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In-Situ Chemical Oxidation of Hydrocarbon Contaminated Groundwater (A Case Study of Baruwa Community, Lagos, Nigeria)

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Abstract. A chemical oxidation of hydrocarbon contaminated site is attempted by using potassium permanganate (KMnO_4) through injection into five hand dug wells within a pilot test area one hectare. The aim is to improve the quality of groundwater by degrading the soluble organic materials for further treatment and polishing, while incorporating bioremediation. The Background characterisations of groundwater and contaminant studied have been previously carried out (Adekunte 2008; Balogun 2009). 50 g/litre of potassium permanganate (KMnO_4) was used as oxidant for the remediation of the Total Petroleum Hydrocarbons (TPH) in the pilot test area, the delivery of oxidant was done by gravity feed to the monitoring wells up to a height of 600 mm (2 ft) above water levels. Oxidation study was carried out by observing the TPH for and other parameters during the process of In-situ Chemical Oxidation (ISCO) remediation for 30 weeks. A reduction in Total Petroleum Hydrocarbons (TPH) ranging from 92.28% to 99.86% was observed within the period. The maximum TPH value of 512 ppm was observed at well W53, while the minimum observed TPH at the end of thirty weeks was 0.7 ppm at the same well.

Keywords: Groundwater · Chemical oxidation · Potassium permanganate · Total petroleum hydrocarbons

1 Introduction

Spills and leaks of petroleum hydrocarbons such as gasoline, diesel, motor oils, and similar materials have caused widespread contamination in the environment. Generally these contaminants are present both in NAPL form (non-aqueous phase liquid; the bulk liquid petroleum hydrocarbon) and also as dissolved contaminants in the ground water.

One of the major environmental problems today is hydrocarbon contamination resulting from the activities related to the petrochemical industry. Accidental releases of petroleum products are of particular concern in the environment.

The goal of site remediation is to restore soil and groundwater quality to precontamination conditions. Site remediation considers the limit of technical expertise, existing government regulations, environmental protection desired and economics. Numerous technologies to remediate sites exist, namely, excavation, air stripping,

carbon bed adsorption, incineration (thermal destruction), bioremediation, soil vapour venting and natural attenuation (Ola and Ojuri 2008).

Most groundwater treatment techniques utilize a combination of technologies. Some of the biological treatment techniques include bioaugmentation, bioventing, biosparging, bioslurping and phytoremediation. Some chemical treatment techniques include ozone and oxygen gas injection, chemical precipitation, membrane separation, ion exchange, carbon absorption, aqueous chemical oxidation, and surfactant enhanced recovery physical treatment techniques including but not limited to pump and treat, air sparging, dual phase extraction and skimming.

Petroleum hydrocarbons such as gasoline are extensively utilized in various transportation and industrial operations. Improper disposal and/or accidental release of these chemicals have resulted in several large scale groundwater contamination problems (Clement et al. 2000; 2002).

Groundwater is a valuable resource both in Nigeria and throughout the world. Where surface water, such as lakes and rivers, are scarce or inaccessible, groundwater supplies many of the hydrologic needs of people everywhere. Groundwater quality impacts resulting from the leaking underground petroleum storage tanks or pipelines are of significant environmental concern due to the sheer number of such underground tanks and pipelines, also the extent of possible environmental contamination when leak. While contamination from petroleum storage tank releases can have significant impact on public health and the environment, active remediation of these contaminated sites can be difficult and expensive. Expectations of having to apply active remediation at all sites has generally not allowed the focusing of resources on those sites representing the greatest threat to public health and the environment (Steele et al. 2008).

2 Background of Study

In some decade ago, the most common technology used for remediating ground water has been to pump the water and treat it at the surface. Although still useful for certain remedial scenarios, the limitations of pump-and-treat technologies have recently been recognized, along with the need for innovative solutions to ground-water contamination (Keely 1989; National Research Council 1994). The ineffectiveness of existing remedial technologies for treatment has created the need for alternative remediation approaches. One such technology, In-situ Chemical Oxidation (ISCO), numerous laboratory column and sand tank studies have demonstrated ISCO effectiveness for the remediation of organic liquid residuals from aquifer materials (Ola et al. 2015).

