Use of Activated Persulfate in the Removal of Petroleum Hydrocarbons from Crude Oil Polluted Soils

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Abstract

Persulfates as very strong oxidants, have found a wide range of applications. Prominent among these is its use in the oxidation of organic contaminants especially hydrocarbons in the environment. Since crude oil is made up of mainly hydrocarbons, it follows that persulfates can be used in the remediation of crude oil polluted soils. The three prominent hydrocarbon groups - Total Petroleum Hydrocarbon (TPH); benzene,toluene, ethylbenzene and xylene (BTEX); and Polycyclic Aromatic Hydrocarbons (PAH) are used in this work to study the ability of persulfates to degrade hydrocarbons in crude oil inundated soils. This was done by spiking soil samples with bonnylight crude oil and subsequently treating the mixture with potassium persulfate solution at acidic, neutral and basic pH ranges. Oil extracts from the treated and an untreated soil samples were later analysed using a gas chromatograph (GC). Efficiency of hydrocarbon removal was selective. While persulfate was good in the removal of the BTEX, it was found not to be so effective in the removal of the PAHs. Percentage hydrocarbon removal for BTEX was about 97%, 95% and 95% at acidic, neutral and basic pH ranges respectively but less than 27%, 3% and 41%, for the PAHs at the acidic neutral and basic pH ranges respectively . The four and five ringed PAHs were degraded more than the three and two ringed ones at the indicated pH ranges. The complete disappearance of the nC_{20} and above hydrocarbons at the neutral pH range was noteworthy.

Key words: Persulfates, bonnylight, TPH, BTEX, PAH, crude oil.

Introduction

Persulfates are strong oxidants that have been widely used in the industries to achieve a wide range of goals. These include clarification of water bodies, micro-etching of cupper printed circuit boards, initiation of emulsion polymerisation, determination of total organic carbon (TOC), in situ and ex situ chemical oxidation of many organic contaminants in water and sediments etc. Among these, its use in the in situ and ex situ chemical oxidation of organic contaminants seems to be the emerging trend[1, 2, 3].

Persulfates are available as ammonium, potassium and sodium salts. The production of ammonia gas limits the use of ammonium persulfate while low solubility of potassium persulfate makes it less desirable than sodium persulfate. As a result, sodium persulfate a yellow crystal is usually used at 10-20% solution. Potassium persulfate, a white corrosive powder is used after the difficulty in dissolution is managed usually by dissolving excess salt in water with moderate and sustained heating. The dissociation of persulfate salts gives the persulfate ion ($S_2O_8^-$) which is a very strong oxidant that is capable of oxidizing most organic substances especially hydrocarbons to carbon dioxide, water and other oxygenated products. The standard reduction potential for the half reaction is +2.01volts. This is very close to that of ozone (2.2v) and more than that of hydrogen peroxide (1.4v) and permanganate (1.7v)[3, 4].

$$S_2O_8^- + 2e^- \longrightarrow 2SO_4^{2-} \quad E^o = +2.01v$$

While the direct oxidation via the persulfate ion is very effective, the free radical oxidation is known to be more effective. The sulphate radical is produced through the activation of the persulfate using heat, electromagnetic radiation or catalysts eg. Iron (II) salts or cupper (I) salts etc. These are species that easily increase their oxidation states by the release of a single electron that acts as initiator for the free radical reaction.[1,5]

$$S_2O_8^- + initiator \longrightarrow SO_4^- + (SO_4^- \text{ or } SO_4^{2-})$$

The free radical mechanism is the preferred method given the high redox potential of SO_4^- Which is 2.6v as against 2.01v of the persulfate ion.[6]

The high redox potential makes it possible for it to be used in the destruction of a wide range of contaminants prominent among which is the petroleum hydrocarbons.

These group of hydrocarbons are ubiquitous in crude oils. They have been loosely grouped into the aliphatics called Total Petroleum Hydrocarbons (TPH) and the aromatics classed into Benzene, Toluene, Ethylbenzene and Xylene (BTEX) and the Polycyclic Aromatic Hydrocarbons (PAH).

These group of hydrocarbons have been found to be susceptible to attack by persulfates.[3, 7]

In this study, the ability of iron (II) sulfate-activated potassium persulfate to degrade petroleum hydrocarbons in a crude oil polluted soil samples is evaluated at the acidic neutral and basic pH media since most radical production reaction are pH dependent. The Bonny light crude - the most abundant crude type in the Niger Delta area of Nigeria is used as the source of petroleum hydrocarbons. The extent of degradation of the hydrocarbons is determined using Gas chromatography(GC) before and after treatment of the soil samples with the oxidant under study.

Material and Methods

250g of sandy soil samples were weighed into three 1L glass beakers with their pHs adjusted to acidic, basic, and neutral using NaOH and HCl. Each of the soil samples in the various containers were then spiked with 20ml of Bonny light crude oil from the Bomu oil field in Rivers state Nigeria.The soil-crude oil mixture in each of the containers were stirred to achieve homogeneity. The sample in the containers were subsequently treated with potassium persulfate (40g in 60ml of water), stirred again and allowed to stand for one week to achieve complete oxidation.

The samples from the three containers i.e at acidic, basic and neutral pHs were taken to the laboratory for analysis together with a sample of untreated Bonny light crude oil/sand mixture used as control.

The three hydrocarbons components mentioned above were all analyzed with a high resolution HRGC MEGA 2 series (FISONS instrument) Gas chromatograph (GC) equipped with a flame detector and the peak areas analyzed with an SRI model peak simple chromatography data system. A silica column of (30 m x 0.25umx 25mm) was used. TPH was analyzed at a column temperature of $60^{o}C$ for 2 minutes to $300^{o}C$ programmed at $12^{o}C/min$ with nitrogen as the carrier gas. Hydrogen and air flow rate were 9psi and 13psi respectively.

