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Obtaining Useful Product From The Degradation Of Polycyclic Aromatic Hydrocarbon Through Fenton And Fenton-Like

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Abstract: *The Photo Fenton and Fenton-like degradation of Polycyclic Aromatic Hydrocarbons (PAHs) using Starch Stabilized Magnetic Nanoparticles (SSMNPs), and Magnetite (Fe_3O_4) in place of Fe(II0 in aFenton reaction has been investigated. The magnetic nanoparticles (SSMNPs) used were synthesized via co-precipitation reaction of Fe(II) and Fe(III) chlorides with weights of starch at 0.06g while the others were without starch. A mixture of 2.0ml crude oil, 8.0ml H_2O_2, 10.0ml H_2O and 0.5g of each of the samples were exposed to sun light for a cumulative period of fifty two (52) hours obtained within study time. The samples were characterised after exposure using the gas chromatography GC-FID model HP 5890 series II spectroscopy. The result obtained showed PAH concentration as 5.39, 7.18, 7.95 and 8.36 ML/L for the two SSMNP and the other two Fentons respectively. A UV-Vis spectroscopy scan at 300-560nm for all four samples revealed the formation of oxidative products like phenols at 350nm and other phenolic derivatives of lower absorptivity in the same wavelength.*
Keywords*: PAH, Magnetite, Nanoparticles, degradation, investigating.*

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I. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are inorganic compounds containing many or more than one aromatic rings of benzene nucleus with molecular mass ranging from 128g/mol in naphthalene to 278g/mol in indenopyrene [1] PAHs are components of fossil fuels (petroleum or coal) that enter the environment through combustion, oil spillage and drill cutting [1,2]. They are hazardous to the environment because of their carcinogenic and immunotoxins ability. Therefore the degradation of PAHs to harmless or environmentally friendly forms is of great interest to researchers and all players of the oil industry. [2,3] Bioremediation and phytoremediation are inefficient in lowering contamination levels beyond the capacity of the microorganisms or plants species that are involved, [3, 4]. In addition, the problem of incomplete degradation of hydrocarbons (HCs) could lead to residual toxins or more harmful intermediate in the environment [4]. However, a combined processes involving chemical treatments like fertilizer application, photoxidation are preferred [2, 5]. The use of Fenton reagent is regarded is the advanced oxidation process (AOPs) and has a promising alternative for the treatment of waste containing Aromatic Hydrocarbons [4, 6, 7, 8].

The Fenton reagent generates hydroxyl radicals (a powerful oxidizing specie with higher oxidation potential than ozone and hydrogen peroxide) insitu [6, 7]. The Fenton reaction involves a transition element like iron [Fe] reacts with hydrogen peroxide to form hydroxyl ions in the equation 1 below.

$$Fe^{2+}_{(aq)} + H_2O_{2(aq)} \longrightarrow Fe^{3+}_{(aq)} + HO^-_{(aq)} + HO^*_{(aq)} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Both the Fe^{2+} and H_2O_2 are more environmentally friendly than most chemicals.
The application of the Starch mediated technique in PAHs degradation has not been reported, though it is cheaper and readily available than SDS [12, 14]. The starch on magnetite (SSMNPs) could increase interactions of carbon chain with PAHs in any water-reactant medium to enhance higher degrading rate. [10], [14].

II. Materials And Methods

The nanoparticles of magnetite (MNPs) were prepared by dissolving 4.40g of $FeCl_2.4H_2O$ with 1.98g of $FeCl_3.6H_2O$ each into 25ML deionized water. The solution were mixed and stirred together. The NaOH(base) was prepared by dissolving 7.0g of NaOH into 250ML distilled or deionized water. Both were mixed together dropwisely on the iron solution while stirring was in progress. The solution turned blackish and a magnet was placed at the side of the test tube to pick the magnetic particles. [10] The particles were dried and analysed using the GC-FID model HP 5890 series II at the ANAL concepts Ltd in Port Harcourt.

