crude oil with H<sub>2</sub>O<sub>2</sub> and water only were also exposed along with the listed samples. The samples were then characterised after exposure using the GC – FID model HP 5890 series II. The results obtained showed PAHs concentration as 5.3, 7.4, 7.2, 7.1, 7.0 and 6.7 for the MNPs and SSMNPs samples respectively. The PAHs of the control (Fenton reaction) crude oil with water plus H<sub>2</sub>O<sub>2</sub> and crude oil only obtained were 7.9, 8.3 and 29.7mg/l respectively. Observation reveals that PAHs with lower molar mass and fewer double bonds were easily degraded relative to those with higher molar masses and many double bonds.

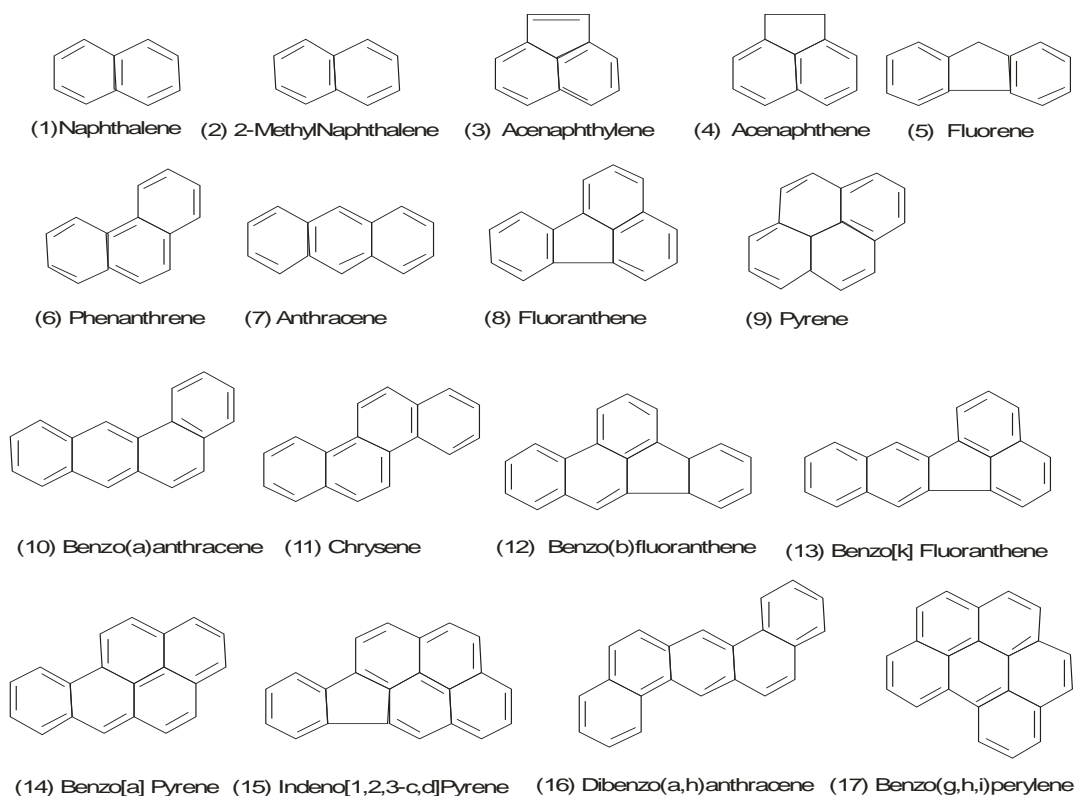
**Index Terms-** Fenton degradation, Synthesis, Nanoparticles, Concentration, Magnetite, Polycyclic hydrocarbons, Reactions, Bulky groups.

## I. INTRODUCTION

The production of viable inorganic reactants of Nano-scale capable of degrading polycyclic aromatic hydrocarbons (PAHs) and monitoring the rate of detoxification with the number of double bonds ( $\pi$  – bonds) in a molecule is the most

relevant issue in this study. <sup>(1)</sup> PAHs are organic compounds of 2-6 fused rings of benzene nucleus with molecular mass ranging from 128g/mol in naphthalene to 278g/mol in indenopyrene<sup>(2)</sup>. PAHs are components of fossils fuels (petroleum or coal) which seep into the soil or water (surface or ground water) through combustion, oil spillage and drill cuttings<sup>(3)</sup>.

