

REMEDICATION OF SURFACE WATER CONTAMINATED WITH DOMESTIC PURPOSE KEROSENE USING FENTON'S OXIDATION

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ABSTRACT

The remediation of surface water contaminated with domestic purpose kerosene (DPK) using Fenton's oxidation was investigated at ambient temperature for effectiveness at optimum conditions established. Results obtained from optimization studies for the Fenton's oxidation employed for the study were 250000 mg/L H₂O₂ and 300 mg/L FeSO₄ at ambient temperature with pH of samples adjusted to 3.0. At the end of the chemical remediation, the Fenton's oxidation was found to be rapid with the reaction being exothermic and followed second order kinetics. About 44.4% of the total petroleum hydrocarbon (TPH) as kerosene removal efficiency was achieved after 90 minutes. The reaction also followed a pseudo-first order kinetics with the rate constant of $3 \times 10^2 \text{ mol}^{-1} \text{ cm}^3 \text{ min}^{-1}$.

Key words: *Total Petroleum Hydrocarbon (TPH); Contaminated Surface Water; Chemical Oxidation; Fenton's Oxidation.*

INTRODUCTION

Hydrocarbons are heterogeneous group of organic substance that are primarily composed of carbon and hydrogen molecules [1,2]. They are quit abundant in modern society; and are used for different variety of multipurpose work. Petroleum and petrochemicals have been the driving force behind the economic development of many developing nations especially Nigeria. The world depends on petroleum and other fossil fuel with vast amount of which is used in transported, processed and stored around the world [3]. In 2003, the total world consumption of petroleum was over 13.1 billion liters per day. The United States energy information administration project in 2006 reported that the world consumption of petroleum will increase to 98.3 million barrels per day ($15.63 \times 10^6 \text{ m}^3 \text{ day}^{-1}$) in 2015 and 118 million barrels per day ($18.8 \times 10^6 \text{ m}^3 \text{ day}^{-1}$) in 2030. With such a large consumption of petroleum, oil spills are inevitable. The most notable oil spills at sea involve large tankers, which spilled thousands of tons of oil due to some human errors [4,5]. These oil spills can cause severe damage to soils, water bodies and other aquatic animals [6]. The apparent oil spillages occurring in Nigeria and other countries are considered forms of major pollution, having adverse effect on the environment when the occurrence is frequent. These oil spillages greatly affects plants and

animals, especially aquatic animals, which may in turn sometimes lead to plants and animals species getting endangered [7,8]. A thick layer of oil inhibits the metabolism of plants and suffocates them to death. This destruction of plants affects the whole food web and decreases the natural habitats of numerous species [9]. The contamination of the environment with petroleum hydrocarbons provides serious problems for many developing countries especially Nigeria. Man has dealt with the cleanup of petroleum products contamination since the first day oil was discovered [10].

The development of petroleum industry into new frontiers, the apparent inevitable spillages that occur during routine operations, the records of acute accidents during transportation has called for more studies into oil pollution problems, which has been recognized as the most significant contamination problem encountered in Nigeria [11]. Thereafter, several studies have examined the fate and effect of petroleum in various ecosystems [12,13]. This work is aimed at investigating the effectiveness of Fenton's oxidation in remediating a kerosene contaminated surface water to contribute to the numerous research works meant to create a convincing chemical remediation technique or method that can be employed to treat a water body when there is a case of oil spillage. This work also investigated the optimum conditions and kinetics needed for better performance of the method employed for the treatment of DPK contaminated surface water.

Materials and Method

All reagents used are of analar grade, the equipment used were washed and dried at appropriate temperatures.

Sampling Area and Sample collection

River Bali is located in Bali local government area of Taraba state, Nigeria, with geographical coordinates of 7° 52' 0" North, 10° 58' 0" East.

The water samples were collected by grab sampling method along the bank of river Bali at different locations to make a representative sample. The water which flows through the Bali main bridge is sampled in a thoroughly washed 25 liter container rinsed with distilled water. A standard domestic purpose kerosene (DPK) Samples were obtained from the Nigeria National Petroleum Commission (NNPC) Filling station of Mile-six Jalingo, Taraba state, Nigeria.

Samples homogenization

To provide a homogenized water sample and to enhance a thorough mixing of the DPK with the water, the water was thoroughly mixed by the use of mechanical shaker. Pollution was simulated in the laboratory by contaminating 45cm³ of the surface water sample with 5cm³ domestic purpose kerosene (DPK) in several different containers, stirred with magnetic stirrer to produce 10% contamination.