PAH was analyzed at a column temperature of $98^{o}C$ for 1minute to $300^{o}C$ programmed at $80^{o}C/min$ and air flow rates were 12psi and 15psi respectively. BTEX was analysed at the initial temperature of $30^{o}C$ for 1minute then increased to $180^{o}C$ at $50^{o}C/min$ and to $230^{o}C$ at $20^{o}C/min$. Helium was used as the carrier gas.

Results and Discussion

TPH: The amount of the aliphatic hydrocarbons in the untreated soil samples is shown in Table-1 and the chromatogram presented in figure-1.The effect of treatment of the sample on the aliphatic components of the crude at the various pH ranges is shown on table-2 and figures-2-4, with the chart on Figure-5 providing a one glance assessment.
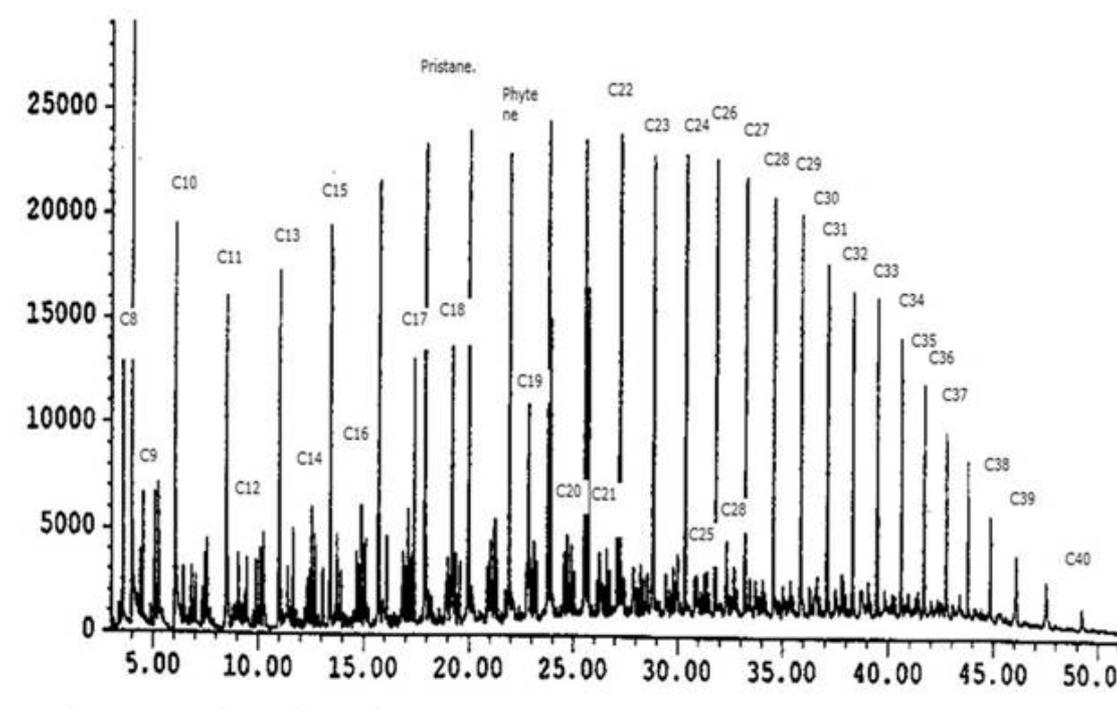

Figure-1
TPH fingerprints of the oil extract before treatment with the oxidants

Table-1
TPH concentrations of the oil extract before treatment with the oxidants

SAMPLE CRUDE.	AMOUNT (mg/kg)	SAMPLE CRUDE.	AMOUNT (mg/kg)
C8	3.0843	C25	27.7663
C9	6.9924	C26	32.5623
C10	1.0983	C27	27.5731
C11	10.7382	C28	36.0934
C12	8.0234	C29	35.7871
C 13	15.7742	C30	32.9731
C14	6.3334	C31	23.0089
C15	19.8349	C32	18.4261
C16	15.9832	C33	17.0245
C17	18.5563	C34	15.6378
C18	19.6672	C35	5.0092
C19	28.0083	C36	18.2231
C20	22.5723	C37	11.0893
C21	29.1120	C38	6.4483
C22	7.2284	C39	5.9734
C23	34.8734	C40	1.1123
C24	16.7663		

Table-2
Distribution of the TPH components of the oil extracts after treatment with potassium persulfate at acidic,
neutral and basic pH media

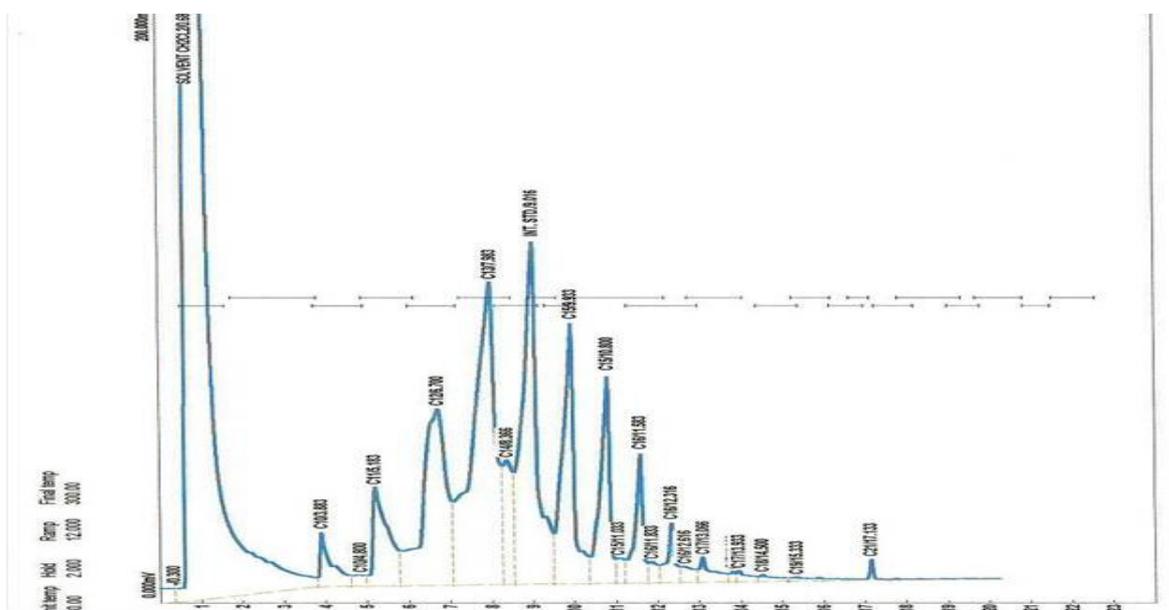| SAMPLE	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}
ACIDIC	-	0.05	0.07	0.11	0.42	-	0.65	0.21	0.01	0.01	0.01	-	0.01	-	-	-	-
BASIC	0.08	0.32	0.54	0.79	1.23	-	0.98	0.62	0.11	0.01	-	-	-	-	-	-	-
NEUTRAL	-	0.38	0.66	0.89	-	1.08	0.75	0.32	0.05	0.05	0.05	0.03	0.04	0.02	0.01	-	0.01

