Remediation of crude-oil contaminated groundwater by Fenton-Oxidative method

Medjor W.O\textsuperscript{1}, Egharevba F\textsuperscript{2}, Akpoveta V.O\textsuperscript{3}, Ize-Iyamu O.K\textsuperscript{4}, Jatto E.O\textsuperscript{5}

\textsuperscript{1} Department of Chemistry, Taraba State University, Jalingo-Nigeria
\textsuperscript{2,3,4,5} Department of Chemistry, Ambrose-Alli University, P.M.B 14 Ekpoma, Edo State-Nigeria

akpovin2@yahoo.com
doi:10.6088/ijes.00202030026

ABSTRACT

Water contamination is a major global problem which requires ongoing evaluation and revision of water resources policy at all levels. It has been suggested that it is the leading worldwide cause of disease and deaths; it accounts for the death of more than 14,000 people daily. Groundwater samples were obtained by grab sampling technique from the tap of chemistry department, Delta state University, Abraka, that has its source from a borehole located within the University. Pollution was simulated in the laboratory by contaminating 90 ml of the groundwater samples with 10 ml of crude-oil in plastic microcosm to produce 10% contamination. Optimum conditions obtained for the Fenton-oxidative method employed in the study were 250,000 mg/l H\textsubscript{2}O\textsubscript{2} and 200 mg/l FeSO\textsubscript{4} at ambient temperature (28-32\degree C). At the end of the chemical remediation experiment, the Fenton-oxidative method was found to be extremely rapid, with the reaction been exothermic and following second order kinetics. The rate constant of the reaction was 0.00052 mol\textsuperscript{-1} dm\textsuperscript{3} hr\textsuperscript{-1} with half-life of 0.38 hour. 86.10% removal efficiency of total petroleum hydrocarbon as crude-oil was achieved after six hours. Control experiment was a microcosm that contained contaminated groundwater sample without the treatment chemical solution. Only about 2.8-3.2% reduction of total petroleum hydrocarbon as crude oil was observed that may be due to evaporation. The Fenton-oxidative method for crude oil-contaminated groundwater gave remediation efficiency of 24.35% (Cd); 31.63% (Pb); 32.58% (Ni) 44.3%; (Cr);98.84% (V). Except for vanadium, where chemical leaching of the metal in acidic medium was very effective, other heavy metal concentrations were higher than maximum permissible levels recommended by World Health Organization (W.H.O). This suggests that Fenton-oxidative method is not effective in the removal of Cd, Pb, Ni and Cr from groundwater polluted with crude-oil. The remediated polluted groundwater sample was found to have most of its physicochemical parameters as close match with the unpolluted groundwater sample and World Health Organization (W.H.O) permissible limits. The overall implication is that crude-oil polluted groundwater remediated by Fenton-oxidative method needs post-treatment to improve on its portability for drinking/domestic and agricultural uses.

Keywords: Groundwater, crude-oil, contamination, heavy metal, chemical leaching

1. Introduction

Water is a constant gift of nature that defines peace in life. It remains a veritable endowment of nature necessary for life sustenance of plants and animals (Gray, 1997). The United Nations (UN) predicts that water shortages could retard the economic growth of some countries and lead to food shortages and possibly, to international conflicts (Turner, 2000). Groundwater and rivers constitute the main sources of water supplies that humans use (for...
drinking, cooking, cleaning, industry and agriculture). These several sources of water supplies are polluted by natural geological sources, pesticides, industrial discharge from various processing industries and oil spillage during oil exploration and exploitations or accidental discharge. Organic substances from oil spillage and petroleum products disposed into water bodies significantly contaminate and degrade them and could possibly elevate the concentration levels of heavy metals. Heavy metals are persistent and can easily enter food chain and accumulate until they reach toxic levels. Traces of heavy metals such as Hg, Cd, Pb, Co, Mn, Cu, Fe and Cr above stipulated levels are toxic to aquatic ecosystem and human (Bowen, 1979; Ademoroti, 1996). Incessant oil spills are known to have caused severe damage to aquatic and terrestrial environment. Crude petroleum, as well as many products derived from it, is shipped from oil-producing locations to oil-consuming locations in ocean-going vessels having huge capacities. Accidents in which the hulls of such vessels are breached and their contents spilled can cause serious damage to the environment. Unfortunately, such accidents are not at all uncommon. Land and offshore oil wells also can be a source of oil spills into ocean waters. Oil spills from such accidents may quickly spread over many square miles of water surface, for example in the Niger-Delta region of Nigeria where there is increasingly oil exploration and exploitation work. Incessant vandalization of pipelines carrying petroleum and its products, massive destruction of oil facilities by irked youths, oil bunkering, industrial and domestic accidents which result in oil spillage and petroleum products deposits into existing water bodies have become the order of the day. Due to their complex composition, crude oils vary widely in their physical/chemical properties.