Quality control

High quality grade n- hexane was used in extracting hydrocarbon from the contaminated surface water in preparing working standards used in constructing calibration curves. The dilute solutions of the analyte employed in the spectrophotometric measurements were homogeneously mixed and found not to associate or dissociate at the time of analysis. Reagent blanks (analyte free water + treatment solutions to be analyzed) were used to correct any absorption of light by n-hexane. Quartz cuvettes free from scratches clean and dried before used [14]

Instrument Requirement

Different hydrocarbons in water shows absorbance at specific wavelengths. Spectrophotometric measurements gave satisfactory accuracy, sensitivity, reproducibility and linearity at different wavelengths. Stable electricity was ensured by via the use of electric generator and an 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 chromogenes.

Optimization studies

Optimization study for the concentrations of H₂O₂, FeSO₄, pH, and temperature was carried out to determine the optimum conditions for the treatment of the DPK contaminated surface water. The same conditions were subsequently used for kinetic studies.

Optimum H₂O₂ Concentration

About 150mg/L FeSO₄ was prepared and kept constant for the sake of the H₂O₂ optimization study. Several solutions of the 10% DPK contaminated surface water taken in ten different

conical flasks which were each added 6 mL of 100 mg/L FeSO₄ and 30 mL of 50,000 – 500,000mg/L H₂O₂ and allowed to undergo remediation for 40 minutes before extraction and analysis. Kerosene in the water layers was extracted using n- hexane. Total Petroleum Hydrocarbon as kerosene was read by UV/Visible spectrophotometer at wavelength of 310 nm. The procedure was repeated for other replicate samples.

Optimum FeSO₄ Concentration

About 250,000 mgL⁻¹ H₂O₂ was observed to be the optimum concentration for the treatment which was used to determine the optimum concentration of iron (II) sulphate. Several solutions of the 10% DPK contaminated surface water taken in eight conical flasks were each added 6 mL of 50-700 mg/L FeSO₄ and 30 mL of 250,000mg/L H₂O₂ and allowed to undergo remediation for 40 minutes before extraction and analysis using T – 60 UV/Visible spectrophotometer.

Optimum pH.

The solution of the 10% DPK contaminated surface water was taken in twelve conical flasks. To each of the several solutions, 6 mL of 300 mg/L FeSO₄ and 30 mL of 250,000 mg/L H₂O₂ were added. Each of the solutions had their pH values varied between 1.5 to 7.0 pH values by the use of 1M H₂SO₄ and 1M NaOH for adjustment, pH meter was used for measurement throughout the adjustment and the samples were allowed to run for 40 minutes before extraction and analysis.

Kinetics studies

Optimum conditions obtained from the optimization study were applied in the kinetic study where aliquot was taken out for extraction and analyzed at time interval of 5, 10, 15, 30, 45, 60 and 90 minutes [14, 15].

Fenton's Oxidation

The optimum conditions established from the optimization and kinetic studies 6cm³ of 300 mg/L FeSO₄, 30cm³ of 250,000 mg/L H₂O₂, pH value of 3, were applied to the several solutions of 10% contamination in conical flasks, stirred with magnetic stirrer and kept for a required time until extraction and analysis. TPH concentration was determined by T-60 UV/Visible spectrophotometer at a wavelength of 310 following laboratory method adopted by [16, 14].

Statistical treatments

Samples were prepared in replicate of three to provide data for statistical treatment. Standard deviation (SDEV), relative standard deviation (RSD) 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 to be of high precision. Blank runs were also conducted to reduce the occurrence of determinate errors [14]

Results and Discussion

The efficiency of a remediation technology depends on several factors; pH, type of water, time, concentration of treatment solutions, nature of catalyst and competition between different pollutants [17]. Various experiments were designed to optimize Fenton's oxidation and to investigate the effect of these environmental factors on Fenton's oxidation [18, 19]. The results on the optimization of hydrogen peroxide concentration, iron sulphate concentration, pH, and temperature for DPK contaminated surface water samples treated by Fenton's oxidation are shown below. Optimum concentrations of 250,000 mg/L H_2O_2 and 300 mg/L $FeSO_4$ solutions were obtained for the kerosene contaminated surface water samples with an average 40.84% remediation efficiency with little or no significant difference. The results are shown in Figs. 1 and 2

