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Persulphate-based degradation of total petroleum hydrocarbons in contaminated water

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Abstract-

The present study investigated the degradation of total petroleum hydrocarbons (TPH) in crude oil polluted water using sodium persulphate as a chemical oxidant. Laboratory-scale contaminations of water and degradation experiments using 0.1 M oxidant were carried out with contact time ranging from 1 to 15 days. The TPH extraction was carried out and analyzed using gas chromatography flame ionization detector (GC-FID) (Agilent 7890A). 72% of ETPH was degraded within 15 days from an initial concentration of ~137 mg/L. Results indicated 99% efficiency in TPH degradation achieved within the first 10 days after initial contamination. Remediation technique on laboratory- and field-scale is promising and could potentially address major oil pollution contamination issues.

Key words: Sodium persulphate, total petroleum hydrocarbons, crude oil, pollution, nano remediation

1. Introduction

Hydrocarbon contamination of soil and groundwater has been a recurring challenge globally, and particularly in oil rich countries such as Nigeria. This has impacted the availability of potable water and arable land in polluted regions. Consequently, local and international authorities are making concerted efforts to address this challenge through the use of innovative and emerging nano remediation techniques. Total petroleum hydrocarbon (TPH) is a term used to define an extensive family of chemical compounds originating from crude oil. They mainly consist of hydrogen and carbon and may contain volatile and semi-volatile compounds such as BTEX (benzene, toluene, ethylbenzene and xylene), n-alkanes and PAHs (polycyclic aromatic hydrocarbons) [1].

TPHs are important environmental contaminants due to their ease and frequency of release via accidental spillage, pipeline vandalism and industrial accidents. Enhanced natural attenuation, which has been largely employed for remediation of petroleum hydrocarbons in the Niger Delta region of Nigeria, has not been effective particularly for degradation of heterocyclic and polycyclic aromatic hydrocarbons [2]. Studies have reported occurrence of hydrocarbon-based contaminants in soil, sediment, water and biota in Nigeria, especially the Niger Delta [3 - 5]. However, chemical oxidants such as persulphates and percarbonates hold promise for environmental remediation.

Chemical oxidation is a process that converts organic contaminants into carbon dioxide and water or other non-hazardous substances. Ozone and permanganates have been widely reported in field and laboratory-scale studies prior to the emergence of persulphates, percarbonates and solid oxygen-supplying peroxides such as sodium and hydrogen peroxide [6]. The strength of



chemical oxidants derives from their oxidation / reduction potential – measured in volts (V) or millivolts (mV), which measures their tendency to be reduced when they acquire electrons. Furthermore, per oxygens such as sodium persulphate (with standard redox potential of 2.1 V) can be activated for greater degradation efficiency by heat [7], UV, ultrasound, and electron beam to generate sulfate radicals [8-10]. Other activation methods include the use of metals, alkaline solution, nanoparticles, organic and inorganic chelates, and mineral-based activation [11]. The aim of this study was to determine the effect of sodium persulphate - a chemical oxidant, on the degradation of total petroleum hydrocarbons (TPH) in crude oil contaminated water.

2. Methodology

2.1 Reagents:

Sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$) and dichloromethane purchased from Merck were used as received. Deionized water was produced with a Milli-Q system from Millipore. Anhydrous sodium sulphate was purchased from Minerals Water Ltd, UK.

2.2 Contamination of water

This study involved laboratory-scale petroleum contamination of water samples. 100 mL of deionized water placed in reaction vessels was contaminated with 15 mg of crude oil and left for 30 days with intermittent/periodic stirring and shaking. The concentration (mg/L) of TPH in water prior to degradation was also determined while the analysis of total petroleum hydrocarbons (TPH) in contaminated water was carried out at intervals within 15 days.