The melting point, boiling point, vapour pressure, partition coefficient and water solubility characteristics of crude oil can differ between oil producing regions as well as within a specific production field. Despite these wide-ranging physical and chemical characteristics, some generalizations can be made regarding the environmental behavior of crude oil. When a release to the environment occurs, components of crude oil will partition into various environmental compartments. The lower molecular weight components may dissolve in water or volatilize to the atmosphere, intermediate fractions may float and spread out on water where they may form emulsions and/or adsorb to soil and sediment, and the viscous, heavy components may agglomerate and float or sink in water or adhere to soil and sediment. The rate at which partitioning occurs depends not only on the nature of the crude but also on the severity of the weathering processes it encounters. When components of crude oil disperse, they may undergo further chemical and physical transformations. Constituents that partition to the air interact with hydroxyl radicals in the atmosphere and thus are subject to indirect photo-degradation. Atmospheric half-lives range from 0.4 days (e.g., n-dodecane) to 6.5 days (e.g., benzene). Crude oils are subject to biodegradation, but biodegradation rates vary considerably, and no crude oils would be considered to be readily biodegradable in standard tests. Low molecular weight components may readily biodegrade, but as molecular weight increases, hydrocarbons become increasingly insoluble in water, so that their bioavailability is limited. In general, hydrocarbons are regarded as being inherently biodegradable, although the degradation rates of the more complex high molecular weight fractions may be very slow. Spills in freshwater environments have been shown to adversely affect the diversity and abundance of the aquatic macro-invertebrate community, with the observed effects associated with oil sorption and substrate coating (Poulton, et al., 1997; Poulton, et al., 1998). Recovery of such communities in some habitats may be rapid (e.g., riffle areas of streams/rivers), while impacts to backwater areas may persist for months. Ultimately, the type of crude oil and the local conditions and habitats will dictate the potential and extent to which crude oil persists and cause effects in the environment. Crude oil is, in general, harmful to aquatic organisms.
In both marine and freshwater environments, a spill event may cause extensive mortality to non-motile susceptible species such as phytoplankton, crustaceans and larvae or eggs of fish and invertebrates. In contrast, spills of crude oil may not acutely affect highly mobile species such as adult fish, and mollusks and polychaete worms have an apparent tolerance to oil contamination. Acute aquatic toxicity of crude oil ranged from 10 to >100 mg/l in studies of whole oil dispersions in water or as water-accommodated fractions (WAFs) (CONCAWE, 2001). Acute toxicity is attributed to those water-soluble hydrocarbon components that are either saturates (aliphatic and alicyclic) or mono-and di-aromatics.

2. Materials and Method

2.1 Sampling Method

Groundwater sample was obtained by the grab sampling method in pre-sterilized 10 litre container from the tap in the chemistry laboratory, Delta State University, Abraka that has its water source from a borehole within the University.

2.2 Source of Crude oil

Crude oil was obtained from Shell Petroleum Development Company (SPDC) Flow Station, Kokori, in Ethiope East Local Government Area of Delta State.

2.3 Preparation of Samples

Pollution was simulated in the laboratory by contaminating 90 ml of the groundwater sample with 10 ml of crude-oil in several plastic microcosms to produce 10% contamination.

