

## **Investigating the effect of pH on potassium ferrioxalate and sodium persulphate (oxidants)'s potentials in the removal of PAH AND TPH from petroleum products contaminated ground water.**

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**Abstract:** Groundwater contamination by organic compounds is a widespread problem worldwide. Particularly, organic compounds from petroleum products (e.g., gasoline, diesel, fuel oil etc.) are frequently detected in groundwater because of different types of spills occurring from pipelines and aboveground storage tanks (AST) or underground storage tanks (UST). In this study, Potassium ferrioxalate and sodium persulfate were used to investigate the effect of the clean-up or reduction of water contamination to a more acceptable level and to achieve this, crude-oil contamination of ground-water was simulated under laboratory conditions using groundwater samples collected from existing hand-dug wells at D Line area of Port Harcourt, Nigeria. Different doses of the oxidants (i.e. Sodium persulphate and Potassium ferrioxalate) were added to samples of ground-water. The treated water samples were left to equilibrate for 7 days, after which the total petroleum hydrocarbon (TPH) and Poly Aromatic Hydrocarbons (PAH) contents of the samples were measured.

**Key words:** Sodium Persulphate, Ground water Simulation, Potassium Ferrioxalate, Petroleum products.

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### **I. Introduction**

Ground water is a global source of drinking water and very vital for both industrial and agricultural purposes. Its pollution affects useful land sites and negatively impacts the surrounding environment especially and cause health hazards through diets, drinking and direct body contacts as drinking contaminated groundwater can result to diseases such as hepatitis, dysentery, cancer etc. (Siegrist, *et al.*, 2001); Liang, *et al.*, (2011) reported that groundwater contamination could result from both organic and inorganic substances especially from common global sources which include: accidental spill/release of petroleum products (e.g. gasoline, kerosene, diesel, and fuel oil) from above ground storage tanks, underground storage tanks, and pipelines.

Organic compounds have been a major pollution problem in groundwater as their presence in water can create hazards to public health as well as the environment. One of the most common sources for PAH-contamination of soil and groundwater are spills involving the release of petroleum products such as gasoline, diesel fuel oil, lubricating oil and heating oil from leaking oil tanks. Because of their polarity and very soluble characteristics, the organic chemicals (PAH) of petroleum products will be able to enter the soil and groundwater systems and cause serious pollution problems. This study focuses on PAH and TPH contaminants, their characteristics and also try to provide information on what they are, why they are a risk to human and environment and how they might be removed through chemical oxidation remediation from contaminated sites.

It has been a problem dealing with the removal of PAH and TPH contaminations since the first-day oil was discovered (Jain, *et al.*, 2011) and the consequent effects have affected the availability of safe drinking water, a very vital need for human existence (WHO, 2011). This means that sufficient and safe supply of water necessary for human development is constantly depleted. Statistics have shown more deaths from effects of insufficient and unsafe water supplies due to hydrocarbon contaminations than from all forms of violence, (WHO, 2002). All over the world especially in developing countries groundwater has become such a vital agricultural and drinking water sources with 49.4% of sampled households from the 2006 Nigerian household census depending on it for their agricultural and domestic use. The high dependence on groundwater stems from the belief that it is free from pathogens freely found in surface waters (Eawag, 2011).

Ground water pollution according to Hoekstra *et al.*, (2011) causes stench and filthiness that ultimately sabotage the quality of the environment, reduce agricultural plantation and growth, restricted land use and development that diminish property values, causing neighbourhoods to suffer reduced property values due to the external health risk in the surrounding areas.