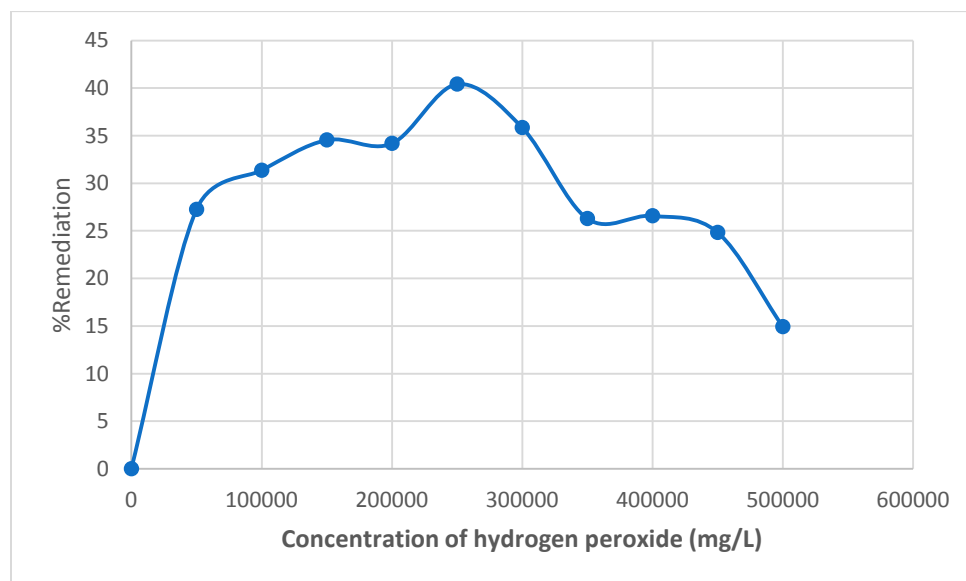


Figure 1: Effect of H_2O_2 concentration on TPH removal efficiency.

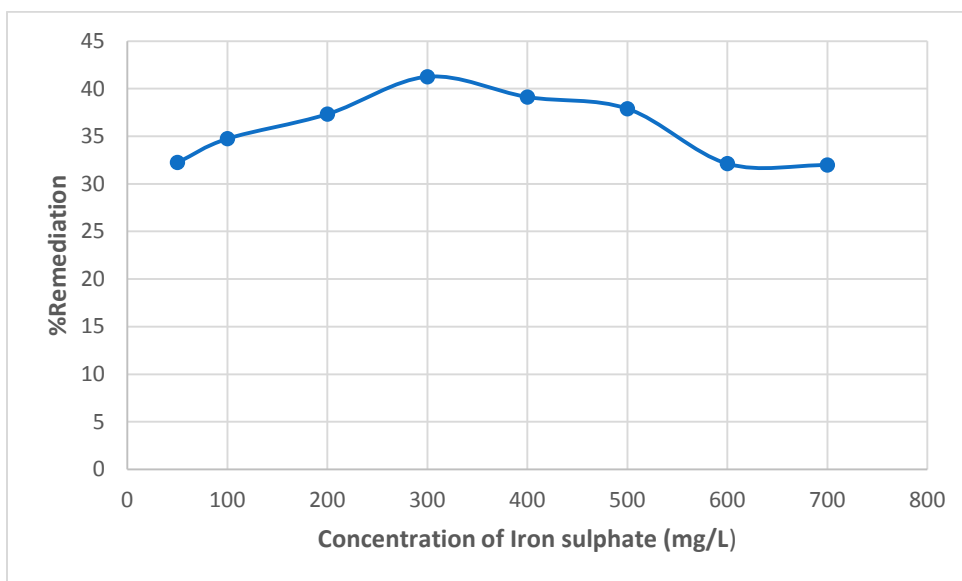


Figure 2: Effect of FeSO_4 concentration on TPH removal efficiency.

Studies found indifferent literatures suggested that the mixture of the hydrogen peroxide and iron (II) sulphate solutions is acidic in nature with an approximate pH value of 4.43, this value was confirmed and an optimum pH of 2.8-3.0 was obtained and ensured for efficiency of the Fenton's oxidation [17, 20].