Table 1

S/N	SAMPLES	PAH MG/L
1.	MNP + 2ML Crude + 10ML H_2O + 8ML H_2O_2	5.39
2.	SSMNP(0.06g) + 2ML Crude + 10ML H_2O + 8ml H_2O_2	7.18
3.	Fe^{2+} + 8ML H_2O_2 + 2ML Crude + 10ML H_2O	7.95
4.	2ML crude 10ML H_2O + 8ML H_2O_2	8.36

ANALYSIS WITH UV –VISIBLE

The four samples were studied on the UV-Vis in order to ascertain the changes in the absorption of the degraded products. Phenols and Phenolic derivatives are likely products of Fenton reactions with PAHs, a wavelength scan between 250-560nm was selected for the measurements. This is because phenols absorb at 350nm [6], [3]

III. Results

Table 2: UV – Visible Readings

No. 1	No. 2	No.3	No.4	
λ/cm^{-1}	MNPs	SSMNPs [0.06%]	Fenton	H_2O_2
300	0.518	0.371	0.535	0.527
350	0.731	0.273	0.532	0.691
400	0.595	0.228	0.276	0.617
450	0.516	0.201	0.226	0.547
500	0.401	0.152	0.179	0.130
550	0.327	0.124	0.137	0.352

UV-Visible Scan

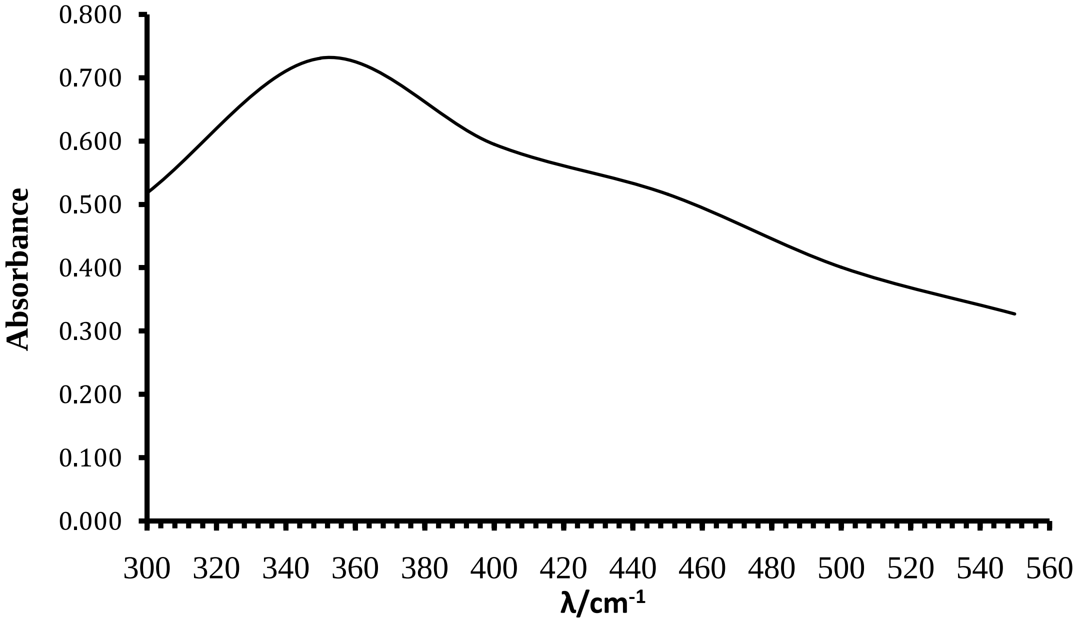


Fig 1 UV- Vis Scan of Sample (1) Reaction with MNPs

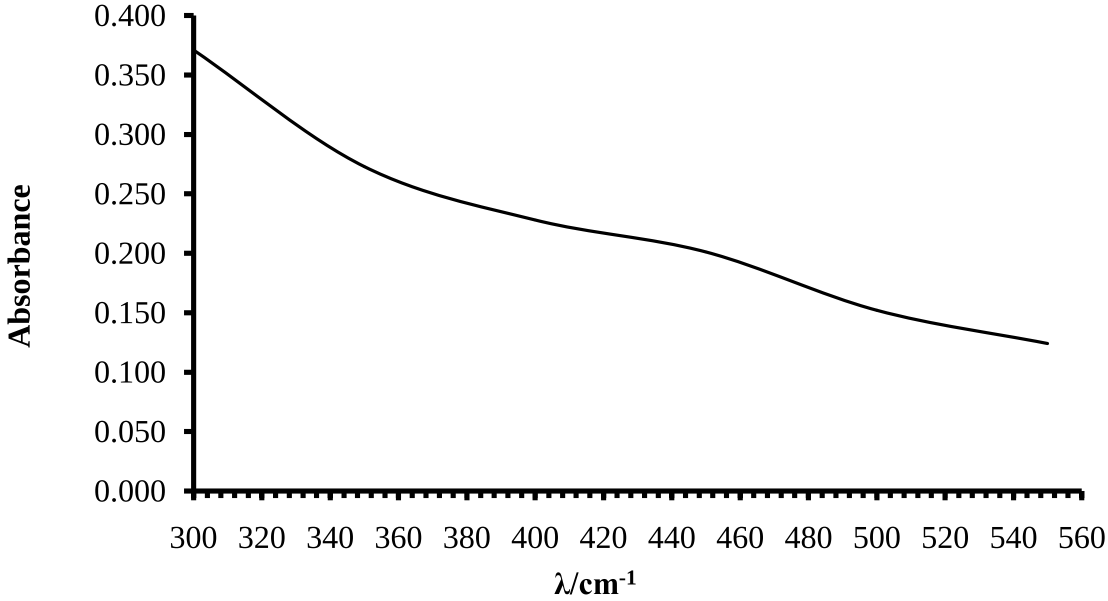


Fig 2 UV- Vis Scan of Sample (2) Reaction with SSMNP [0.06%]