2.4 Chemical Reagents

High analytical grade hydrogen peroxide, iron(II) sulphate and hexane were used for the experiment.

2.5 Quality Control

Good quality assurance was ensured by taking the following measures:

2.5.1 Solution requirements

High purity quality hexane was used in extracting hydrocarbon from water and in preparing working standards used in constructing calibration curves.

The dilute solutions of the analyte employed in the spectrophotometric measurements were homogeneous and found not to associate or dissociate at the time of analysis. Reagent blanks (analyte-free water analyzed with the samples) were used to correct any absorption of light by hexane. Quartz cuvettes free from scratches and found to be clean were used.

2.5.2 Instrument requirements

Different hydrocarbons in water show absorbance at specific wavelengths. Spectrophotometric measurements gave satisfactory accuracy, sensitivity, reproducibility and
linearity at different wavelengths used. Stable electricity was ensured via the use of generator and uninterrupted power supply (UPS) device for reliable performance. In this study a spectrophotometer was used in preference to a colorimeter to reduce the interference from unwanted chromogen.

2.5.3 Recovery Study

Recovery Study was carried out by spiking water sample with crude to prepare a known concentration of 1000mg/l. 98.9% of crude oil was recovered. Similar recovery studies were carried out for Pb, Cd, Cr, Ni and V with recovery percentages of 98.3, 96.7, 97.53 and 99.13% for the heavy metals respectively.

2.6 Statistical treatments

Samples were prepared in replicate of three to provide data for statistical treatment. Standard deviation, relative standard deviation and coefficient of variation (CV) calculations were used to checkmate indeterminate (random) error. Sets of replicate results obtained from the study were found to have measurement uncertainty of less than 2% in terms of their coefficient of variations in all cases. Therefore the results are said be of very high precision. Blank runs were also conducted to reduce the occurrences of determinate errors.

2.7 Optimization Study

Optimization study was carried out to determine the optimum conditions for pH, concentration of treatment solutions and temperature. These conditions were subsequently applied to kinetics studies.

2.7.1 Fenton-oxidative Method

Treatment Concentration: 300ppm FeSO\textsubscript{4} + 50,000-500,000ppm H\textsubscript{2}O\textsubscript{2} in 1:5 ratio by volume. Several solutions of 10% contamination of crude-oil /90ml H\textsubscript{2}O was prepared and 6cm\textsuperscript{3} of 300ppm FeSO\textsubscript{4} + 30cm\textsuperscript{3} of 50,000-500,000ppm H\textsubscript{2}O\textsubscript{2} was added to each solution and kept for 30minutes until extraction and analysis. TPH as crude-oil was determined by T-60 UV/Visible spectrophotometer at a wavelength of 460nm following laboratory method adopted by (Macgill, 2000).

2.7.2 FeSO\textsubscript{4} Concentration

The best concentration of hydrogen peroxide obtained in 2.7.1 was used to determine the optimum concentration of FeSO\textsubscript{4} for the experiment. Several concentrations of FeSO\textsubscript{4} (50-700 ppm) was used to treat the water samples contaminated with crude-oil and kept for 30 minutes until extraction and analysis.

2.7.3 pH adjustment: pH=3 and pH= 8

The effect of pH on Fenton-oxidative method was investigated by adjusting the pH of two water samples contaminated with crude-oil to pH=3 and pH=8 using 1M H\textsubscript{2}SO\textsubscript{4} and 1M NaOH respectively and then was treated with the optimal treatment concentrations obtained from 2.7.1 and 2.7.2, kept for 30 minutes until extraction and analysis.
2.8 Kinetics Study
Optimum conditions obtained from the optimization study were applied in the kinetic study where aliquot was taken out for extraction and analysis at an hourly interval until optimum remediation was achieved.

2.9 Physicochemical Parameter
Physicochemical parameters such as pH, conductivity, turbidity, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), alkalinity, ammonia (NH₃) were determined by standard methods as adopted by Macgill, 2000. Heavy metals were determined by atomic absorption spectrophotometer using laboratory methods adopted by (Caroline et al., 2007).

