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# Application of Fenton's Oxidation in the Remediation of Surface Water from River Yedzaram Contaminated with Diesel

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**Abstract**

Surface water contamination is a significant problem for municipal authorities. It can lead to pollution on a large scale and be a cause of major illness in humans. The remediation of surface water from river Yedzaram contaminated with diesel using Fenton's oxidation was studied at ambient temperature for effectiveness at some optimum conditions. Results obtained from optimization studies for the Fenton's oxidation employed for the study were 20000 mg/L $H_2O_2$ and 350 mg/L $FeSO_4$ at ambient temperature with pH of samples adjusted to 3.0. The result obtained at end of the chemical remediation studies shows that the Fenton's oxidation was found to be spontaneous with the reaction being exothermic which followed by a second order kinetics. Around 43.9% of the total petroleum hydrocarbon (TPH) as diesel removal efficiency was achieved after about 105 minutes. The kinetics of the reaction has proven too and followed the pseudo-first order kinetics with the rate constant of $3x10^2$ $mol^{-1}cm^3min^{-1}$ which is similar to that of Kerosine.

**Keywords;** Total Petroleum Hydrocarbon (TPH); Contaminated Surface Water; Diesel; Fenton's Oxidation

## Introduction

Surface water contamination is a significant problem for developing many countries especially Africa Nigeria in particular. It can lead to pollution on a large scale and be a cause of major illness in humans and the ecosystem. The contamination of surface and ground water with hydrocarbons resulting from oil exploration activities and production highlights the need for efficient and environmentally friendly technology to mitigate this form of water pollution (Afzal *et al.*,2019;Shinggu *et al.*, 2019). Environmental pollution with petroleum and petrochemical products (complex mixture of hydrocarbon) has been recognized as one of the most important serious current problem. People working in garage and mechanical workshops are always exposed with oily sludge which is a potent immunotoxicants and carcinogenic (Jain *et al*., 2011).

Hydrocarbons are heterogeneous group of organic substance that is primarily composed of carbon and hydrogen molecules (Wang, 1993). 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. Jain *et al* (2011), reported that the total world consumption of petroleum was over 13.1 billion liters per day. The United States energy information administration project in 2006 also reported that the world consumption of petroleum will increase to 98.3 million barrels per day ($15.63x10^6$ $m^3day^{-1}$) in 2015 and 118 million barrels per day ($18.8x10^6$ $m^3day^{-1}$) in 2030. With such a large consumption of petroleum, oil spills into surface and ground waters are inevitable. The most notable oil spills at sea involve large tankers, which spilled thousands of tons of oil due to some human errors (Paine *et al* 1996; Albaiges *et al.*, 2006). These oil spills can cause severe damage to soils, water bodies and other aquatic animals (Whitfield, 2003). The obvious 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 especially in the Niger delta may greatly affects plants and animals, especially aquatic animals, which may in turn sometimes lead to plants and animals species getting endangered (Edwer *et al.*, 2004 ; Wells, 2001).

According to Dadrasnia and Agamuthu,(2013) the largest concentrations of the hydrocarbon molecules that make up crude oil and petroleum products are highly toxic to many organisms, including human. Stroud *et al* (2007) reported the same trend which is estimated to be between 1.7 and 8.8 million metric tons of oil is released into the world's water and soil every year (Abu and Dike 2008). This is directly related to human activities including deliberate waste disposal is also estimated that to about 30 % of the spilled oil enters freshwater systems (Henry 2001). 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 (HELMCOM, 2003). 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 (EPA, 1999). 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 (Snape, 2001). Thereafter, several studies have examined the fate and effect of petroleum in various ecosystems (Whittaker, 1999; Boehm, 1995). This work is aimed at investigating the effectiveness of Fenton's oxidation in remediating a diesel contaminated surface water to contribute to the numerous research works meant to create an efficient 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 therefore investigative studies of the optimum conditions and kinetics needed for better and effective method employed for the treatment of diesel contaminated surface water in River Yedzaram in Mubi, Adamawa State, Nigeria. .

**Materials and Method**

The reagents used for this study are all of analar grade obtained from sigma Aldrich. The apparatus and glass wares used were washed and dried at appropriate temperatures.