The results of the pH test condition demonstrated that the most effective removal was at pH 3 with percentage removal of 42.59%. The effect of pH seemed to be less effective in TPH removal at higher pH values. At lower pH values, the removal was quite high (pH: 2 = 35.6%, pH: 2.5 = 37.25%, pH: 3 = 42.59%). With increasing pH, the percentage TPH removal dropped linearly as shown in Fig.3. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species [17]. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. The drop in efficiency on the acid side is less dramatic given the logarithmic function of pH, and is generally a concern only with high application rates. The result shows that ferrous iron could react with H_2O_2 efficiently under acidic conditions [21]. Thus pH of 3 is the optimum for the DPK contaminated surface water treated by Fenton oxidation.

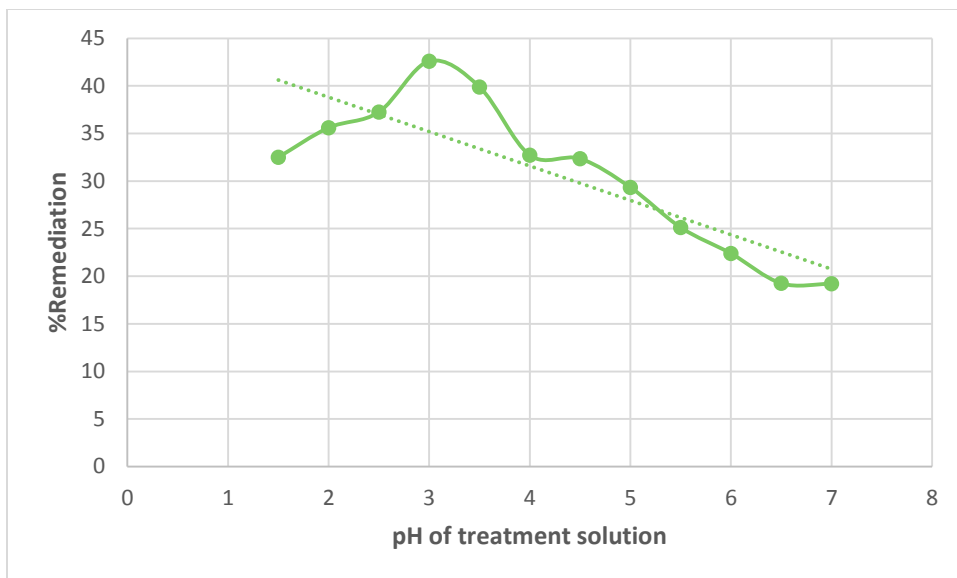


Figure 3: Effect of pH on TPH removal efficiency.

Optimum temperature range of 25 – 30⁰C was **obtained;** this is in agreement with other studies found in literature. The rate of reaction with Fenton’s reagent increases with increase in temperature, with the effect more pronounced at the range of 25 to 30⁰C. However, as the temperatures increase above 40⁰C, **statistically there was a significant change as** the efficiency of Fenton’s oxidation declines. This is due to the accelerated decomposition of H₂O₂ into water and oxygen [17, 22]. This discussion is illustrated in Figs. 4 below

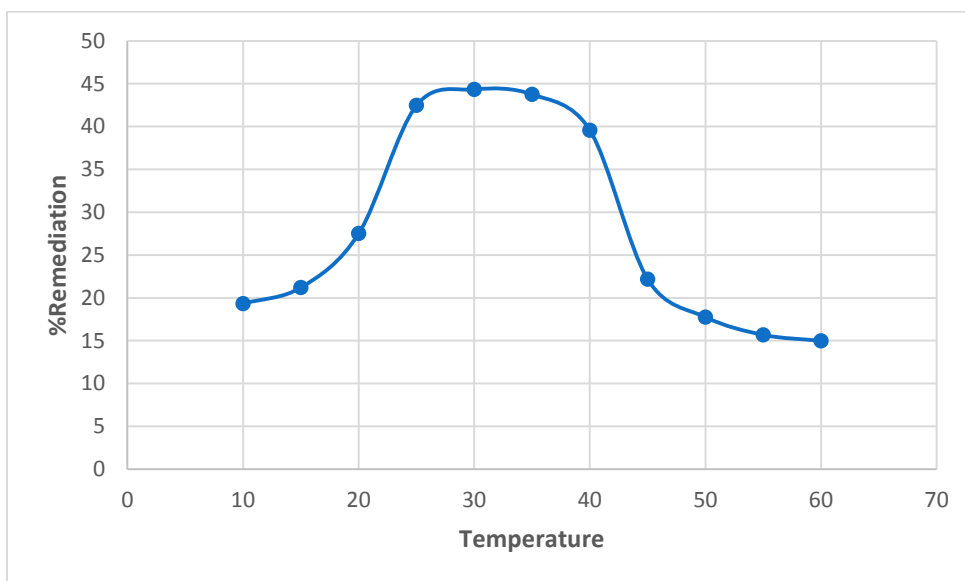


Figure 4: Effect of temperature on TPH removal efficiency.