The tendency for contaminated soil water to leach into the ground water is largely controlled by forces operating from either the ground surface (infiltration, evaporation) or from the bottom layers of the zone of generation which eventually leads to the development of soil water potential gradient, first in the vertical direction (NRC, 1993). Groundwater contamination from petroleum hydrocarbon has indeed become a major environmental concern because of its wide usage and many contamination incidences. In the United States of America alone, it is reported that there are up to 400,000 contaminated groundwater sites. (Thiruvkatachari *et al.*, 2008). Currently, both ex-situ and insitu remediation technologies are being improved in order to solve this environmental problem, (Gavrilescu, 2005). Reports also have it that in recent times, technologies are becoming more popular, (Hoekstra *et al.*, and 2011)); however, it is difficult to select an optimal method and processes at low overall costs (Liquang *et al.*, 2001). Though many techniques have been used to develop support tools for site remediation decision-making, it should be known that carrying out more studies on this subject will help to create management systems for petroleum contaminated sites in which desired remediation methods will be the lowest cost and time efficient as well as guarantee safety of the environment and public health. Many remedial methods are available but chemical oxidation has been rated high and proven for the remediation of groundwater contaminated with petroleum products (Julien *et al.*, 2011; Thompson *et al.*, 2008). The Greater number of scientific researchers are currently shifting attention to chemical oxidation because it is a preferred remedial alternative to other remediation techniques for hydrocarbon contaminated ground water due to observed limitations of conventional ground water clean-up technologies (Liang *et al.*, 2011). Regenesis, (2007) has noted that chemical oxidation method is fast and efficient for remedial mass reduction at a lower overall cost because there are no moving parts that could break down, no discharge or effluent disposal permits, it generates specific data and allows optimisation prior to full implementation (refine chemistry, incorporates efficiency and cost saving).

The chemical oxidation method is a more promising technology in view of its advantages over others as its surface disturbance is limited when compared with other methods. The saying that anything that has advantage also has a disadvantage shows that chemical oxidation is however not without its side effects and challenges; for instance, its capital, technical and operational costs are high and very site specific. According to Mulligan *et al.*, (2000), this kind of information is indispensable for decision makers and all stakeholders in the selection of appropriate technology for the treatment of hydrocarbon contaminated groundwater resources. It will also provide among other things, a general overview of chemical oxidation technology by examining various oxidants and their reaction chemistry, the effect of geology and hydrogeology on oxidant performance, oxidant delivery methods and future research needs.

Chemical oxidation is a form of oxidation technique known to be the most rapid, cost saving and innovative treatment method for the remediation of soil or ground water contaminated by targeted environmental contaminant concentrations (Crimi and Taylor, 2007; Liang *et al.*, 2011). The successful use of chemical oxidation remediation is dependent on several site-specific factors viz: composition of contaminants, the geology of the site, ground water properties and temperature prevalent on site of remediation. Chemical oxidation is useful for the treatment of a variety of organic compounds including those that are resistant to natural degradation, Liang *et al.*, (2011). This treatment method constitutes one-half of a redox reaction in which there is usually a loss of electrons; one of the reactants in the reaction becomes oxidized, or loses electrons, while the other reactant becomes reduced, or gains electrons. According to ITRC, (2005), chemical oxidation oxidizing compounds are used to reduce contaminants to less harmful or totally harmless compounds. Chemical oxidation therefore, involves the introduction of chemical oxidant(s) into the ground water with an intention to converting inherent hazardous contaminants to non-hazardous or less toxic compounds that are more stable, less mobile and/or inert (ITRC, 2005). The oxidizing agents commonly used include hydrogen peroxide catalysed with ferrous in Fenton's reagent (Claudia *et al.*, 2006; John *et al.*, 1993), potassium permanganate (David *et al.*, 2004) and sodium persulphate (Julien *et al.*, 2011). For proper application of different oxidants, laboratory studies must be carried out to choose the most suitable one and concentration, because each oxidant has its specific advantages and disadvantages.

In Nigeria few studies have been undertaken to determine the effects of ingesting groundwater with elevated levels of petroleum hydrocarbon especially PAH and other toxic substances, hence user awareness of such contaminations despite health risks associated with their ingestion are absent.

## **II. Methodology (Materials and methods)**

### **List of materials/equipment**

Materials include: 1. Erlenmeyer flasks 2. Shaker 3. Double de-ionized water 4. 4-litre plastic buckets. 5. pH meter. 6. Thermometer while reagents are: Sodium Persulfate and Potassium Ferrioxalate.

Degradation and Control experiments were conducted in 250ml Erlenmeyer flasks to determine a suitable type of oxidant and under what concentrations they will effectively oxidize selected contaminants {Transformer oil, Diesel (AGO) and Crude oil} in contaminated water samples through treatment. The reagent grade chemicals

(Potassium Ferrioxalate and Sodium Persulfate) used in all the tests conducted were obtained from Chris Colon Scientific Company, No.1 Obi Street, Diobu, Port Harcourt, Nigeria.

