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Full Length Article

Optimization, kinetics, physicochemical and ecotoxicity studies of Fenton oxidative remediation of hydrocarbons contaminated groundwater

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ABSTRACT

Fenton oxidation remediation of hydrocarbons contaminated groundwater was investigated for efficiency and effectiveness. 10% pollution was simulated in the laboratory by contaminating groundwater samples with diesel and domestic purpose kerosene (DPK) in two different experimental set ups. Optimum conditions of concentrations of the treatment solutions and pH were established: 300 mg/L ($FeSO_4$), 150,000 mg/L (H_2O_2) and pH = 3 for the kerosene contaminant; 100 mg/L ($FeSO_4$), 300,000 mg/L (H_2O_2) and pH = 3 for the diesel contaminant. The results from kinetics study show that the remediation process is pseudo-first order reaction with a rate constant of 8.07×10^4 $mgL^{-1}hr^{-1}$ and 3.13×10^4 $mgL^{-1}hr^{-1}$ for the diesel and kerosene contaminants in that order with 95.32% and 79.25% reduction in chemical oxygen demand (COD) for diesel and kerosene contaminated samples at the end of the remediation process respectively indicated that remediation have occurred significantly. Percent reduction in Total Petroleum Hydrocarbon (TPH) as kerosene was 89.84% and that of the diesel contaminant as 91.87% after 6 hours of remediation. The general pollution index (GPI) for the hydrocarbons contaminated samples was in the range of 6.70–7.52 against the background value of 4.39 for the control groundwater sample. After treatment the GPI had dropped to 4.13–4.43 which depicts remarkable remediation although the samples remained impaired. Therefore there is the need of post-treatments to make the groundwater fit for domestic and agricultural uses. The application of the Fenton oxidative process is found to be very efficient, effective and rapid in reducing total petroleum hydrocarbon as kerosene and diesel as target contaminants.

1. Introduction

The world is over-dependent on crude oil. In spite of the advent of the new technology of production of alternative energy source from Shale oil (crude oil distilled from shale), massive activities of exploration, exploitation, production and transportation of crude oil have continued to be in the increase yearly across the globe. It has been predicted that the World use of petroleum and other liquid fuels would grow from 90 million barrels per day (b/d) in 2012 to 100 million b/d in 2020 and to 121 million b/d in 2040. The petroleum and other liquid fuels act as primary feedstock for majority of petrochemical industries and also general transport system [1]. Petroleum hydrocarbons represent high-volume global trade materials [1]. Chemically oil is known to consist mainly of aromatic and aliphatic compounds. These compounds are persistently toxic and difficult to deal with; particularly the benzene, toluene, ethyl benzene, xylene isomers (BTEX), and phenols [2]. In 2000 the world population was 6.2 billion. The United Nation has a projection of an additional 3 billion by 2050 with most of the growth from developing countries that are already experiencing water stress [3]. Groundwater and rivers form the main sources of water supplies that humans use (for domestic, industrial and agricultural uses). These several sources of water supplies are polluted by natural geological sources, pesticides, industrial discharge from various processing industries and oil spillage. As long as the longing urge for these global material persist, the unfortunate problems of pollution would remain with us and the quality of our environment remains largely compromised

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and therefore leading to serious environmental problems [4]. The toxicity of the oil adversely affects the soil, plants and water resources. The devastating effects of pollution makes fresh water no longer useable without incurring painstaking high clean up costs [5].

Advanced oxidation process (AOP) via the use of hydrogen peroxide has been one of the most celebrated chemical remediation technologies in the treatment of petroleum refinery wastewaters to ameliorate the problems associated with pollution [6–11]. In most of the works cited in literatures optimum conditions of pH and concentrations; kinetics of remediation methods employed, physicochemical characterizations and ecotoxicity of samples after treatments are not usually discussed in details or referred to scantily. This present work is poised to investigate the optimum conditions, kinetics, physicochemical characterization and ecotoxicity of Fenton oxidation remediation of diesel and domestic purpose kerosene contaminated groundwater for efficiency and effectiveness.

2. Materials and methods

2.1. Materials

Automatic gasoline oil (diesel) and Domestic purpose kerosene (DPK) were obtained from Petroleum Marketers at Agbor, Delta State, Nigeria. All plastics and glassware used in the study were thoroughly pre-washed with detergent water solution, rinsed with tap water and soaked for 48 hours in 50% HNO_3, then rinsed properly with deionised water and air-dried in the laboratory.