In the process, called In-Situ Chemical Oxidation or ISCO, chemical oxidants are delivered in the subsurface to destroy (converted to water and carbon dioxide or to nontoxic substances) the organics molecules. The oxidants are introduced as either liquids or gasses. Oxidants include air or oxygen, ozone, and certain liquid chemicals such as hydrogen peroxide, permanganate and persulfate. Ozone and oxygen gas can be generated on site from air and electricity and directly injected into soil and groundwater contamination. The process has the potential to oxidize and/or enhance naturally occurring aerobic degradation. Chemical oxidation has proven to be an effective technique for dense non-aqueous phase liquid or DNAPL and LNAPL when it is present.

Permanganate (MnO_4^-) is available both $NaMnO_4$ and $KMnO_4$, the sodium form is distributed as a liquid available at 40% concentration by weight. Potassium permanganate is most commonly available in a crystalline form, and has a solubility of approximately 6% by weight in water at 20 °C. While permanganate is most commonly delivered as an aqueous solution, it may also be mechanically mixed into soil or introduced via pneumatic or hydraulic fracturing. Permanganate dissociates to produce the permanganate anion, an oxidizing agent with an oxidation potential of 1.7 V. The permanganate anion has an affinity for carbon-carbon double bonds (Wiberg and Saegbarth 1957).

3 Materials and Methods

3.1 Description of the Study Area

Baruwa area (Latitude 06° 35' 12" N, Longitude 03° 16' 21" E) is located in Ipaja, between the popular Iyana-Ipaja Bus-stop and the Ikotun Area of Alimosho Local Government Council of Lagos State, South West Nigeria. It is about 2.5 km from Iyana-Ipaja Bus Terminal, and is bounded by residential estates namely, Gowon Estate and Abesan Estate to the right and left respectively, while coming from Iyana-Ipaja Bus Terminal. It is accessible by a network of roads through Ipaja and Ayobo, which is a densely populated residential area with a population of over 100,000 inhabitants. The existence of Baruwa dates back to the early 20th Century, but it became prominent in

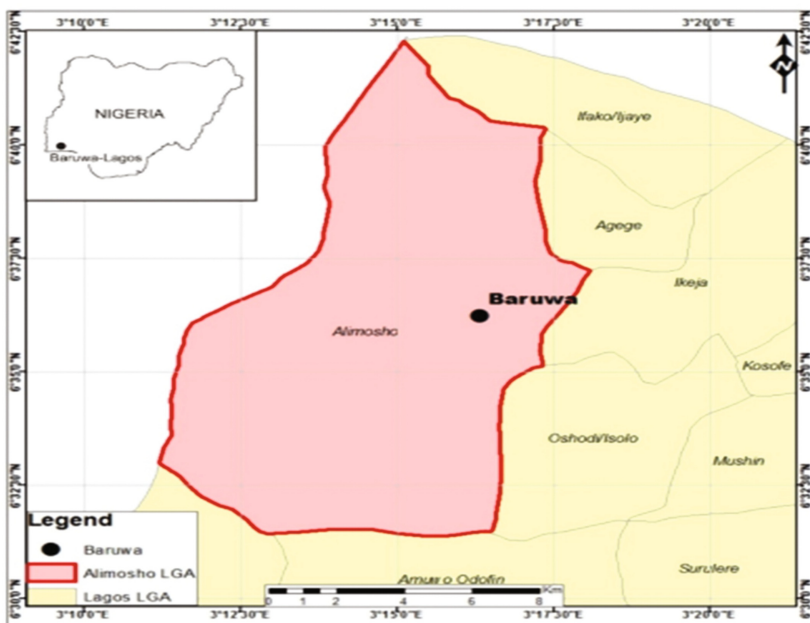


Fig. 1a. Map of Lagos State showing Baruwa Community the case study site.