3. Results and Discussion
Results obtained have shown that groundwater samples contaminated with crude oil gave an optimum remediation of 61.88% when treated with 250,000mg/l H₂O₂ and 200mg/l FeSO₄ (Table 1 and figure 1)

| CONC. | TPH MEAN | STDEV | RSD | CV | % REMEDIATION |
|-------|-----------|-------|-----|----|---------------|
| 0     | 5018.25   | 7.75  | 0.001544 | 0.1544 | 0             |
| 150000| 3024      | 4.67  | 0.001544 | 0.1544 | 60.26         |
| 200000| 3044.57   | 4.70  | 0.001544 | 0.1544 | 60.67         |
| 250000| 3105.29   | 4.80  | 0.001544 | 0.1544 | 61.88         |
| 350000| 3044.57   | 4.70  | 0.001544 | 0.1544 | 60.67         |
| 400000| 2931.16   | 4.50  | 0.001546 | 0.1546 | 58.41         |

STDEV =Standard deviation; RSD= Relative standard deviation; CV =Coefficient of variation

Figure 1: Optimization graph showing % remediation against concentration in fenton-oxidative method of groundwater contaminated with crude oil

Table 1: Optimization data in Fenton-oxidative Method

Figure 1: Optimization graph of % remediation against concentration.
Changes in pH was found to affect the remediation efficiency of total petroleum hydrocarbon as crude oil in the fenton-oxidative method. At pH of 3.00 and 8.00, remediation efficiencies of 55.56 and 53.53% were attained respectively. It implied that acidic medium favoured remediation of TPH as crude-oil more than the basic medium at ambient temperature(28-32°C). Similar studies found in literature suggest that remediation is more effective and efficient at pH range of 3-6 for the Fenton-oxidative method (Olexandre, et al., 2009). The optimum conditions of concentration of hydrogen peroxide, iron(II)sulphate, pH and temperature obtained from the optimization studies were applied to the kinetic study.

4.1 Kinetics Study of Fenton-oxidative Method

Kinetics of Fenton oxidative method was investigated for its order of reaction. The concentration of total petroleum hydrocarbon left was plotted against time using data provided in table 2 and represented in figure 2. It was observed that TPH decreased with time as reaction progressed. This was a strong indication that there was interaction between total petroleum hydrocarbon molecules and the reacting species of the treatment solution in the Fenton-oxidative method employed in the study.

| Time/hours | TPH mean left as crude oil | 1/ TPH left |
|------------|---------------------------|-------------|
| 0.00       | 5018.25±7.75              | 0.000199    |
| 1.00       | 713.59±1.10               | 0.001400    |
| 2.00       | 673.95±1.04               | 0.001480    |
| 3.00       | 591.51±0.91               | 0.001690    |
| 4.00       | 534.94±0.99               | 0.001870    |
| 5.00       | 417.36±0.83               | 0.002396    |
| 6.00       | 301.84±2.96               | 0.003313    |

Values are means of three triplicate readings ± standard deviations

Figure 2: Fenton-oxidative method was tested for a second order reaction kinetics.
This finding is in agreement with works of EPA, (2000) on kinetics of Fenton reagent on contaminant of common concern. The equation 1/(TPH left) = Kt + (initial TPH) establishes the relationship between TPH concentration and time for a second-order reaction, where t=time and K= rate constant. Plot of 1/(TPH left) against time using the data in table 2 gave a graph of good linearity confirming second order reaction kinetics for the Fenton–oxidation method for crude oil as represented figure 3.