Their presence in the environment is of great concern to humanity because they are potential health hazards (carcinogens). Therefore, the reduction of PAH to harmless or environmentally friendly forms is of top most interest to all players of the oil and gas industries<sup>(3,4)</sup>. Many biological and chemical methods have been used for PAH degradation; these include phytoremediation, bioremediation and chemical remediation. Chemical remediation could involve the use of fertilizers, photooxidation and Fenton reagents etc<sup>(5)</sup>. Majority of the chemical methods are expensive, less effective and toxic<sup>6</sup>. Fenton's reagent which consists of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> are more environmentally friendly with subtlety than other chemical methods. Fenton's reagent has been applied in the remediation of crude oil contaminated soil and water samples<sup>(6,7,8)</sup>. The substitution reaction of Fe<sup>2+</sup> with magnetite (Fe<sup>II</sup>, Fe<sup>III</sup> species) in a catalysed chemical oxidation appears to be potentially active than Fe<sup>2+</sup> alone. Such reagent is called Fenton-type reagent<sup>(9)</sup>. Precipitation of magnetite nanoparticles with different sizes was achieved through coating with varying percentage concentrations of starch<sup>(9)</sup>. The use of magnetite with varying starch concentration in the degradation of spilled oil has not been reported<sup>(10)</sup>. This research therefore seeks to apply starch stabilized magnetic nanoparticles (SSMNPs) in the degradation of PAHs of spilled oil exposed to sunlight<sup>(10)</sup>. It would be expected that the rate of degradation could be manipulated with starch coatings to such an extent that greater efficiency is achieved. Degradation rate was expected to follow a pattern that as the number of double bonds increase, the rate of degradation decreases<sup>(11)</sup>.



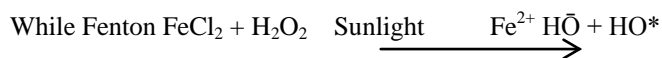
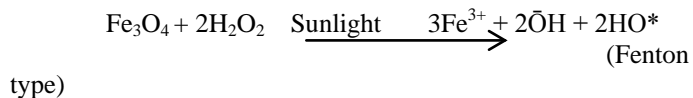
## II. METHODOLOGY

Chemicals used were obtained from BDH Analar Ltd, Poole, England. The salt was purchased from a Chemical sales outlet in Port Harcourt, Nigeria.

0.7m NaOH was prepared by dissolving 7.0g of the pellets into 250ml of deionised water. Each mass of 0.02g, 0.04g, 0.06g, 0.08g and 0.10g of starch solution was dissolved into 100ml deionised water. Out of this, 61ml of starch solution was used to dissolve Fe<sup>2+</sup> and Fe<sup>3+</sup> hydrated chloride. The mixture was infused in nitrogen gas for ten minutes and shaken gently. To facilitate precipitation of magnetite, 143ml NaOH was added drop wisely to 61ml solution of the Fe<sup>2+</sup> and Fe<sup>3+</sup> as a mixture. After the precipitation of the magnetite, filtration was done through a Buckner funnel and was filtered using a vacuum pump. The magnetite was dried in an ovum until the crystals became strong.

## III. REACTIONS

The Fenton type is a combination of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hydrogen peroxide H<sub>2</sub>O<sub>2</sub> in the presence of UV radiation



Fenton

8ml H<sub>2</sub>O<sub>2</sub> + 2ml crude oil + 0.5g SSMNP + 10ml H<sub>2</sub>O – to make a slurry. Each of the 10 slurries were transferred into a conical flask and exposed to sunlight (IIV light) for 50 hours. The samples were taken for characterization and analysis in GC-FID mode HP 58090 series II.