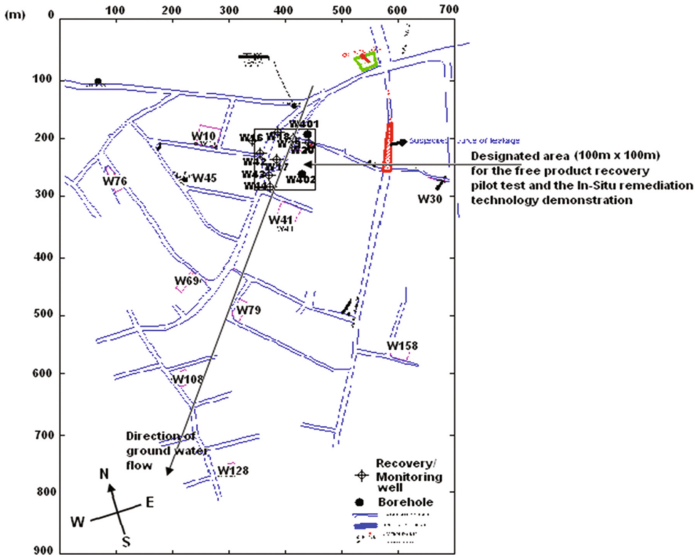


Fig. 1b. Field site (Baruwa, Nigeria) diagram showing location of *In-situ* chemical oxidation remediation

the 1970s due to population explosion witnessed in Lagos, that led to the development of satellite communities (Adekunte 2008). Figure 1a shows the map of Baruwa, in Lagos, Nigeria indicating the position of the study area (Baruwa). The area has a few cottage industries with small scale enterprises, and has a fair to good supply of electricity, with a network of earth roads without a proper drainage systems, which subsequently leads to impassability of some roads during the rainy season, and Fig. 1b shows the 100 m by 100 m designated for the pilot scheme test.

3.2 Field Experimental Programme

The study employed the collection of field data from the contaminated site in Baruwa, using equipment and methods to sufficiently characterize the hydrocarbon contamination within the area. Characterization of the study area was conducted utilizing the methodology prescribed by United States Environmental Protection Agency, US EPA (2001).

3.2.1 Field Tools and Equipment

(a) *Oil/Water Interface Characterization*

Volumetric characterization of the pure phase hydrocarbon in the monitoring wells was monitored with the aid of water/oil interface meter (Fig. 2), the depth to the surface of liquid, thickness of the pure phase hydrocarbon and the water in the monitoring wells were determined with the equipment.



Fig. 2. Model 122 (CSA) interface meter, P8/LM3/60 m (Solinst)

(b) *Pure Phase Hydrocarbon Skimming*

Model 8 Oil skimmer was used in skimming off the pure phase hydrocarbon from the monitoring wells within the pilot test area. The oil skimming technology was adopted to remove hydrocarbon contamination from groundwater without the pumping of groundwater with the contaminant. This is indicated in Figs. 3a and 3b.

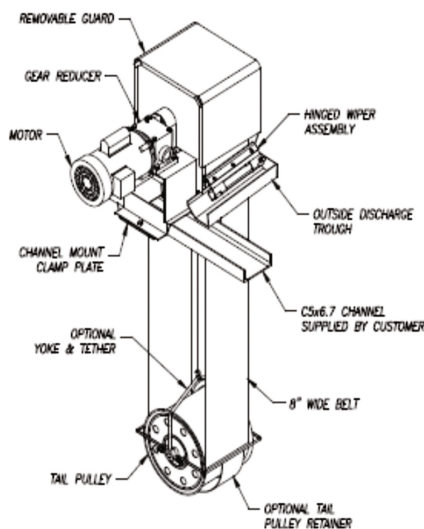


Fig. 3a. Oil grabber skimmer model 8 (Abanaki Corporation USA)

(c) *In-situ Chemical Oxidation of the Pilot Test Area*

50 g/litre of potassium permanganate (KMnO_4) was used as Oxidant for the remediation of the Contaminant of Concern (COC) in the pilot test area; the delivery of



Fig. 3b. Oil skimmers with fussy belt

oxidant was done by gravity feed to the monitoring wells. Oxidation study was carried out by observing the concentration of COC for a period of 30 weeks

(i) Determination of Concentration of Contaminant and Physico-chemical Characterization

Pre-injection test was carried out on water samples before injecting the subsurface with oxidant so as to determine the concentration of contaminant of concern (COC); subsequently water samples were taken periodically, after the injection of oxidant (Post-injection) in order to monitor the rate of reduction of contaminant of concern



Fig. 4a. PHA-100 - Portable Hydrocarbon



Fig. 4b. Testing of water samples with PHA analyzer (FCI environmental)

per time. Unique Portable Hydrocarbon Analyzer (PHA) (Figs. 4a and 4b) was used for the purpose of monitoring the concentration of contaminant of concerns per time.