***Sampling Area and Sample collection***

River Yedzaram is located in Mubi north and south local government areas of Adamawa state, Nigeria, with geographical coordinates of 10°16′N 13°16′E / 10.267°N 13.267°E / 10.267; 13.267. The water samples were collected by grab sampling method along the bank of River Yedzaram at different locations to make a representative sample. The water which flows through the Mubi three bridges cross the river is sampled at different locations in a thoroughly washed 20 liter container rinsed with distilled water. A standard diesel samples were obtained from the Total Filling station in Mubi, Adamawa State, Nigeria.

***Samples homogenization***

To provide a homogenized and composite water samples and to enhance a thorough mixing of the diesel with the surface water, the composite was thoroughly mixed with the help of mechanical shaker. Pollution was simulated in the laboratory by contaminating 50 $cm^3$ of the surface water sample with 10 $cm^3$ diesel in several different conical flask and 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 (Medjor *et al.,* 2012)

**Optimization studies**

Optimization study for the concentrations of $H_2O_2$, $FeSO_4$, pH, and temperature was carried out to determine the optimum conditions for the effective treatment of the diesel contaminated surface water. The same conditions were subsequently applied for the kinetic studies.

***Optimum $H_2O_2$ Concentration***

About 150 mg/L $FeSO_4$ was prepared and kept constant for the sake of the $H_2O_2$ optimization study. Several solutions of the 10% diesel contaminated surface water taken in ten different conical flasks which were each added 5 mL of 100 mg/L $FeSO_4$ and 25 mL of 5,000 –50,000 mg/L $H_2O_2$ 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 all other replicate samples.

***Optimum $FeSO_4$ Concentration***

About 25,000 $mgL^{-1}$ $H_2O_2$ 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% diesel contaminated surface water taken in eight conical flasks were each added 5 mL of 50-700 mg/L $FeSO_4$ and 25 mL of 25,000 mg/L $H_2O_2$ and allowed to undergo remediation for 45 minutes before extraction and analysis using T – 60 UV/Visible spectrophotometer.

***Optimum pH.***

The solution of the 10% diesel contaminated surface water was taken in different conical flasks. To each of the several solutions, 5mL of 300 mg/L $FeSO_4$ and 25 mL of 25,000 mg/L $H_2O_2$ were added. Each of the solutions had their pH values varied between 1.5 to 7.0 pH values by the use of 1M $H_2SO_4$ and 1M NaOH for adjustment, pH meter was used for measurement throughout the adjustment and the samples were allowed to run for 45 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 (Medjor *et al*.,2012)

***Fenton's Oxidation***

The optimum conditions established from the optimization and kinetic studies 5$cm^3$ of 250 mg/L $FeSO_4$, 25 $cm^3$ of 25,000 mg/L $H_2O_2$, 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 nm following laboratory method adopted by (Pignatello *et al*., 2006)

***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 (Medjor *et al.*, 2012)

**Results and Discussion**

The efficiency of a remediation technology depends on several physical factors; pH, type of water, time, concentration of treatment solutions, nature of catalyst and competition between different pollutants (Sylvia,2018; Shinggu *et al*.,2019). Various experiments were designed to optimize Fenton's oxidation and to investigate the effect of these environmental factors on Fenton's oxidation (Bautista, *et al*., 2008). The results on the optimization of hydrogen peroxide concentration, iron sulphate concentration, pH, and temperature for diesel contaminated surface water samples treated by Fenton's oxidation are shown below. Optimum concentrations of 25,000 mg/L $H_2O_2$ and 250 mg/L $FeSO_4$ solutions were obtained for the diesel contaminated surface water samples with an average 41.0% remediation efficiency with little or no significant difference as shown in Figures1 and 2 below.