**Sample collection and treatment:**

Contaminated water samples were prepared by adding hydrocarbon products (transformer oil obtained from Nigeco Nig. Ltd., Port Harcourt, diesel and crude oil obtained from the Port Harcourt refinery) into a double de-ionized water in 4-liter plastic buckets. These mixtures were vigorously shaken for 15 – 30 minutes to saturate. 5ml of ameliorant solution was added to 30ml of each of the saturated water sample in the Erlenmeyer flask. These were then shaken in an orbital shaker centrifuge for twelve hours after initial pH meter readings.

**Analysis for the reduction of PAH and TPH.**

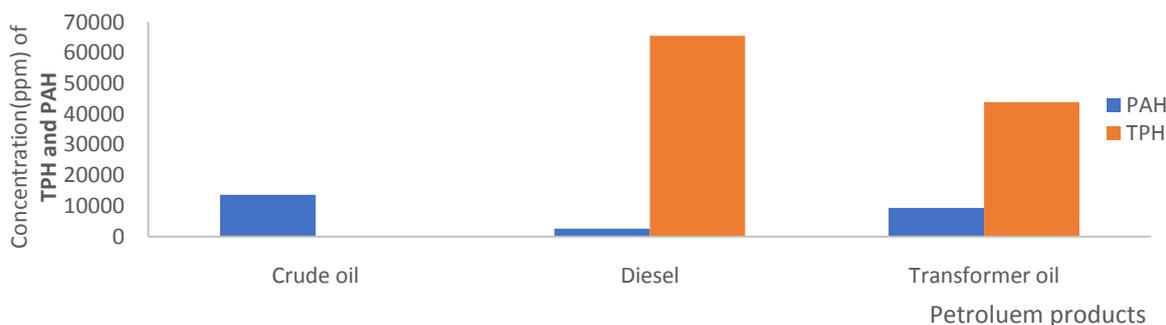
200ml of the contaminated water was mixed with 20ml of different oxidants in a 4 litre plastic bucket, covered and left to stand for 60mins at a temperature of 29°C and optimum pH of 7.2. At the end of the time, the petroleum products were separated and the concentrations of PAH and TPH were determined using GC-FID.

**Analysis for the effect pH**

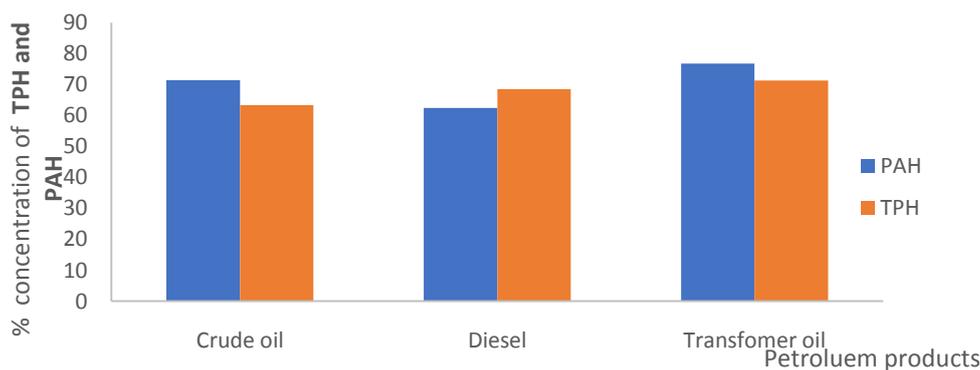
The pH of the contaminated water were adjusted to values, 3.0,4.5,6.0,7.5,8.0,9.5,11.0 and 12.5 using 0.1M HCL and 0.1M NaoH reagents. Then 10 ml of the oxidants each were added. The mixture was thoroughly shaken in a shaker for 1 hour (60minutes) over 29°C. The mixture was then separated using separating funnel and the concentrations of TPH and PAH determined using GC-FID.