Figure-2
Chromatogram showing TPH components after treatment of the soil
with potassium persulfate at the acidic medium

The most striking feature of the treatment with persulfate as the oxidant is the disappearance and the near complete disappearance of some hydrocarbon fractions. The average percentage reduction/removal of the hydrocarbons at the different pH ranges is above 96% with some hydrocarbon species especially the C_{20} and above hydrocarbons experiencing complete disappearance at the neutral pH medium.it could be that the shorter chain aliphatics were completely oxidized while the longer chain aliphatics were partially attacked with some breaking down to the short chain hydrocarbons. This could also be deduced from the not-too-pronounced unresolved complex mixtures (UCM) found in the chromatograms.

Also it can be seen especially from the chart in figure 5 that the oxidation of the aliphatic components of the oil in the soil using potassium persulfate was not seriously affected by pH of the soil under study.

PAH: The PAH distribution of the untreated crude oil and its GC chromatogram is presented in table-3 and figure 6. It is particularly worthy of note that pottasium persulfate is not a very good oxidant in the removal of PAHs from crude oil polluted soil, unlike the other hydrocarbon groups discussed above .This can easily be seen from table-4 and figures-7-10.

Table-3
PAH distribution of the crude oil extract before treatment with persulfate oxidant

SAMPLE CRUDE OIL	Amount (mg/kg)	SAMPLE CRUDE OIL	Amount (mg/kg)
Acenaphthene(A1)	9.2333	Naphthalene(A7)	10.6470
Phenanthrene(A2)	12.0993	Chrysene(A12)	14.9940
Anthracene(A8)	24.7055	Fluorene(A9)	21.7326
Fluoranthene(A4)	12.3286	Dibenzothiophene(A13)	1.0884
Pyrene(A5)	1.1235	Acenaphthylene(A10)	12.9644
Benzanthracene(A6)	17.2210		

Table 4
PAH distribution of the oil extract after treatment with the oxidant
(persulfate) at the different pH media

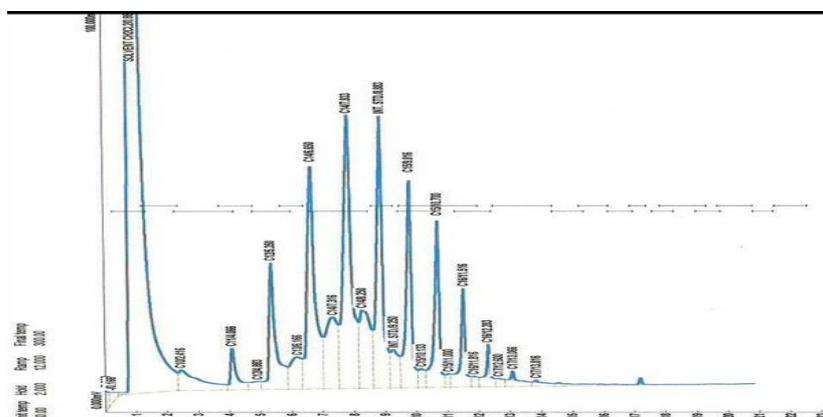| PAH (mg/kg)	Acidic	Neutral	Basic
Acenaphthene	17.85	33.18	24.09
Phenanthrene	6.25	6.4	7.30
Anthracene	4.87	11.87	6.91
Fluoranthene	1.55	3.06	2.43
Pyrene	0.89	1.53	1.12
Benzanthracene	18.47	49.29	48.12
Naphthalene	-	66.28	1.87
Chrysene	-	-	-
Fluorene	11.17	19.99	14.21
Dibenzothiophene	-	-	-
Acenaphthylene	1.93	3.5	2.76

Figure-3
TPH components of the soil treated potassium persulfate at the neutral pH medium