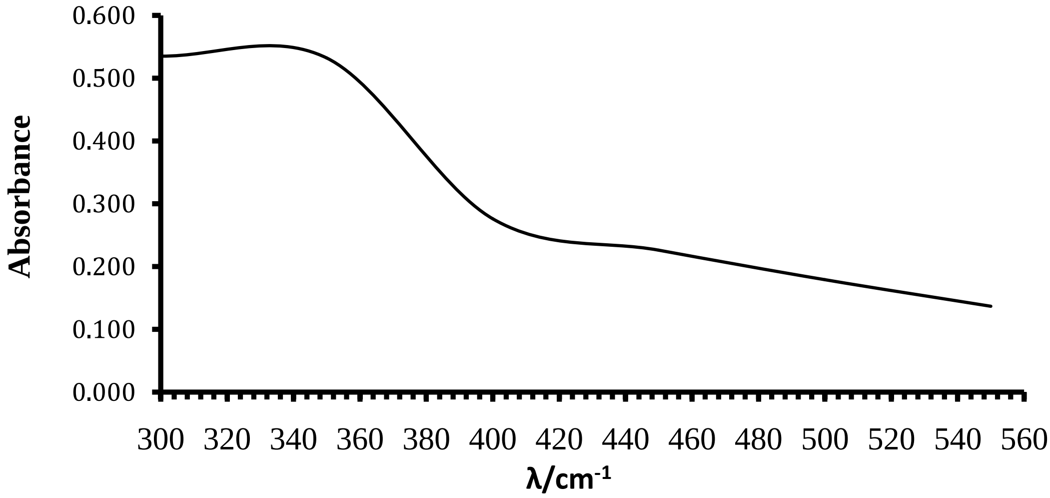


Figure 3 UV- Vis Scan of Sample (3) Reaction with Fenton

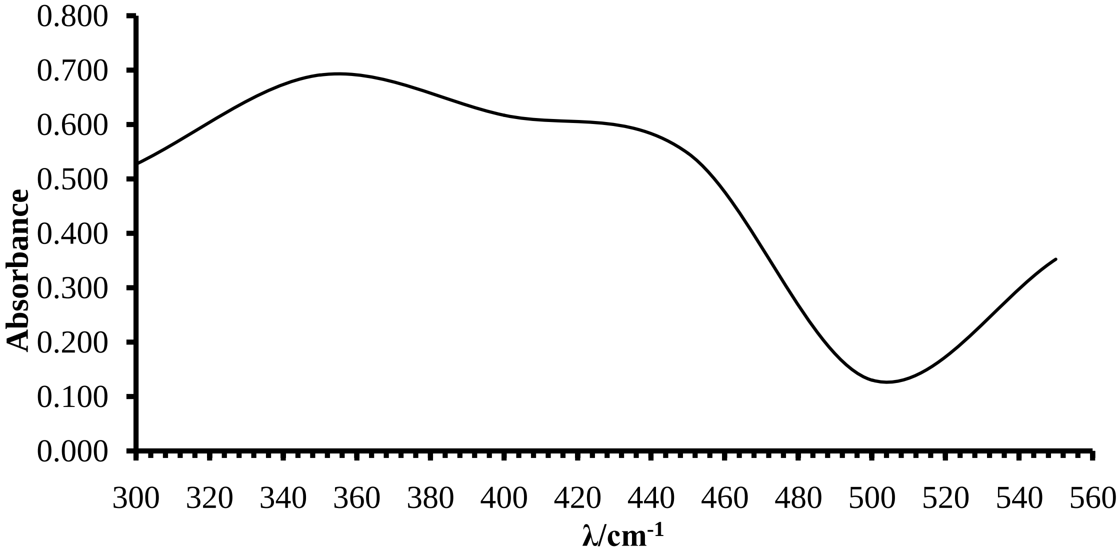


Fig 4 UV- Vis Scan of Sample (4) Reaction with H_2O_2
Plots of AbsorbanceVs Wavelength