**III. Results and discussion**

Data used for this study were obtained from both primary and secondary sources. The primary data are concentrative of contaminated groundwater over time in laboratory condition while secondary data sources are academic literatures from journals, books and conferences. Results obtained in this study are as plotted in figures below:



**Fig.1:** TPH and PAH in the petroleum products.



**Fig.2:** TPH and PAH in the contaminated water using sodium persulfate.

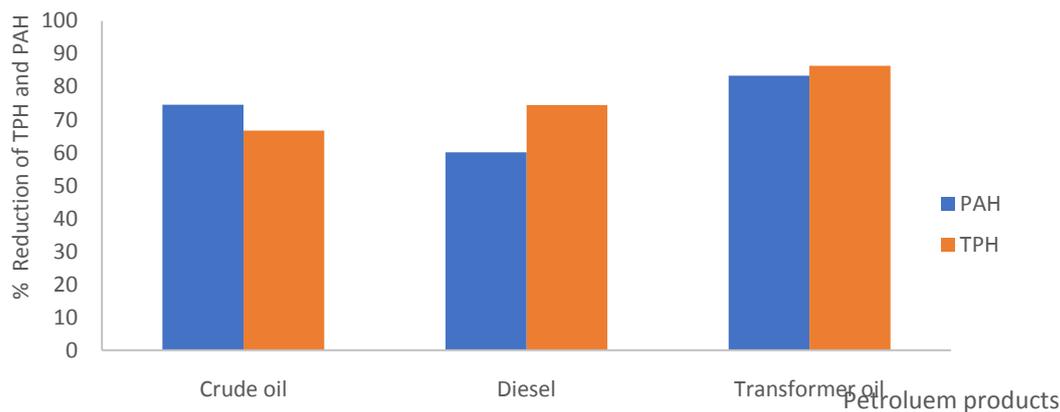


Fig. 3: TPH and PAH from contaminated water using potassium ferrioxalate.

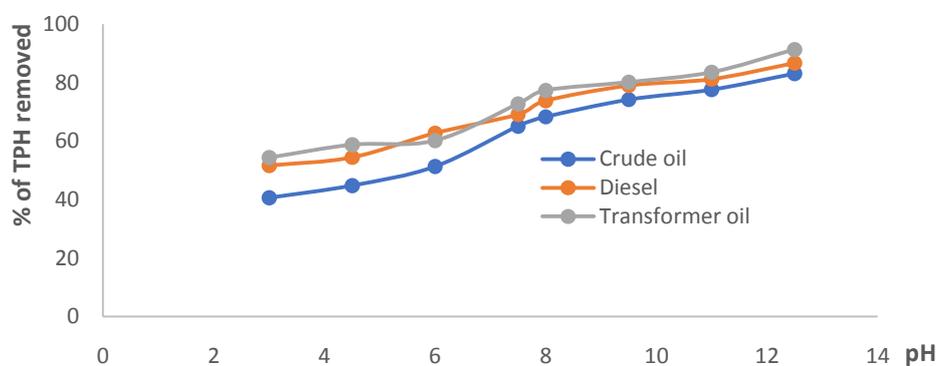


Fig. 4: Effect of pH on the removal of TPH from contaminated water using sodium persulfate solution.

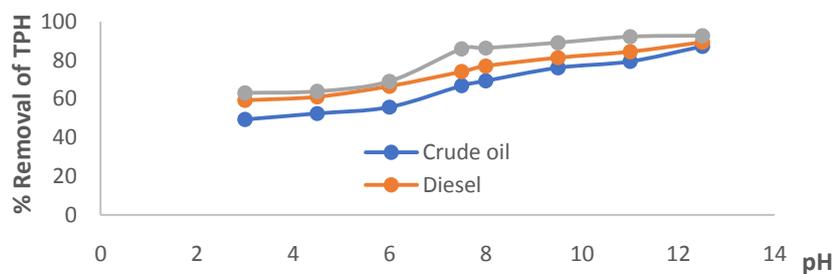


Fig. 5: Effect of pH on the removal of TPH from contaminated water using potassium ferrioxalate solution.