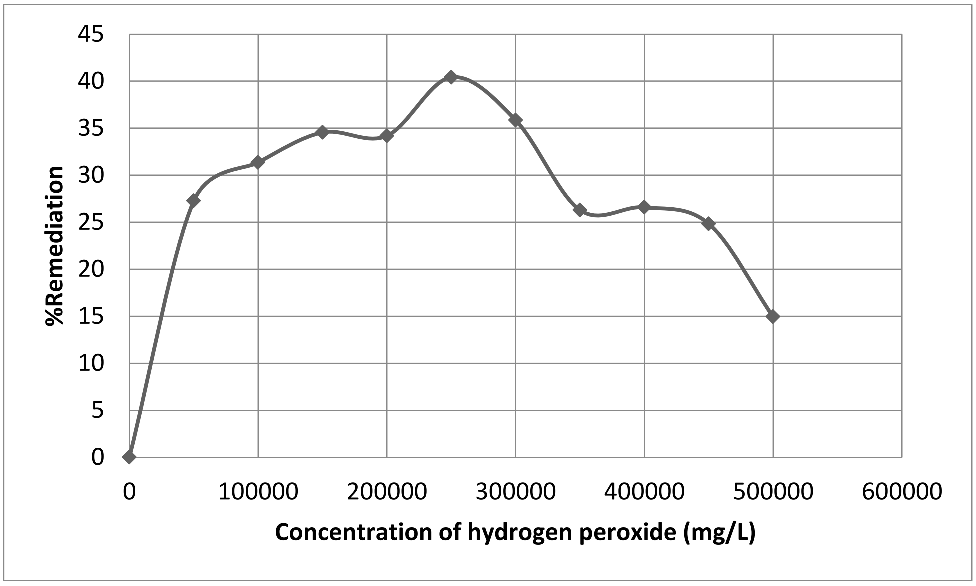


**Figure 1:** Effect of $H_2O_2$ concentration on TPH removal efficiency.

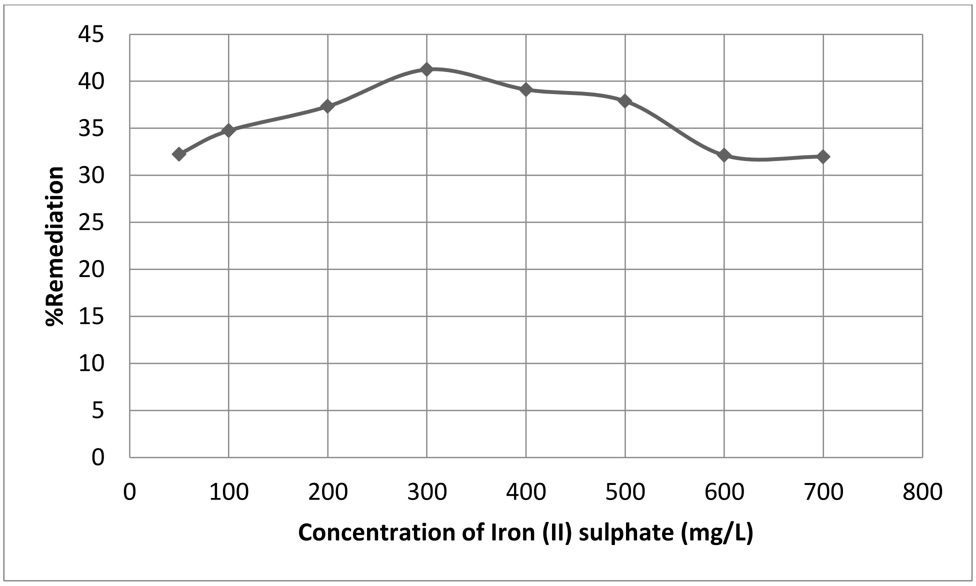


**Figure 2:** Effect of $FeSO_4$ concentration on TPH removal efficiency.

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 ( Sylva 2018; Medjor *et al.*,2012).

The results of the pH test condition demonstrated that the most effective removal was at pH 3 with percentage removal of 42.29%. 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 = 34.8%, pH: 2.5 = 36.95%, pH: 3 = 42.29%). 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 Sylva (2018). 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 (US Peroxide, 2013). Thus pH of 3 is the optimum for the diesel contaminated surface water treated by Fenton oxidation.