2.2. Preparation of samples

Pollution was simulated in the laboratory to mimic such occurrences in the natural environment. Seven plastic containers were each filled with 90 mL groundwater sample. 10 mL of kerosene was added to each of the containers and stirred thoroughly using a magnetic stirrer to obtain 10% contamination. These preparations were repeated in each experimental set up and for the diesel contaminant in replicates of five.

2.3. Preparations of treatment solutions

2.3.1. Preparation of hydrogen peroxide treatment solution for Fenton-oxidative method

Several concentrations of 50,000–500,000 mg/L of hydrogen peroxide were prepared by adding 5–50 mL of hydrogen peroxide solutions into several 100 mL volumetric flasks and made up to marks using distilled water.

2.3.2. Preparation of Iron(II) sulphate treatment solution for Fenton-oxidative method

Several concentrations of 100–700 mg/L of iron(II) sulphate solutions were prepared by dissolving 100–700 mg of iron(II) sulphate in seven different volumetric flasks (1000 mL), thoroughly shaken and made up to marks using distilled water.

2.3.3. Optimization of concentration of treatment solutions and pH

Optimization of concentration of hydrogen peroxide, iron(II) suulphate and pH of treatment solutions were determined to ascertain the optimum conditions for TPH removal for each of the two contaminants employed in the study.

2.3.4. Optimization of concentration of hydrogen peroxide on Fenton-oxidative method

TPH as kerosene was determined by molecular spectrophotometry following standard procedure adopted by Wang et al. [12] with slight modification of drying the wet extracts with anhydrous sodium sulphate to avoid unnecessary interference of impurities. Several solutions of the 10% kerosene contaminated groundwater taken in seven conical flasks were added to each 6 mL of 300 mg/L $FeSO_4$ and 30 mL of 5–35% wt H_2O_2 and allowed to undergo remediation for 30 minutes before extraction and analysis. Kerosene in the water layers was extracted using hexane. The wet extracts were passed through 5 g of anhydrous sodium sulphate on Number 42 Whatmann filter paper in different filtration set ups in order to obtain clean and dry extracts. TPH as kerosene was read off by UV/Visible spectrophotometer (made in the United Kingdom, 2007 model) at wavelength of 310 nm. The procedure was repeated using the other four replicates samples. Experiment was repeated using diesel contaminated groundwater samples at wavelength of 350 nm.

2.3.5. Optimization of concentration of $FeSO_4$ on Fenton-oxidative method

The optimum concentration of hydrogen peroxide obtained in this same study was used to determine the optimum concentration of iron(II) sulphate. The 30 mL of the optimum concentration of hydrogen peroxide was added to 6 mL of several concentrations of $FeSO_4$ (50–700 mg/L) in eight conical flasks; to each flask was added 10% kerosene contaminated groundwater sample and allowed to undergo remediation for 30 minutes before extraction and analysis. Kerosene in the water layers were extracted using hexane. TPH as kerosene were determined standard method adopted by Wang et al. [12] and read off at wavelength of 310 nm using T – 60 UV/Visible spectrophotometer (made in United Kingdom, 2007 model). Experiment was repeated using diesel contaminated groundwater samples at wavelength of 350 nm.

2.4. Kinetics studies on Fenton-oxidative method

The pH of the domestic purpose kerosene of contaminated groundwater samples were adjusted to pH = 3 and treated with concentrations of 150,000 mg/L of hydrogen peroxide and 300 mg/L of iron(II) sulphate obtained from the optimization study in this same study and allowed to undergo remediation at an hour interval for 6 hours and extraction and analysis was carried out at an hourly interval . Kerosene in the water layer was extracted using hexane and TPH as kerosene were determined by UV/Visible spectrophotometer at wavelength of 310 nm using standard method adopted by Wang et al. [12] with modifications described in the same work.

The concentrations of TPH as kerosene left were plotted against time. Typical pseudo-first-order rate plot for the remediation process was tested by plotting $Ln[B]_o - Ln[B]_t$ against time using the experimental kinetics data. The slope of the graph is the first order rate constant, k. The actual pseudo-first order rate constant was obtained by multiplying the value of the slope from the graph with the optimum concentration of the treatment solution that was used in excess, $[A]_o$ in the optimisation experiment in this same work. Experiment was repeated using diesel contaminated groundwater samples at wavelength of 350 nm with pH of the solutions adjusted to pH = 3; 300 mg/L of iron(II) sulphate and 300,000 mg/L of H_2O_2.

2.5. Controlled experiments

Two plastic containers were each filled with 90 mL groundwater sample with known background hydrocarbon level for each of the contaminant. 10 mL of diesel and 10 mL of kerosene was added to each of the set ups to produce 10% contamination. The simulated control samples without the Fenton oxidation treatment solutions were left to undergo remediation in the laboratory for an optimum

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