Physico-chemical characterization was determined in-situ with the aid of YSI professional multi-parameter water quality meter, also water samples were taken for other physico-chemical tests.

4 Results/Discussion

4.1 Distribution of Free LNAPL at the Study Area

The Light Non-aqueous Phase Liquid (LNAPL) thickness was monitored in all the six wells within the pilot scheme area. Figure 5a displays hydrocarbon thicknesses of the monitoring wells reported by Adekunle (2008) and Figs. 5b and 5c present the contours of free hydrocarbon thicknesses of all the six wells monitored within the pilot area and reports of all wells monitored showing the various thicknesses of free hydrocarbon product and water respectively in 2014. The free hydrocarbon thickness in the wells varies from 0.491 m to 0.001 m. W17 had the highest thickness of free hydrocarbon, and the least thickness of hydrocarbon occurred in W44 and W41.

(i) Volume of the Skimmed-off Pure Phase Hydrocarbon

Table 1 and Fig. 6 present the summary of the volume of free product skimmed-off from the wells within the pilot test area using the Model 8 Abanaki oil skimmer shown in Figs. 3a and 3b. About 800 litres of free hydrocarbon product was skimmed-off from the monitoring wells within the pilot scheme area and deposited at the closet depot of the national oil regulatory body in Nigeria (NNPC/PPMC depot at Ejigbo, Lagos). Thereafter, pumping of water from subsurface was carried out with the help of sub-surface pumping machine. The pumping out of groundwater was done so that contaminants trapped between the monitoring wells could migrate to the wells during aggressive pumping. This was carried out for over 6 months. This operation was

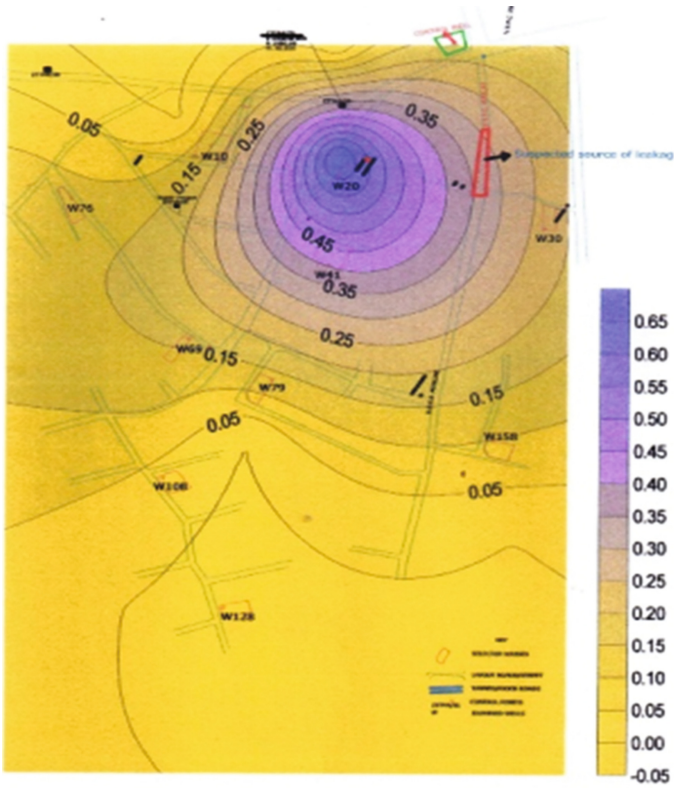


Fig. 5a. Free hydrocarbon thickness for monitoring wells within the study area (2006) (Adekunte 2008)