![Figure 3: Second order profile](image)

The rate constant of the Fenton-oxidative method used in the treatment of crude oil contaminated groundwater samples was obtained from its second-order reaction kinetics plot as 0.00052mol⁻¹dm³hr⁻¹. The half-life of second-order reaction kinetics is inversely proportional to the initial total petroleum hydrocarbon concentration, given as \( t_{1/2} = 1/K[\text{initial TPH}] \) where \( t_{1/2} \) =half-life and K=rate constant of a second-order reaction kinetics. The half-life of Fenton-oxidative method employed in remediating crude oil contaminated groundwater samples was calculated as 0.38 hours. The reaction is exothermic and extremely very fast, particularly in the first 23 minutes that covers the half life period employed in the study. This is a very good result because the half-life should be shorter in the early stage of the reaction when more of reactant molecules were present to collide with each other. It was observed that an effective removal of crude oil from the contaminated groundwater samples required an optimum period of 6 hours achieving a remediation of 86.10%.

### 4.2 Physicochemical Parameters from Fenton-oxidative Studies

Table 3 summarized the results for pH, DO, BOD, electrical conductivity, NH3, alkalinity and heavy metals (Co, Cr, Ni, Pb and V) determined in crude oil polluted groundwater sample remediated by Fenton-oxidative method, unpolluted groundwater sample and polluted groundwater sample without treatment.

#### 4.2.1 Water Quality Parameters

The pH of crude oil polluted groundwater sample remediated by Fenton-oxidative method was found to be 8.8 as seen in table 3. pH is an important quality parameter which indicates
the aesthetic quality of water such as taste and has no serious health significance (Ogamba, 2004). The value was within the standard for pH set by W.H.O (6.5-9.5) for drinking/domestic and agricultural uses. The concentration of alkalinity in crude oil polluted groundwater sample remediated by Fenton-oxidative method showed a change in its alkalinity values from 0.001 to 0.005mg/l after remediation as seen in table 3. Alkalinity is due to the presence of hydrocarbonate, carbonate and hydroxyl ions in water. It is the acid neutralizing capacity of water and a function of all titratable bases present in water (Denloye, 2004). The alkalinity value of the remediated sample was below the W.H.O permissible level for drinking water/domestic and agricultural uses.

Table 3: Physicochemical properties of unpolluted, polluted and remediated groundwater samples

| Parameter | pH  | EC<sup>a</sup> (µs/cm) | DO<sup>b</sup> (mg/l) | BOD<sub>5</sub> (mg/l) | Turb<sup>e</sup> (NTU) | Alk<sup>d</sup> (mg/l) | NH<sub>3</sub> (mg/l) | Pb (mg/l) | Cd (mg/l) | Ni (mg/l) | Cr (mg/l) | V (mg/l) |
|-----------|-----|------------------------|----------------------|-----------------------|---------------------|---------------------|------------------|-----------|-----------|-----------|-----------|---------|
| FEN-C     | 8.80±0.44 | 0.27±0.0 | 7.60±0.1 | 3.00±0.0 | 5.20±0.7 | 81 | 0.00±0.5 | 0.10±0.0 | 0.15±0.0 | 0.13±0.0 | 0.08±0.0 | 0.01±0.0 |
| SC        | 8.50±0.40 | 0.00±0.0 | 2.67±0.1 | 120 | 0±2 | 120 | 0.00±1 | 0.00±0.0 | 0.00±0.0 | 0.00±0.0 | 0.15±0.0 | 1.03±0.0 |
| S1        | 7.30 | 0.00±1 | 3.60 | 1.80 | 0.00±1 | 0.00±3 | <0.1ND | ND | ND | ND | ND |

Key:
S1 = Unpolluted groundwater sample
SC = Crude oil polluted groundwater sample without treatment
FEN-C = Crude oil polluted groundwater sample remediated by Fenton-oxidative method
EC<sup>a</sup> = Electrical conductivity
DO<sup>b</sup> = Dissolved oxygen
BOD<sub>5</sub>=Biochemical Oxygen Demand
Alk<sup>d</sup> = Alkalinity
Turb<sup>e</sup> = Turbidity

The turbidity of the groundwater samples polluted with crude oil was 1200NTU. This astronomically high value is an indicator that the prepared sample was highly polluted compared to Rump, H. H (1991) who reported turbidity value of 100-275mg/l for highly polluted water. Crude oil polluted groundwater sample remediated by Fenton-oxidative method had turbidity value less than 20NTU. This suggests low levels of dissolved suspended particles and very high quality water (WHO 2010). The crude oil polluted groundwater sample had its dissolved oxygen value as 2.67mg/l indicating very high pollution.