The effect of reaction time on Fenton's oxidation of surface water contaminated with domestic purpose kerosene was tested based on the optimum conditions established earlier. It was found that the rate of TPH removal increased from the initial time of 5mins to 10mins. There was increase in time until about 45 minutes where the removal rate became steep and steady with gradual increase from 60 to 120 minutes. Appreciable TPH removal percentage was achieved within 90 minutes of reaction time. A plot of TPH left against time represented in Figure 5, gave a reciprocal relationship between TPH left and time of reaction, which clearly indicate a reduction in TPH concentration with time.

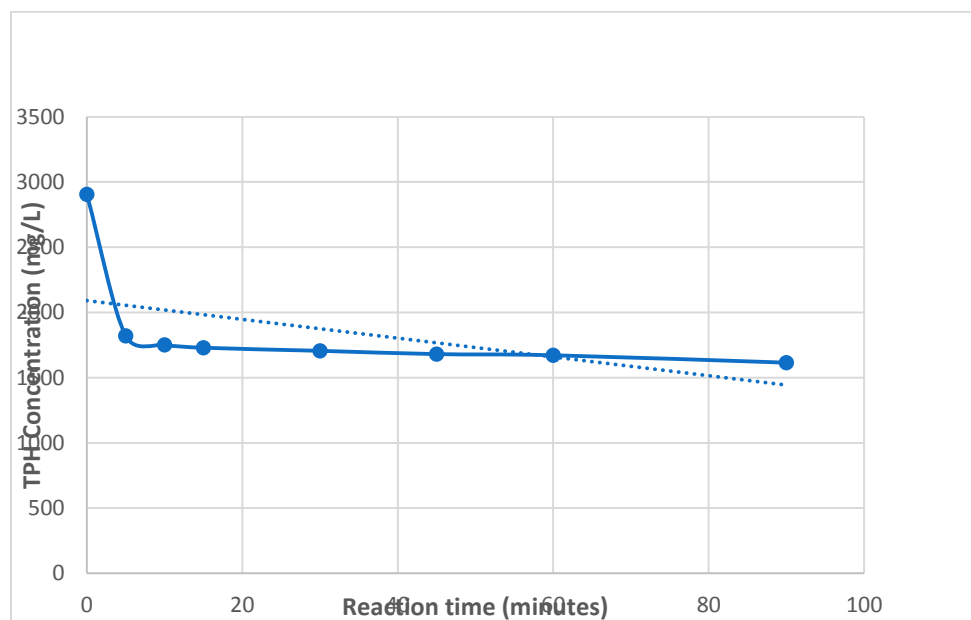


Figure 5: TPH left after remediation with different reaction time.

The result obtained from the kinetic study, showed that surface water contaminated with kerosene gave appreciable TPH removal of 44.4% when the reaction was allowed to run for 90mins. A graph of percentage remediation against reaction time was plotted to illustrate this. This is shown in Figure 6