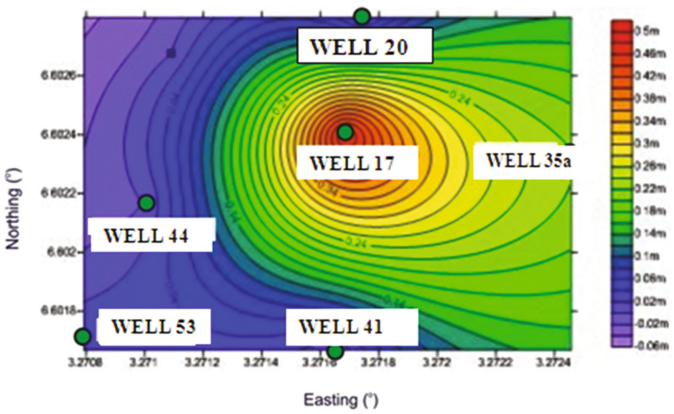


Fig. 5b. Free hydrocarbon thickness for monitoring wells within the study area



Fig. 5c. Reports of all wells monitored showing the various thicknesses of free hydrocarbon product and water

Table 1. Summary of the volume of LNAPL skimmed-off from the monitoring wells

Observation wells	W(20)	W(17)	W(41)	W(35A)	W(44)	W(53)
Thickness of LNAPL(m)	0.004	0.491	0.001	0.221	0.001	0.033
Diameter of wells (m)	1.765	0.820	1.930	1.650	1.111	0.799
Vol. of LNAPL skimmed (Litres)	9.67	259.4	2.926	472.7	0.969	16.540

successfully concluded when there was no more sheen on the surface of the groundwater in each of the monitoring wells. *In-situ* Chemical Oxidation (ISCO) process commenced only when no hydrocarbon sheen could be noticed in any of the six pilot wells.

(ii) Dissolved Oxygen Values during ISCO

The DO concentration usually reflects its organic contaminant load (that is, the lower the DO, the greater the contaminant concentrations). The DO increases significantly for all the observation wells dosed with the oxidant (KMnO₄) from the second week of injection of oxidant, except for the observation well (W17) that exhibited a contrary results at the second week of ISCO, the DO reduces from 1.8 mg/l to 1.4 mg/l, but significantly increases as ISCO progresses (Fig. 7). DO is electron acceptors and abundance of electron acceptors is helpful in the success of bioremediation.