Figure-4
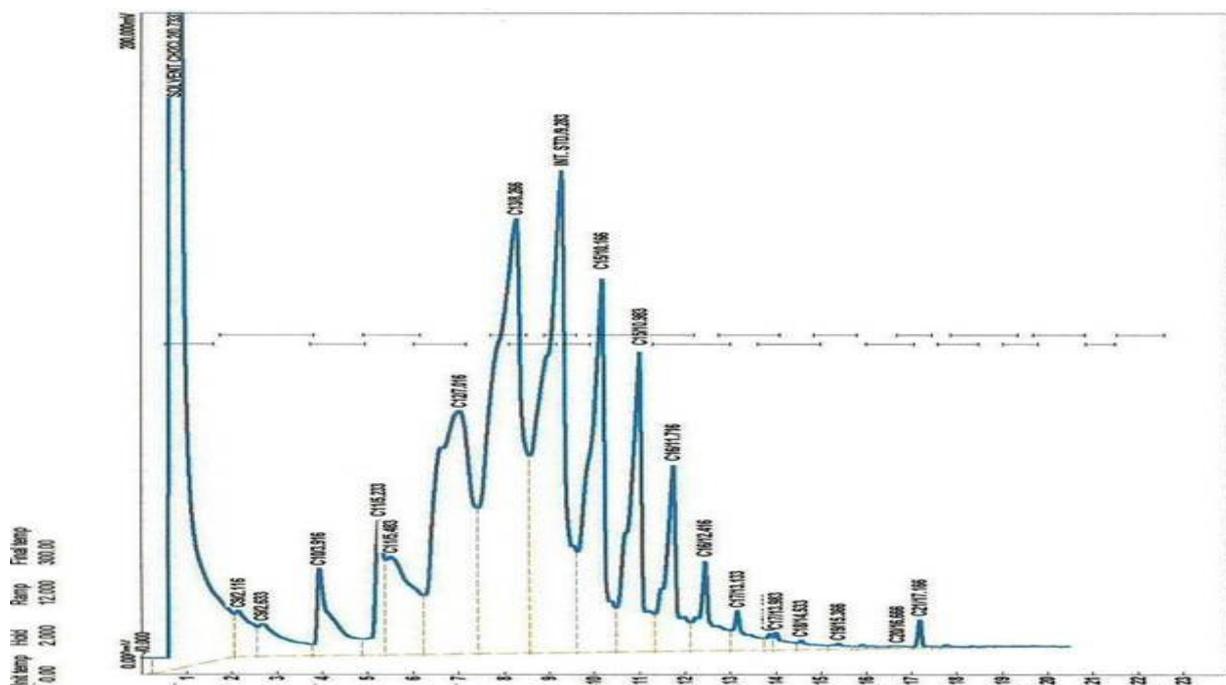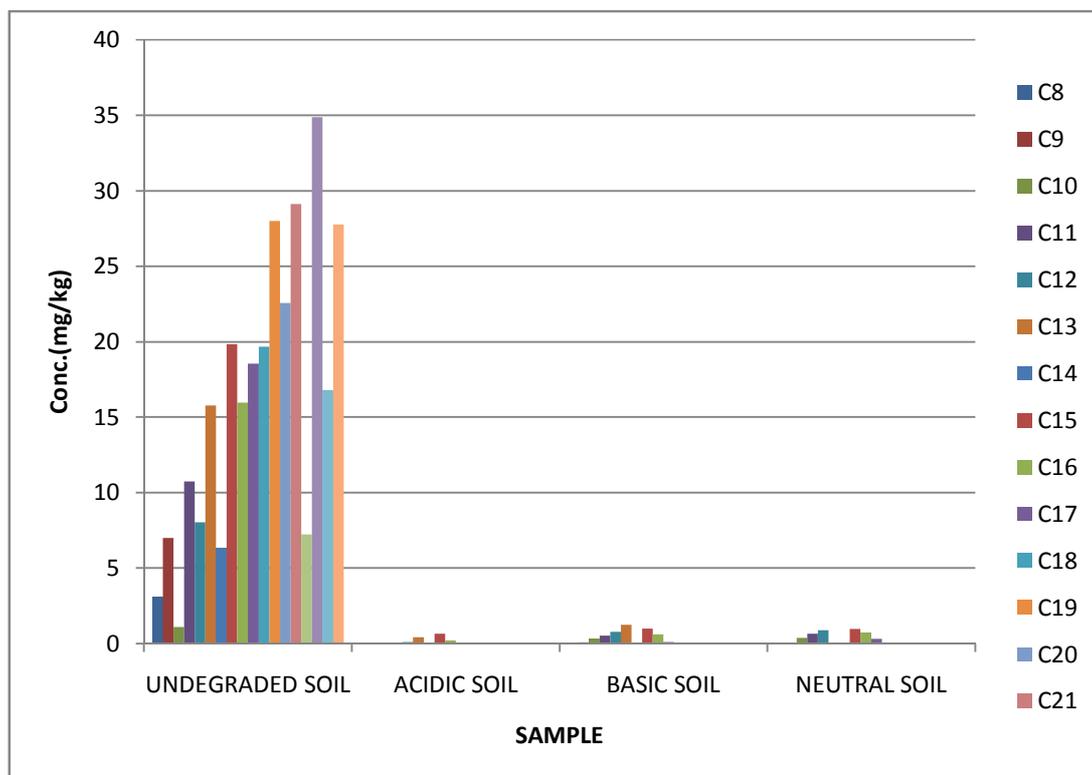**TPH components after treatment with persulfate at the basic pH medium**