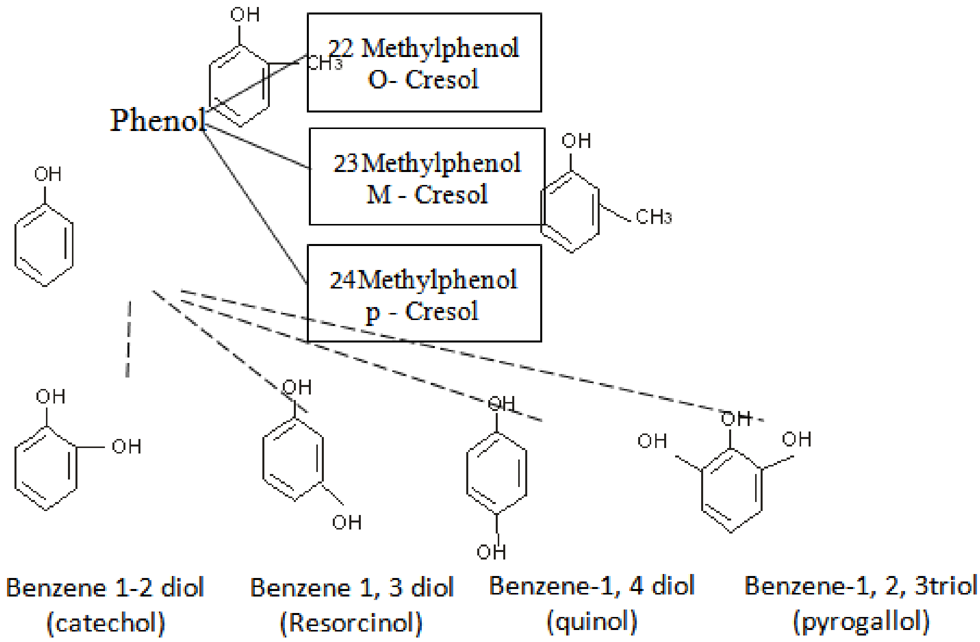
IV. Interpretation And Discussions

The UV-Visible readings of the samples analysed namely: MNPs (1), SSMNPs (2), Fenton (3) and H_2O_2 (4). Oxidative degradation of benzene as well as PAHs often results in phenols and phenolic derivatives as primary products before further breakdown to other substances. Phenols absorb at 350nm in the UV region. [6]

The plot of absorbance versus wavelength of figures 1 and 2 showed that, there was a gradual increase in absorbance from 300nm up to a maximum peak at 350nm. There after a gradual decline was observed from 360nm down to a maximum at 560nm. This implied that phenol was the likely major primary degradation product present in the sample of MNP (1), [7, 8].

Similarly, a rise in absorbance was observed for the Hydrogen Peroxide (H_2O_2). Sample 4 from 300nm to 350nm. However, unlike the MNPs sample, a broader peak was observed before a gradual decrease with a sharp drop to minimum at 500nm. Unlike the MNP sample, another sharp rise in absorbance was observed from 500 to 560nm. These broad peaks at 350-460nm suggested slower degradation to other oxidative products. The sharp drop and rise at 500nm also suggested the presence of different oxidative products from those observed for the MNPs. On the other hand, the SSMNP – No2 showed a continuous gradual decrease in absorbance from 300nm down to 560nm as shown in the figure above. This showed that there was a direct transformation to other oxidative products without the formation of phenols which absorbed maximally at 350nm. This result showed that the presence of starch in the SSMNPs caused a significant change in the catalytic property of the iron oxide –magnetite compared to what was observed for the MNPs.

The Fenton sample – No 3 absorbed maximally with broad peak within 300-360nm but dropped sharply from 360-400nm with a gradual decrease to a maximum at 560nm. This result implied that the primary product (phenols) had possibly undergone further transformation into other products with lower absorptivity.



V. Conclusion

The synthesis of nanoparticles of magnetite MNP, the starch stabilized magnetic particles and Fenton reagents via a simple co-precipitation reaction has been reported. The particles find use in the degradation of Polycyclic Aromatic Hydrocarbons (PAH). A close investigation of their degradations reveals that, useful product of phenols and phenolic derivatives come from the PAH due benzene.

A UV-Vis scan exposes the presence of phenols, catechol, resorcinol, quinol, pyrogallol solutions just to mention but a few.

Other reagents are the cresol derivatives. Phenol is a useful solvent of bench reagent. It is a precursor for other intermediates and laboratory reagents. Phenols and its derivatives are useful in making nylon, epoxy resins, dyestuffs, explosives and pharmaceuticals.

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