2.3 Chemical oxidation of TPH

Experiments were performed to evaluate the chemical oxidation of contaminated water using 0.1 M sodium persulphate over a 15-day period. Batch studies were performed without pH adjustment (circumneutral), room temperature (20 – 25°C), in the absence of light (using aluminum foil coverings). 0.1 M sodium persulphate was added to contaminated water samples and degradation of TPH determined at 2, 4, 6, 8, 10 and 15 days, respectively. Reaction was then stopped by adding methanol to each batch.

2.4 Extraction and analysis

Water samples were first extracted with dichloromethane before iodometric titration was carried out. The total petroleum hydrocarbons concentration was analyzed using a GC-FID 7890B from Agilent Technologies. A standard mixture was used to define the integration limits of the chromatogram area, corresponding to $\text{C}_{10}\text{H}_{22}$ and $\text{C}_{34}\text{H}_{70}$.

3. Result and discussions

The results of the concentration (mg/L) of TPH after oxidation and in water prior to degradation are presented in Table 1 and Figure 2, respectively. The result of analysis of total petroleum

hydrocarbons (TPH) in contaminated water carried out at intervals within 15 days is as shown in Figure 3.

The concentration of TPH in contaminated water was found to be 137.33 mg/L from initial spiking of 15 mg/100 mL in each reaction vessel. This represents a recovery of about 96% from initial contamination. The concentration of TPH in water decreased with time over a 15-day period with the lowest concentration (33.41 mg/L) obtained after day 15. Results indicated that about 72% of TPH had been degraded within this period. Of this percentage, 99% degradation was achieved within the first 10 days. The results indicated that increasing contact time increased the percentage of TPH removal. This can be attributed to decrease in surface activity for the uptake of pollutant particles. For instance, within 6 days, 38% of TPH had been degraded. This increased to about 71% after 10 days of contact between contaminated water and oxidant, representing 33% increase in degradation efficiency within 4 days. However, increasing contact time to 15 days only achieved 1% increase in TPH degradation.

Table 1: Concentration of total petroleum hydrocarbons in water after oxidation

Time (days)	TPH concentration (mg/L)
Initial concentration	137.33
Day 2	111.83
Day 4	91.40
Day 6	85.35
Day 8	58.76
Day 10	39.87
Day 15	33.41

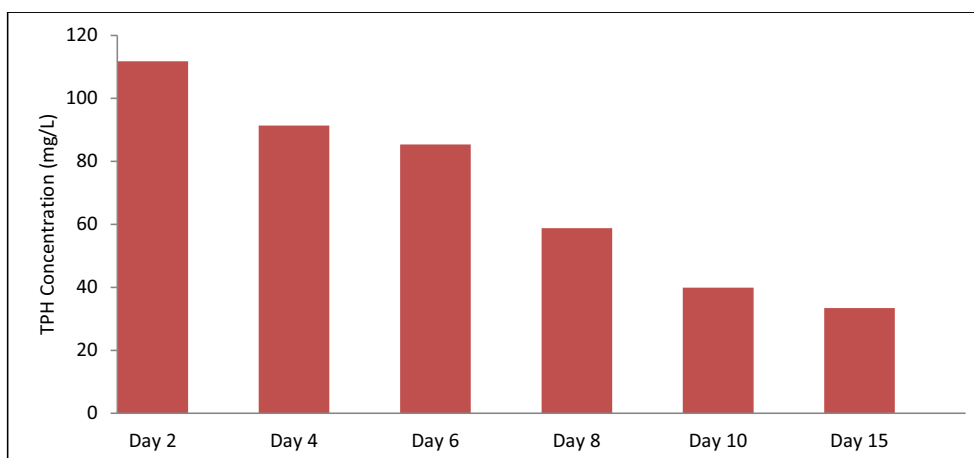


Figure 1: Chart showing effect of oxidant on ETPH concentration within 15 days.