Figure-5
Chart showing extent of TPH depletion of the samples after treatment with potassium persulfate at the various pH ranges
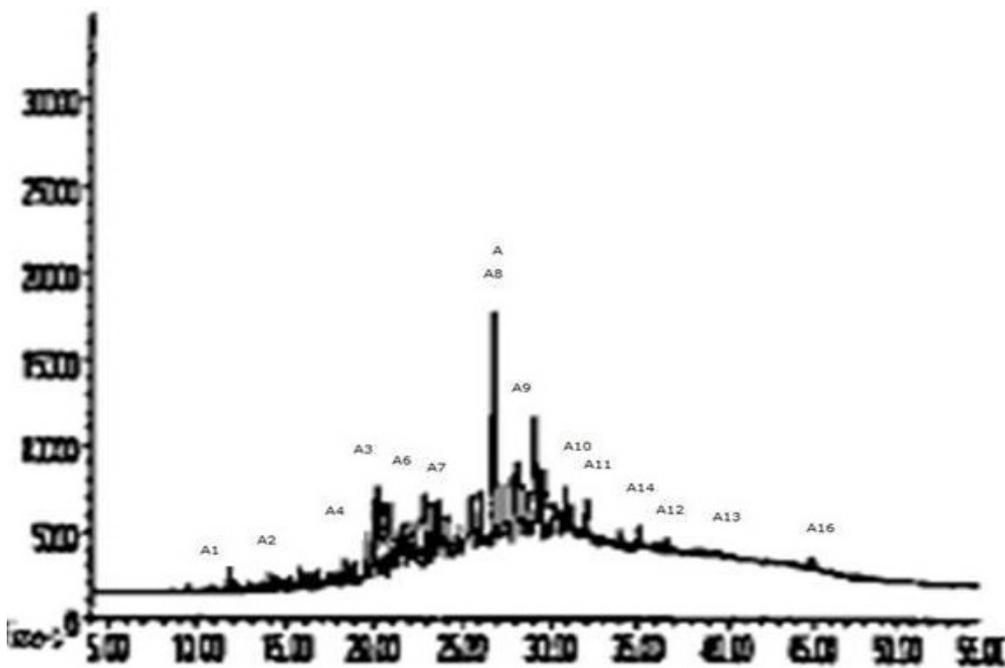
Figure-6
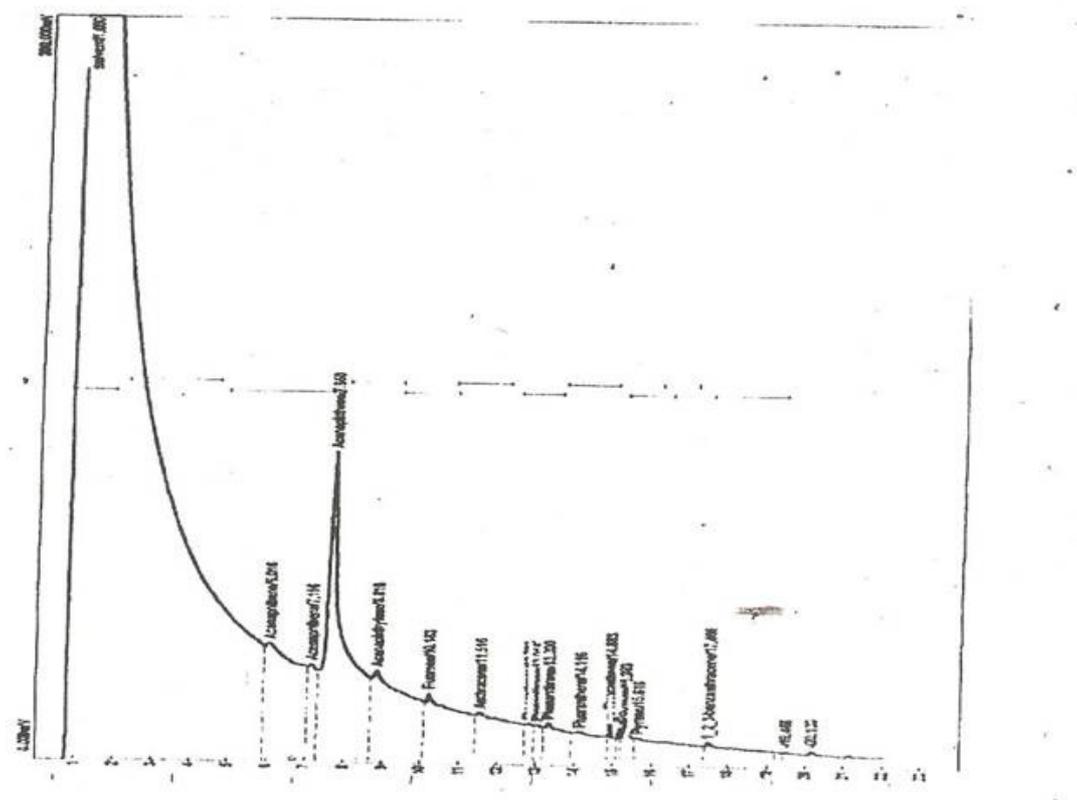**PAH distribution of the crude oil extract before treatment with the oxidants**

Figure-7
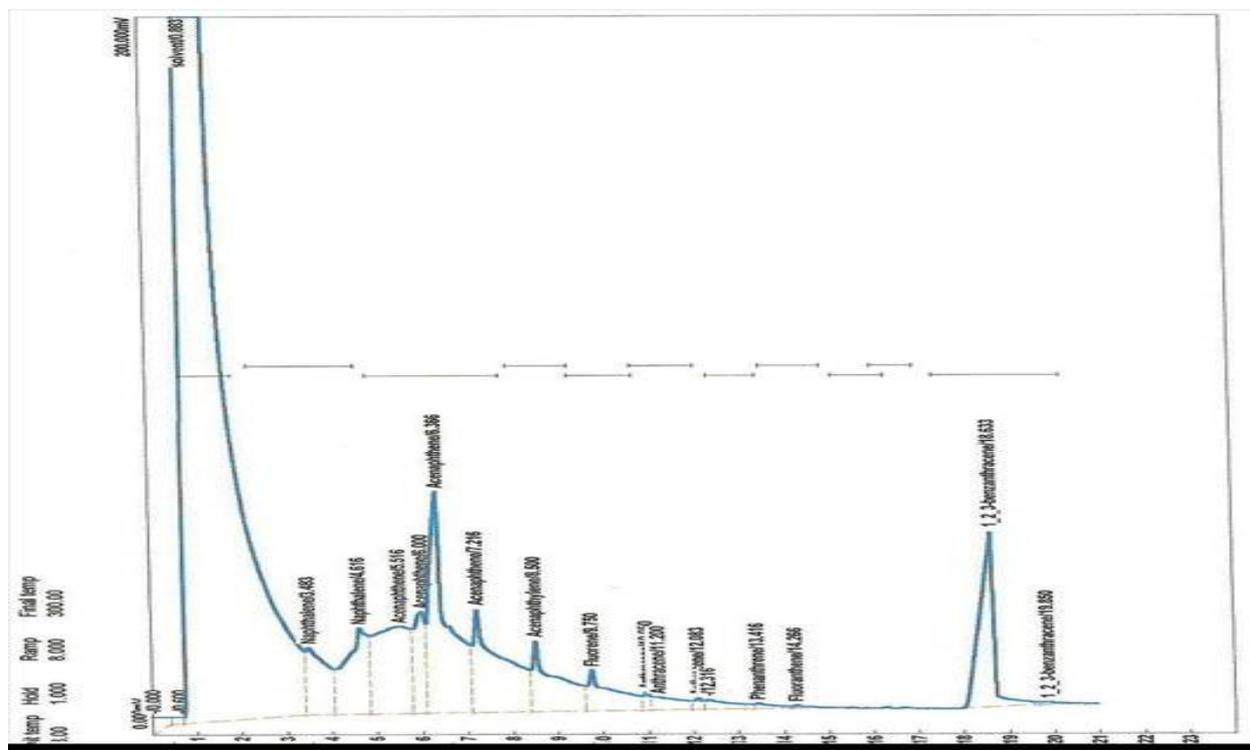**PAH fingerprints of the soil sample after treatment with potassium persulfate**