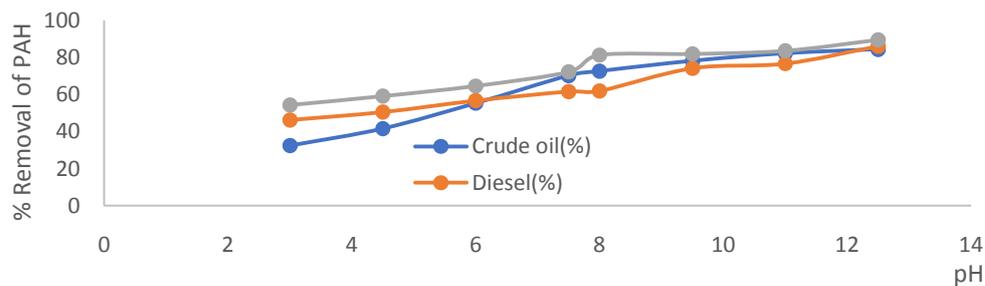
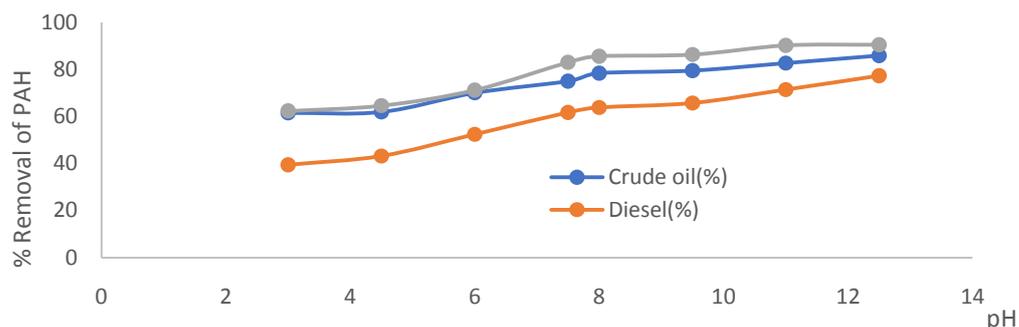


Fig. 6: Effect of pH on the removal of PAH from contaminated water using sodium persulfate oxidant.



**Fig. 7: Effect of pH on the removal of PAH from contaminated water using potassium ferrioxalate solution.**

#### IV. Discussion

Fig.1 shows the concentration (ppm) of TPH and PAH in the petroleum products used in the study. Results of total polycyclic aromatic hydrocarbon (PAH) in this study recorded elevated values of 13617.60 ppm for crude oil and 9417.53 ppm for transformer oil with slightly lower average concentration of 2613.87 ppm for diesel. TPH showed higher concentrations in diesel with 65471.78 ppm, transformer oil with 43860.1 ppm and very low concentration of 258.78 ppm in crude oil. The low concentration of TPH in crude oil could be attributable to the fact that refined petroleum products are more toxic compared to crude oil due to alteration of metal speciation as well as addition of new metal in the matrix during refining process (Ogoka; (2014).

Also from fig.1, it is evident that amongst the petroleum products, crude oil contains the highest amount of PAH (13,617.60 ppm) and lowest TPH (258.78 ppm). Diesel has the highest amount of TPH (65,471.7 ppm) and lowest amount of PAH (2613.87 ppm), while Transformer oil has the lowest amount of TPH (43,860.1 ppm) and PAH (9417.53 ppm).

Fig. 2 shows the %Reduction of PAH and TPH in the petroleum products (diesel, crude oil and transformer oil diesel) using sodium persulfate. Removal efficiency of hydrocarbons by sodium persulfate has been studied by several authors. Accordingly, fig. 4.2 shows that it was most efficient in Transformer oil (76.80%), Crude oil (71.40%) then least in diesel (62.40%). Similarly, the removal efficiency of sodium persulfate in TPH was highest also in Transformer oil (71.30%), least in Crude oil (63.39%) and Diesel (68.50%).

From fig.2, it is glaring that removal efficiency of TPH & PAH with Sodium persulfate was highest in Transformer oil. This could be attributed to chemical alterations of the substance during refining of crude oil. Removal of TPH from water sample using sodium persulfate activated by  $Fe^{2+}$  or alkaline conditions produced removal rates of between 63.39% and 71.30%, respectively. Higher % (71.40) reduction of PAH in crude oil than TPH. The reverse is the case for transformer oil which showed higher % (71.30) reduction of TPH. Persulfate anions ( $S_2O_8^{2-}$ ) according to Ogoka (2014) dissociates in water –Activators such as heat, ferrous iron, chelated iron, high pH, and peroxide increase oxidative strength through formation of sulphate radicals ( $SO_4^{\cdot-}$ )

This method is effective over a wide pH range as shown in figs. 2 and 3.

Fig. 3 shows the %Reduction of PAH and TPH in the petroleum products using potassium ferrioxalate.