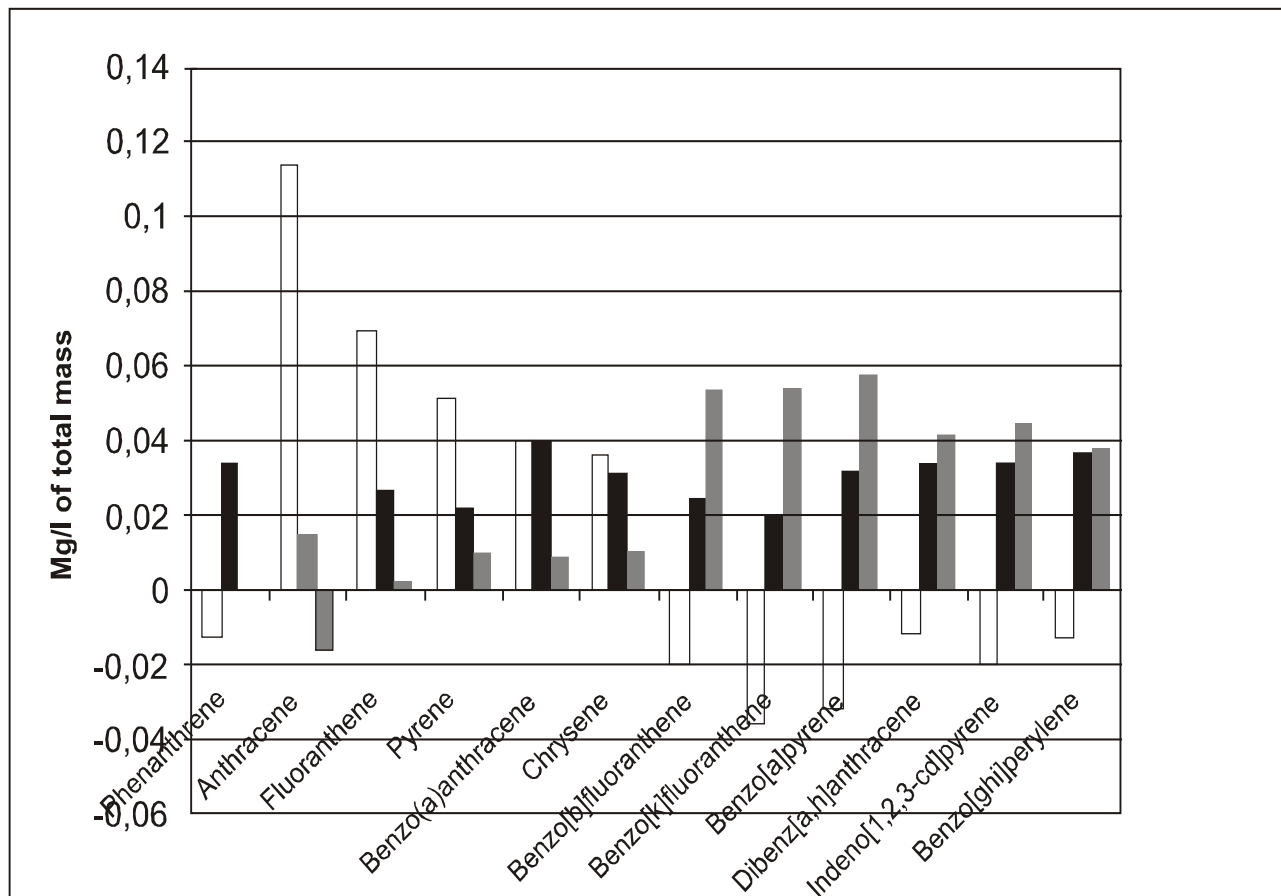
## IV. DATA PRESENTATION

Results of GC-FID are hereby presented as analysed. Table 1 shows the total signal count as obtained. The signal count was directly proportional to the concentration of constitutions in the vapour phase.

**Table 1: Table 1: Total signal count of PAH in the samples.**

Total PAH in the samples.