Figure-8
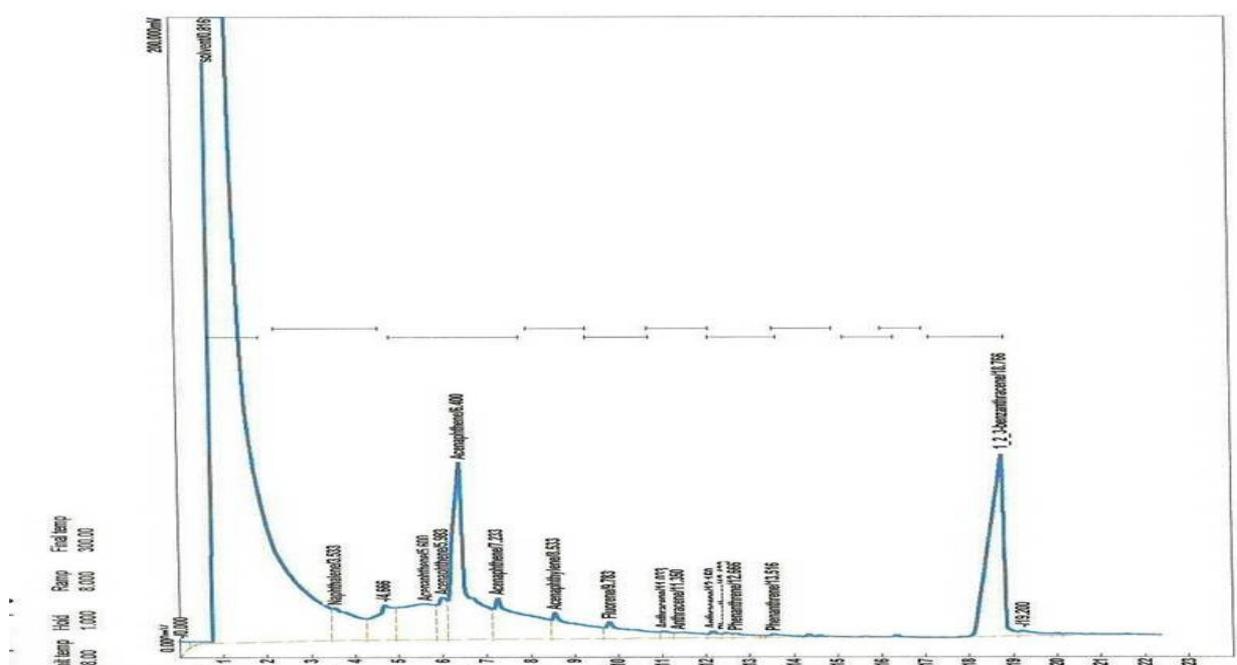**Chromatogram showing the PAH distribution of the treated soil sample at the neutral medium**

Figure-9
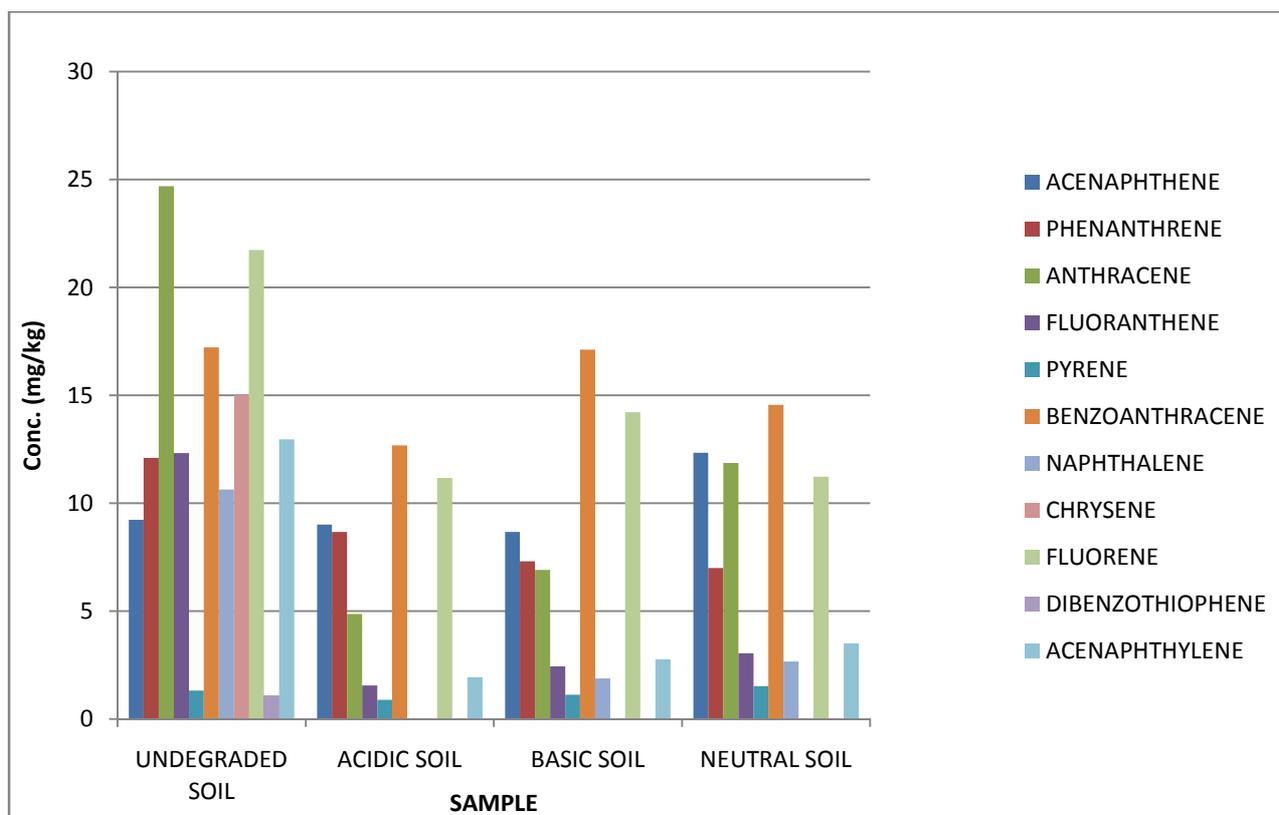**PAH Fingerprints of the soil sample treated with potassium persulfate at the basic pH medium**