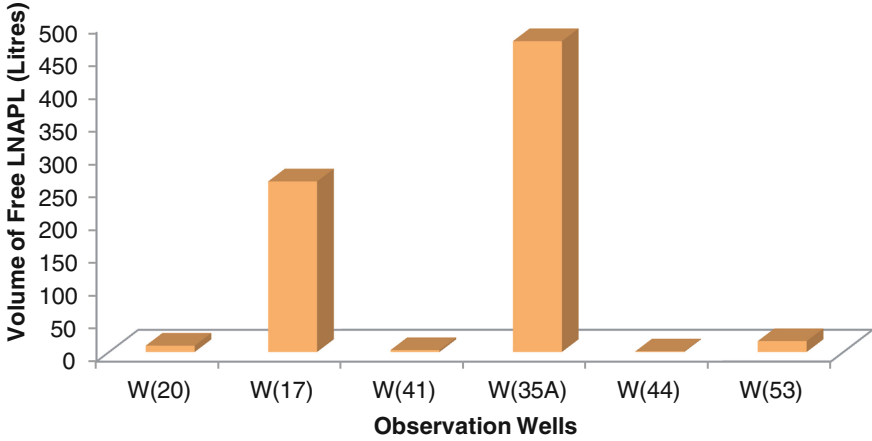


Fig. 6. Volume of LNAPL in skimmed-off prior to ISCO

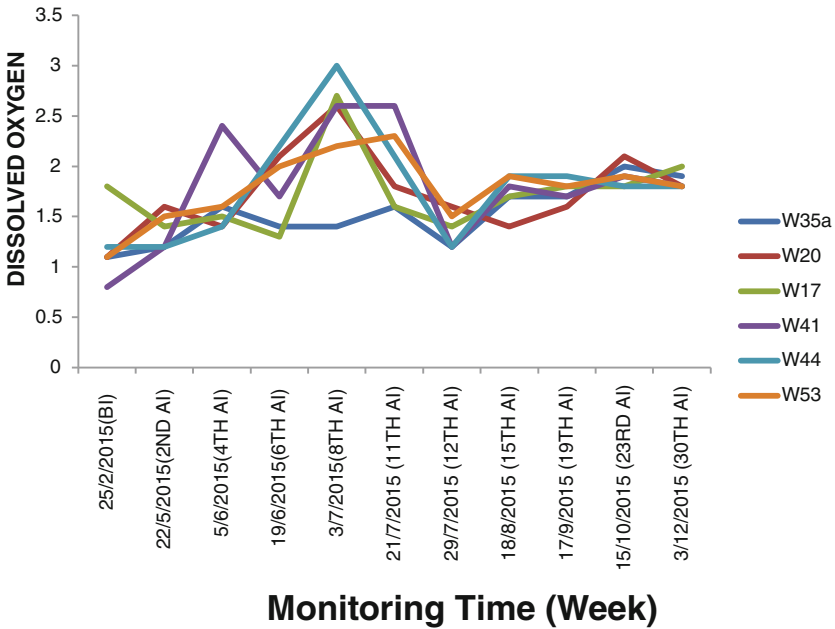


Fig. 7. Dissolved oxygen values against monitoring time

(iii) **Total Petroleum Hydrocarbon (TPH) in the Groundwater during ISCO Remediation**

Figure 8 shows the plot of TPH values for W35a, W20, W17, W41, and W53. For monitoring well W35a, the TPH value reduced from 350 ppm to 20 ppm at the end of thirty weeks of injection. The monitoring well W20 reduced from 299 ppm to 30 ppm

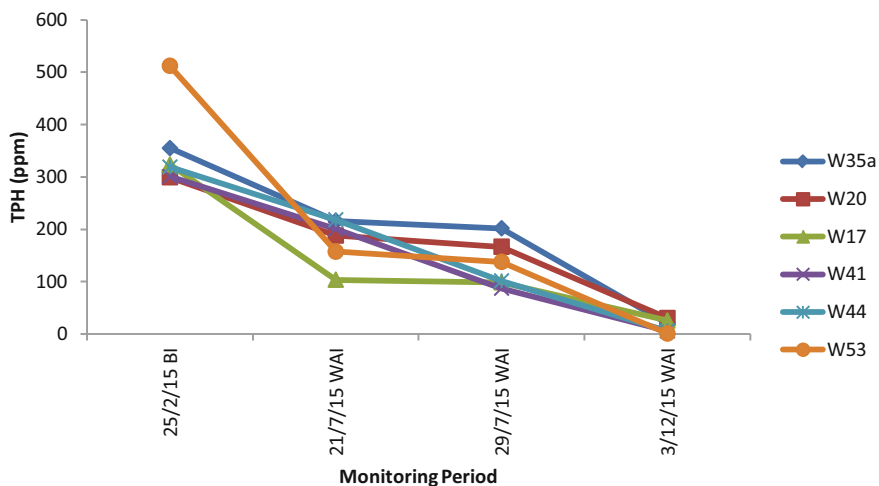


Fig. 8. Total petroleum hydrocarbon in the groundwater for monitoring wells during ISCO.

at the end of thirty weeks of injection. The TPH value of monitoring well W17 reduced from 324 ppm to 25 ppm at the end of thirty weeks of injection, also W41 reduced from 300 ppm to 6 ppm on the same time after injection.

At the monitoring well W44, TPH value before injection of oxidant was 319 ppm which reduced to 6 ppm at the end of thirty weeks after injection of oxidant; also, W53 reduced from 512 ppm to 0.7 ppm at the end of thirty weeks of injection of oxidant

5 Conclusion

The maximum record of thickness of LNAPL of 0.49 m was recorded in monitoring well W17 and 259.4 litres of the free product was skimmed off, 472.7 litres of LNAPL was skimmed off from W35a and the least product was skimmed from W20. The total volume of LNAPL skimmed off was about 800 litres. Thus, all the free products have been effectively removed in all the wells in the pilot scheme area

The DO increases significantly for all the observation wells dosed with the oxidant, the DO increases from a range of 0.8 mg/l to 8.4 mg/l.

Oxidation study was carried out by observing the concentration of COC for and other parameters during the process of ISCO remediation for 30 weeks. A reduction in Total Petroleum Hydrocarbons (TPH) ranging from 92.28% to 99.86% was observed within the period. Maximum TPH values in monitored well was 512 ppm, while the minimum observed TPH at the end of thirty weeks was 0.7 ppm (W53).

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