	1	2	3	4	5	6	7	8	9	10
	0.02 SSMNP	0.4 SSMNP	0.06 SSMNP	0.08 SSMNP	0.10 SSMNP	MNP+Crude +H <sub>2</sub> O <sub>2</sub> +H <sub>2</sub> O	Fe <sup>2+</sup> +H <sub>2</sub> O <sub>2</sub> + Crude	Crude H <sub>2</sub> O <sub>2</sub> (exposed)	Crude + H <sub>2</sub> O <sub>2</sub> (dark)	Crude oil
Naphthalene	0.0	0.0	0.0	0.0	0.0	0.00120	0.0	0.0	0.0	0.64496
2.Methyl Naphthalene	0.0	0.0024673	0.003131	0.00489	0.0073694	0.0	0.0	0.0118328	0.0	0.139196
Acenaphthylene	0.0427658	0.101149	0.0981817	0.109408	0.0982450	0.0415888	0.0624836	0.192043	0.0929269	0.830863
Acenaphthlene	0.0352772	0.68476	0.652298	0.0734941	0.0258336	0.0153664	0.0516715	0.126491	0.0710564	0.350980
Fluorine	0.349822	0.375122	0.156692	0.388679	0.150263	0.111861	0.380491	0.639776	0.266153	0.822233
Phenathrene	0.154867	0.890924	0.114934	0.108828	0.288689	0.539167	0.730630	0.941200	1.00762	0.513217
Anthracene	0.143929	0.107088	0.293870	0.0604345	0.498458	0.259563	0.416004	0.510786	0.675475	2.46836
Fluoranthene	3.39596	3.48993	2.80756	2.90314	2.11843	0.507891	0.748927	0.846853	4.11410	11.02290
Pyrene	0.146636	0.184032	0.0900955	0.239152	0.26599	0.153844	0.542410	0.513164	0.303787	1.14129
Benz (a) anthracene	0.192712	0.334427	0.551218	0.53959	0.364707	0.201125	0.221320	0.238425	0.735564	1.67016
Chrysene	0.503380	0.294974	1.15166	0.757463	0.273578	0.664790	1.29277	0.436932	1.19958	2.80554
Benzo (b) fluoranthene	0.813206	0.295529	0.313277	0.2549	0.2676763	0.085696	0.290618	1.04341	0.491517	0.992418
Benz (k) Fluoranthene	0.200494	0.614580	0.482582	0.537924	0.554790	0.140454	0.255184	0.267061	0.812327	3.01070



**Fig 1: Graphical display of all PAHs**

The tallest peaks were those of crude oil sample as expected due to high concentration and absence of catalyst  $H_2O_2^{(11)}$  However, few PAHs in the crude oil were degraded even lower than those of other samples. For example, acenaphthene and benzo (a) pyrene peaks of crude oil sample were lower than 0.02% SSMNPs and even MNPs respectively

### PAH Degradation due to Molar Mass and $\pi$ – Bonds of Benzene Nucleus

The table above shows GC – FID was not able to detect 2 – member rings of Naphthalene for samples of FL 1-5. The four rings member of pyrene and fluoranthene with molar mass 202g resisted photochemical oxidation. There values were 0.15ppm

and 0.50ppmm. This must have been due to their large molecular mass and ring number of 4.

### Degradation rate of PAH Relative to Double bonds and Molar Mass.

Observed resistance to degradation is likely due to the number of double bonds as well as the molar mass of each compound. Five double bonds in naphthalene were easily degraded by Fenton and Fenton type. The trend was slow at higher numbers like Pyrene and Benzo pyrene of nine and eleven double bonds respectively.

**Table 2: Degradation rate of PAH Relative to No. of bonds and Molar Mass.**

PAH	Rings Group	Molar MASS	Degradation pt after 50hrs ppm
Naphthalene	2	128	0.00
Acenaphthylene	3	166	0.10
Anthracene	3	178	0.06
Phenanthrene	3	178	0.08
Fluorene	3	166	0.37
Pyrene	4	202	0.180
Benzo (a) Anthracene	4	228	0.33
Chrysene	4	228	0.29
Dibenzo (a,h) anthracene	5	278	0.18

## V. DISCUSSION

Degradation of PAHs was higher with the lower members of the compounds. These are Naphthalene, 2. Methyl Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene and Anthracene. Those higher members with very high molecular mass number were more resistant to degradation; however, degradation is feasible with strong oxidizing agents like the Fenton’s and Fenton type. The number of double bonds in PAHs compounds is also a factor that could be considered. Benzo(a)pyrene, Indeno (1,2,3-c, d) pyrene with many pi-bonds showed resistance to degradation while Naphthalene did not considerably resist degradation.

## VI. CONCLUSION

The size of a molecule of PAH plays significant role in resistance to its degradation. Most advanced methods of remediation’s like Fenton, Fenton type are only useful in degrading higher members of PAHs. Therefore, the study recommends the chemical remediative methods strongly for effective and complete clean-up of any polluted environment (soil or ground water).

Nanoparticles have proved very active in the remediations of hydrocarbon polluted environment. Modern improved methods of Fenton type are most useful in remediating a large polluted environment. The MNPs and SSMNPs could indeed be used as heterogeneous catalyst in reactions in order to attain best

results in remediations and other environmental clean ups. The larger members of the PAHs offered resistances in degradation. Therefore, bulky groups of PAHs with many double bonds with its associated resonance stabilized benzene nucleus of the kekule’s structure are the results and opposition to environmental purity.

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