Figure-10
Chart showing the extent of depletion of PAH components of the sample at different pH media after treatment with potassium persulfate

The amounts of benzoanthracene and naphthalene experienced a surprising increase in concentration after treatment with potassium persulfate at the basic pH medium. This could be as a result of conversion of the five or six ringed-PAHs in the crude oil to the two or three ringed PAHs in question. Also the average amount of the PAH removed by the oxidant is about 26% for the acidic medium, 2.7% for the neutral and about 46% for the basic medium. This is a far cry from the average of about 95% hydrocarbon removal reported in the use of Fenton's reagent as the oxidant.[6, 8.]

This notwithstanding, a 50% hydrocarbon removal within one week from any crude oil polluted site in the Niger- Delta , described as most crude oil polluted province in the world is a welcome development. The complete or near complete disappearance of the four and five-ringed PAHs (Chryslene & Pyrene) is also worthy of note. This may be a pointer that the oxidation of PAHs with potassium persulfate may not only be dependent on the moleculer weigth of the PAH but may also be a function of the structure of the hydrocarbon. The heterocyclic ring, dibenzothiophene is also completely removed after treatment with the persulfate oxidant.

BTEX: The concentration of the BTEX fingerprints of the crude oil under study is presented in figure-11 and table-5. The untreated crude is dominated by the Xylenes (ortho and para).

Hydrocarbon removal at the pH ranges studied was efficient. The average percentage hydrocarbon removal was about 97.5%, 95.8% and 95.2% for acidic, neutral, and basic pH media respectively. This is interesting given the dangerous nature of the aromatic hydrocarbons in the environment, with some of them known as carcinogens. It is also interesting to note that the use of persulfate as an oxidant reduced the amount of hydrocarbons (BTEX components) to less than 1mg/kg except the ethylbenzenes. This is very good for the Niger Delta soils given the benchmark set by the department of petroleum resources (DPR) for water and sediments in the Niger Delta area of Nigeria. The oxidation of the simple aromatic components of the oil under study using potassium persulfate at the different pH media could be said to be complete as can be seen from table-6 and figures-12-14. There were no UCMs in the chromatograms and hydrocarbon reduction was very efficient especially at the acidic pH medium

Table-5
BTEX concentrations of the oil extract before treatment with the oxidants

BTEX	Amount (mg/kg)
BENZENE	10.4630
TOLUENE	09.0730
ETHYLBENZENE	15.6402
P,M-XYLENE	16.5656
O-XYLENE	20.6321

Table-6
BTEX concentration of the soil samples at the acidic, neutral and basic pH media
after treatment with potassium persulfate

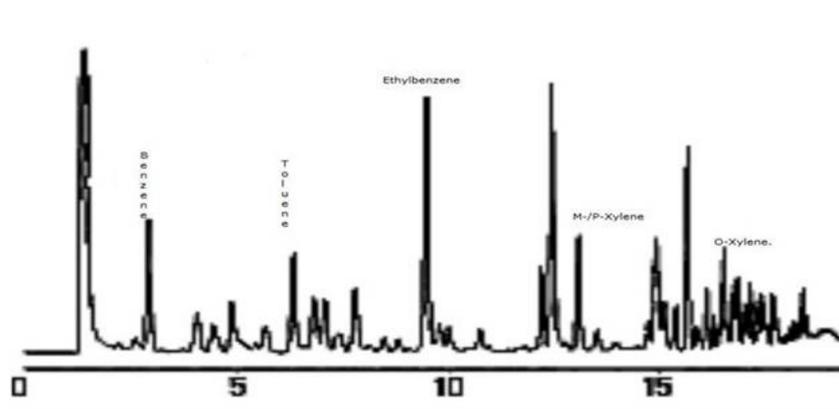| BTEX (mg/kg)	Acidic	Neutral	Basic
BENZENE	0.3201	1.0721	0.2361
TOLUENE	0.1091	0.5160	0.5002
ETHYLBENZENE	1.2370	1.2621	1.6566
P,M-XYLENE	0.0065	0.0098	0.4137
O-XYLENE	0.1012	0.1025	0.6603

Figure-11
BTEX fingerprints of the oil extract before treatment with the oxidants