In a related development, Fig. 3 shows efficient removal of PAH and TPH by using Potassium Ferrioxalate. From the results, removal efficiency was highest (83.46%) for transformer oil, next is Crude oil (74.60%) and least in diesel: Similarly, removal efficiency of TPH using Potassium Ferrioxalate was highest (86.40%) in the same transformer oil. The next is diesel (74.50%) and least in Crude oil (66.70%). These results are further shown in Fig. 3. It should be noted that transformer oil and diesel are refined products recording the highest removal efficiencies of TPH. This implies that refining processes must have altered the resistance of the substances to the effect of the oxidants.

Fig. 4 shows the effect of pH on the removal of TPH from groundwater contaminated with petroleum products using sodium persulfate solution. The effect of pH on the chemical breakdown of substances has been widely studied to show that pH plays significant role in the chemical oxidation of substances (Ogoko, 2014).

From fig.4, it is clear that high pH favours the chemical breakdown or removal of TPH from the contaminants in the presence of sodium persulfate. Also, high pH which is alkaline condition, favours the removal of the contaminants and the rate of removal is greatest in transformer oil (91.3%), followed by diesel (86.70%) and Crude oil (83.10%) at a very strong alkaline environment of 12.50. Generally, this also supports

the fact that better results are obtained with high pH values (alkaline environment). Persulfate decomposition due to enhanced formation of reactive surface hydroxo complexation was accelerated with pH increases (Li, et al; 2017).

In the case of removal of the contaminants using potassium Ferrioxalate solution, Results shown in Fig. 4.5 also favours a high removal efficiency. The percentage removal efficiency is slightly higher than that of sodium persulfate at similar pH situation. According to fig.5, at a very strong alkaline; pH of 12.50, the removal efficiencies are 92.70%, 89.30% and 87.20% for transformer oil, diesel and crude oil respectively.

Fig.6 shows the effect of pH on the removal of PAH from ground water contaminated with petroleum products using sodium persulfate oxidant.

Similar to fig. 5, the effect of pH on removal efficiency of PAH by Sodium persulfate also favours the alkaline environment. Although, it is less than that of TPH, fig.6 reveals that, its removal efficiency is still highest with transformer oil (89.50%), diesel (86.10%) and Crude oil (84.40%).

Fig.7 also shows a related reduction in the amount of PAH present in the contaminants using potassium ferrioxalate solution in the alkaline environment.

In comparison with other literatures, the effect of changes in pH in chemical breakdown of PAH and TPH cannot be over emphasized (Hao, et al.; 2016).

The analysis also shows that the removal efficiency is highest at a very strong alkaline condition.

From this study, it could be deduced that with pH being acidic as in most soils of the Niger Delta, the implication is that chemical oxidation using the above oxidant is not a favourable option of remediating impacted sites, unless pH of the site is highly madealkaline.

## **V. Conclusion/Recommendation.**

While polycyclic aromatic hydrocarbons (PAHs) refers to an ubiquitous family of several chemically related environmental importunate organic compounds of various structures and with different levels of toxicity, TPH is a term which describes a wide variety of derived petroleum compounds and its by- products. This TPH measures the gross quantity of these petroleum hydrocarbon products present in the environment rather than seeking to measure individual component separately which could be tedious and non-practicable.

Polycyclic aromatic hydrocarbons (PAH) especially are a large class of organic compounds with two or more fused aromatic rings. These compounds carry only carbon and hydrogen atoms with no substituent atoms or groups, whereas the general term, Polycyclic Aromatic Compounds (PACs) refer to those carrying substituent functional derivative (Srijata and Pranab 2011). PAHs are an important class of environmental contaminants because of their persistence and demonstrated adverse health effects. They are usually a ubiquitous class of organic compounds which have since been identified in ground and wastewaters (WHO, 2002). They however have very low water solubility, but soluble in organic solvents and highly lipophilic. It has, therefore become critically important at this period in time that areas with high concentration of hydrocarbon contaminants (PAH and TPH) be known and remediated to safeguard the environment and health of citizens. This has become necessary because most people in the suburban areas depend on untreated groundwater for drinking as well as other domestic purposes.

Further studies are recommended to be carried out by applying these oxidants on petroleum products polluted sites in order to determine their efficacy on large scale remediation.

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