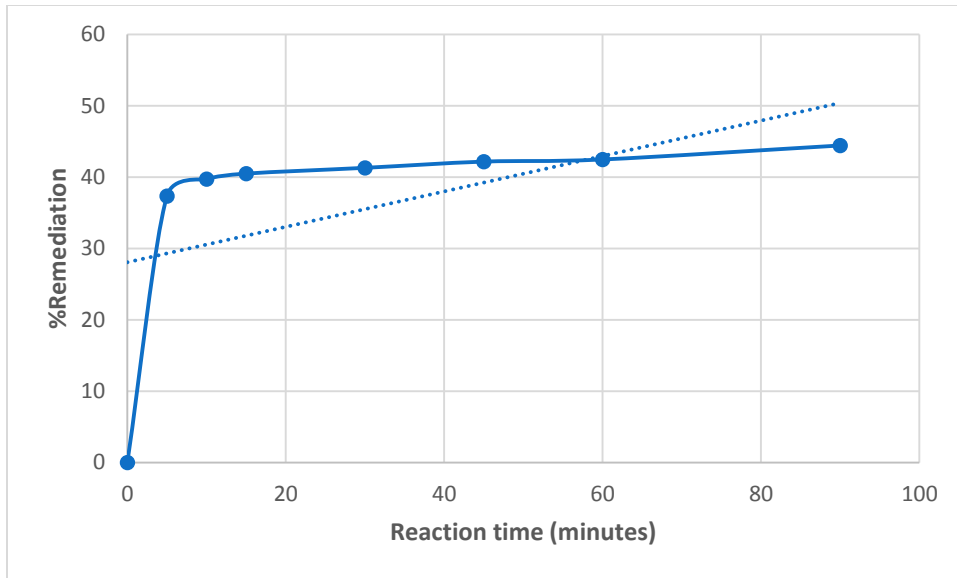


Figure 6: Percentage remediation against reaction time

The equation $\ln[B]_0 - [B]_t = kt$ against Time, establishes the relationship between TPH concentration and time for a second order kinetics as represented in Figure 7. The plot is of good linearity, which shows that the obtained data fits into a Pseudo-first order kinetics. This is illustrated below

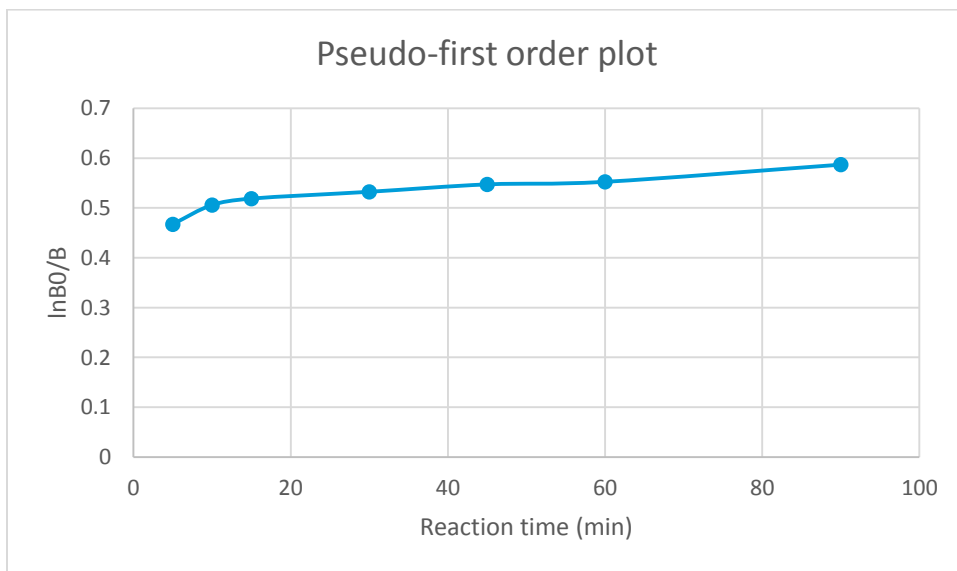


Figure 7: Second order reaction kinetics (Pseudo – first order plot).

The rate constant of the Fenton's oxidation used in the remediation of kerosene contaminated surface water samples was obtained from its second order reaction kinetics plot (pseudo-first

order plot) as $3 \times 10^2 \text{ mol}^1 \text{ cm}^3 \text{ min}^{-1}$. The half-life of second-order reaction kinetics which is inversely proportional to the initial total petroleum hydrocarbon concentration ($t_{1/2} = 1/k_{[\text{initial TPH}]}$) was calculated as 1.146×10^{-6} minutes. This shows that the half-life was shorter in the early stage of the reaction when more of the reactant molecules were present.

Conclusion

The results obtained from this have shown that Fenton's oxidation is an efficient technique in remediating DPK contaminated surface water. The study has revealed that various factors such as pH, type of water, type of hydrocarbon, H_2O_2 concentration, FeSO_4 concentration, temperature and reaction time can affect the efficiency of Fenton's oxidation.

Fenton's oxidation was found to be more effective in acidic environment than in basic environment. This suggests that the environment to be treated must be slightly acidic before treatment. The environment must also not be too acidic as H^+ would compete with contaminants for OH^\cdot radicals.

DPK polluted surface water remediated by Fenton's oxidation may need post-treatment to improve on its portability for industrial, domestic and agricultural uses.

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