Similarly, other studies have explored the use of sodium persulphate for oxidation of TPH. Desalegn et al. [12] reported >90% TPH degradation in oil sludge contaminated sediment within one week using persulphate activated with biosynthesized iron nanoparticles. The TPH concentration was analysed using GC-FID [9]. Results of a study on degradation of TPH in aged contaminated harbor sediments in France carried out by [13] has been reported. A comparative study using activated and unactivated sodium persulphate was employed with improved TPH degradation efficiency observed for the former. <5% degradation was observed when sodium persulphate alone was used for hydrocarbon oxidation. Improved hydrocarbon degradation efficiency using activated persulphate is due to the fact that ferrous iron (activator) used reacted with persulphate ion to produce stronger radicals. Furthermore, in a laboratory study on use of potassium persulphate for degradation of TPH, polycyclic aromatic hydrocarbons (PAHs) and BTEX in soil samples contaminated with bonny light crude oil, near complete oxidation was achieved for BTEX (>95%) under acidic pH within one week degradation of TPH and PAHs was less effective under similar conditions [14].

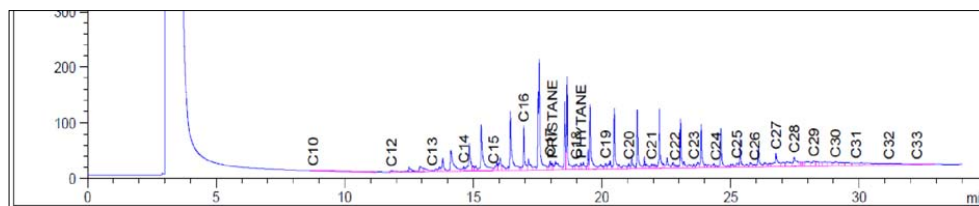


Figure 2: Chromatogram of initial concentration of total petroleum hydrocarbons in water.

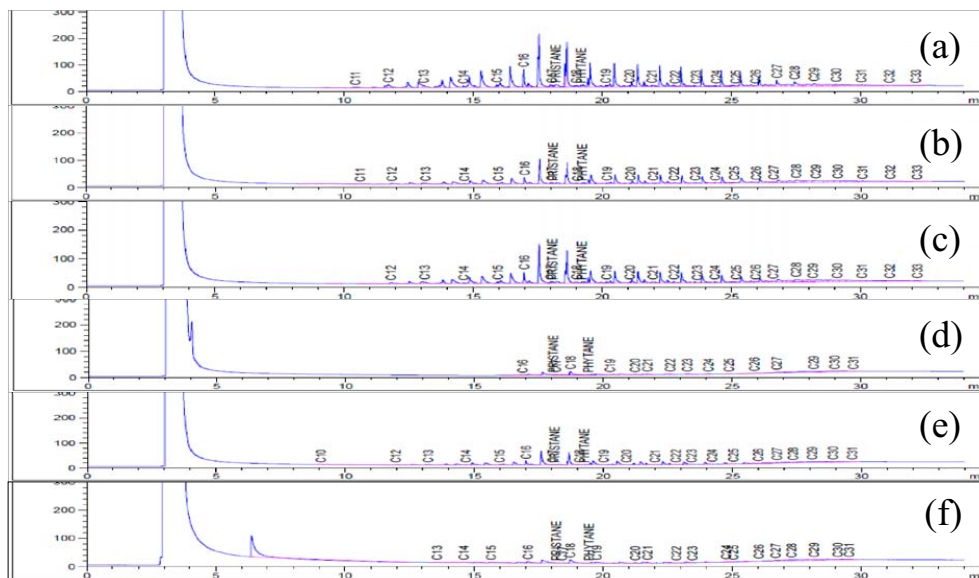


Figure 3: Stack chromatograms showing TPH concentration in water at 2, 4, 6, 8, 10 and 15 days, respectively.

4. Conclusion

About 70% degradation of TPH in petroleum-contaminated water was achieved within 10 days using sodium persulphate (0.1 M) as a chemical oxidant. The remediation technique used in the present study is effective and promising, as further studies involving activation might yield improved degradation efficiency within shorter time.

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