The dissolved oxygen (DO) in the polluted groundwater samples remediated by Fenton oxidative method was found to be 7.60mg/l. This value is >6mg/l recommended by Rump, H.H (1999) for water of good quality. Crude oil polluted groundwater sample remediated by Fenton-oxidative method had its BOD<sub>5</sub> to be 3.00mg/l which is within the BOD<sub>5</sub> range of (2-6mg/l) for water of good quality (Rump, H.H., 1999). The remediated sample obtained from the chemical method had its ammonia concentration as 0.10mg/l which indicates water of good quality (Rump, H.H 1999). The Fenton-oxidative method for groundwater polluted with crude oil gave remediation efficiency of 24.35%(Cd); 31.63%(Pb); 32.58%(Ni); 44.3%(Cr);
98.84% (V). Except for vanadium where chemical leaching of the metal in acidic medium was very effective, other heavy metal concentrations were higher than the maximum permissible levels recommended by World Health Organisation (W.H.O). This suggests that Fenton-oxidative method is not effective in the removal of Cd, Pb, Ni and Cr from groundwater polluted with crude-oil.

The remediated polluted groundwater sample was found to have most of its physicochemical parameters as close match with the unpolluted groundwater sample and World Health Organisation (W.H.O) permissible limits. The overall implication is that crude-oil polluted groundwater remediated by Fenton-oxidative method needs post-treatment to improve on its portability for drinking/domestic and agricultural uses.

5. References

1. Ademoroti, C.M.A., (1996(b)), “Standard Methods of Treatment of Water and Wastewaters”. Fodulex Press Ltd., Ibadan.

2. Bowen, H.J.M., (1979), “Environmental Chemistry of Elements”. Academic Press, London, pp 155-157.

3. Caroline, M., Luis, R., Juan, S., (2007), A Comparison of two digestion methods for the analysis of heavy metals by flame atomic absorption spectroscopy, University of Valencia, Spain.

4. CONCAWE., (2001), “Environmental classification of petroleum substances-summary data and rationale”. Report No. 01/54. Brussels: CONCAWE Constium Registration (2003) American Petroleum Institute, Petroleum HPV Testing Group.

5. Denloye, S.A., (2004), Quality parameters for packaged water NAFDAC Laboratory Experiment IPAN News.

6. EPA., (2000), Kinetics of Fenton reagent on contaminant of common concern.

7. Gray, N.F., (1997), “Drinking water quality; problems and solutions”. John Wiley and Sons.

8. Macgill., (2000), Macgill Environmental Research Laboratory(MERL)-Analysis Manual.

9. Ogamba, A.S., (2004). Packaged drinking water, how safe? Professionalism IPAN News.

10. Olexandre, K., Vira, L., Elena, K., Volodymyr, N., (2009), “Chemical oxidants for remediation of contaminated soil and water”. A REVIEW. chemistry & chemical technology

11. Poulton, B.C., Finger, S.E., Humphrey. S.A., (1997). “Effects of a Crude Oil Spill on the Benthic Invertebrate Community in the Gasconade River, Missouri”. Archeology, Environmental Contamination and Toxicology, 33, pp 268-276.
12. Poulton, B.C., Callahan, E.V., Hurtubise, R.D., Mueller. B.G., (1998), “Effects of an Oil Spill on Leaf pack-Inhabiting Macro-invertebrates in the Chariton River, Missouri”. Environmental Pollution, 99, pp 115-122.

13. Rump, H.H., (1999), Wiley-VCH:Weinheim.“Laboratory Manual for the Examination of Water, Wastewater and Soil.

14. Turner, S., (2000), “Will There Be Enough Water In The Next Century?” Encarta Yearbook, February 2000.

15. World Health Organization., (2010), Guidelines for Drinking Water.