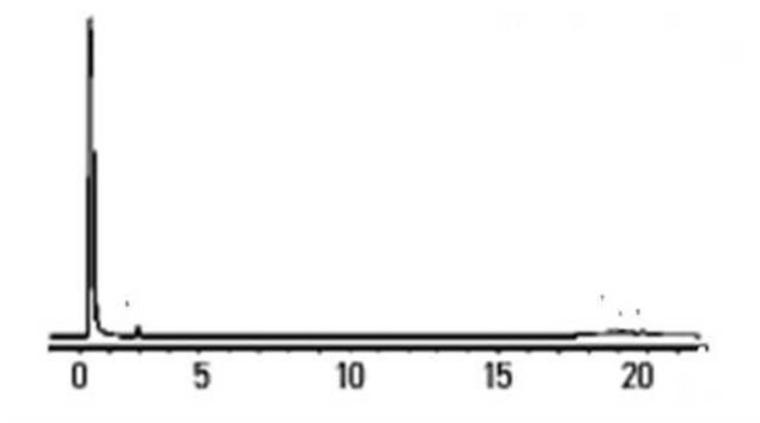**Figure-12**
Chromatogram showing the BTEX concentration of the soil sample after treatment with potassium
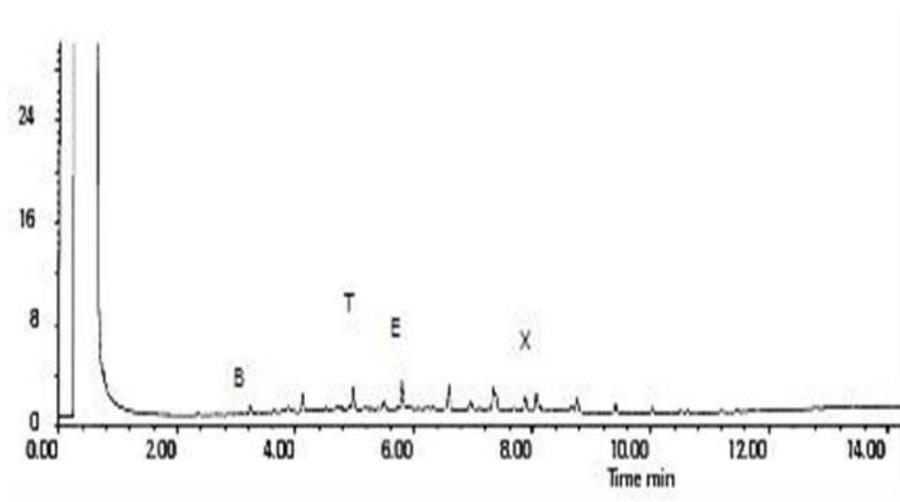**persulfate at the acidic pH range**

Figure-13
Concentrations of the BTEX components of the soil samples after treatment with potassium persulfate at the neutral pH medium

Figure-14
Chromatogram showing the BTEX concentrations of the soil samples after treatment with potassium persulfate at the basic pH medium
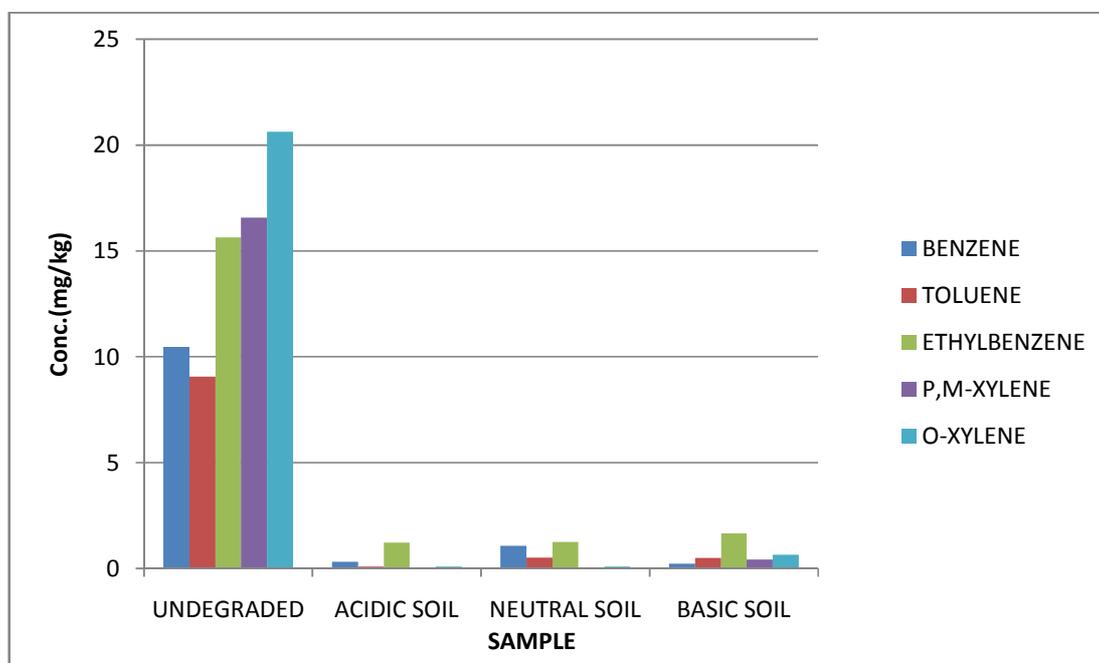

Figure-15
Chart showing depletions of the BTEX components of the samples at the different pH media after treatment with potassium persulfate

Conclusion

This work has shown that potassium persulfate is a promising oxidant for management of crude oil polluted soils. The results has shown that the oxidant will work well in sites polluted by light crudes that are dominated by the aliphatic hydrocarbons and the one-ring aromatics, but may not be well suited for the remediation of sites polluted by heavy crudes or ashphaltic crudes that are dominated by polycyclic aromatic hydrocarbons.

Acknowledgement

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