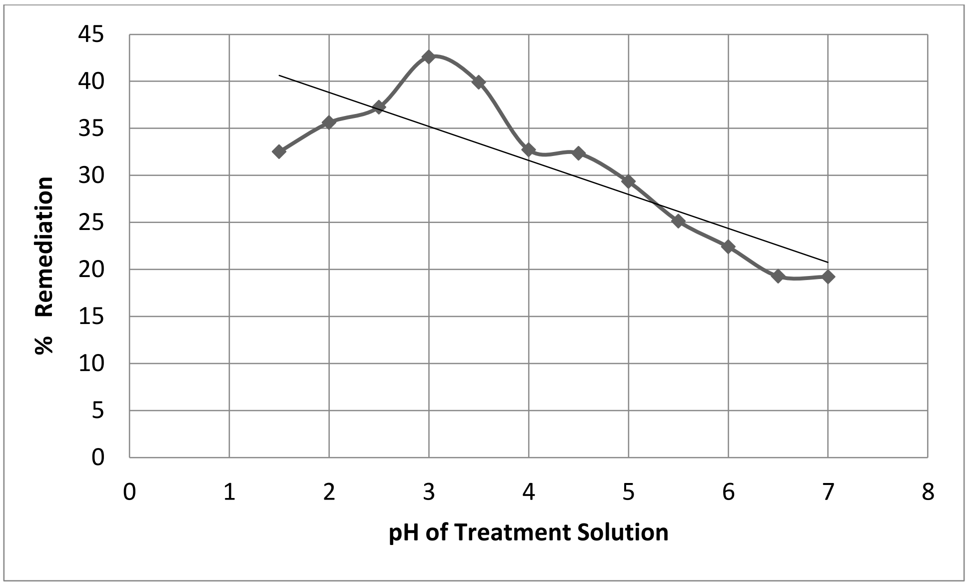


**Figure 3:** Effect of pH on TPH removal efficiency.

Optimum temperature range of 25 – 30$^0$C 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 30$^0$C. However, as the temperatures increase above 40$^0$C, statistically there was a significant change as the efficiency of Fenton's oxidation declines. This is due to the accelerated decomposition of $H_2O_2$ into water and oxygen Figure 4 below (Sylvia 2018; Huang *et al.*,1993).The speciation of iron, and hydrogen peroxide decomposition are both affected by pH activities which show decrease in removal efficiency. This can explain as follows: at lower pH (< 2.5), the formation of $[Fe(H_2O)_6]^{2+}$ complex occurs rather than the formation $[Fe(OH)(H_2O)_5]^{+}$ complex , which reacts slowly with the hydrogen peroxide and, therefore, produces less amount of reactive hydroxyl radicals thereby reducing the degradation efficiency as reported by Mota *et al.*,(2008). In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes important at a very low pH and also the reaction of $Fe^{3+}$ with hydrogen peroxide is inhibited (Pignatello, 1992).

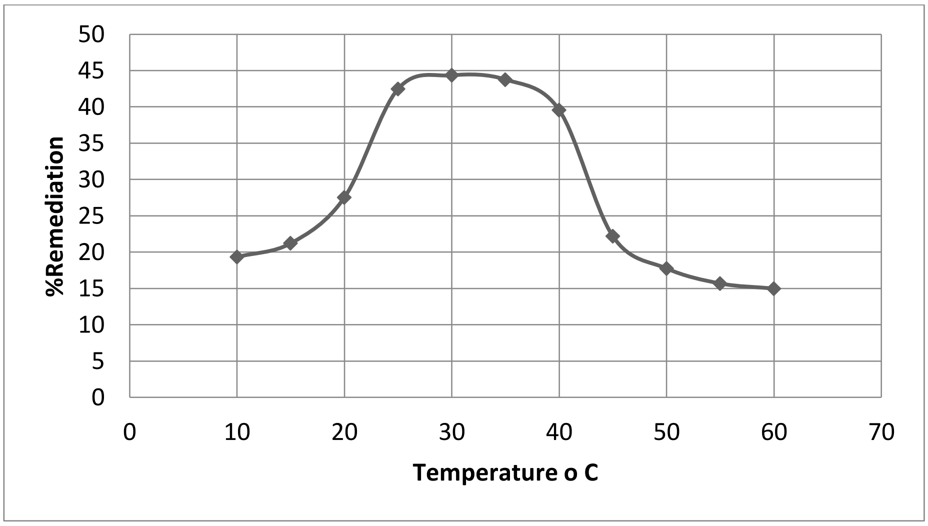


**Figure 4:** Effect of temperature on TPH removal efficiency.

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 5 mins to 10 mins. 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 105 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. The result shows that only a marginal effect on degradation performance was obtained which is similar to Shinggu *et al* (2019). The result of this study agree with the report of Mustafa *et al (*2013), which also coinciding with Rivas *et al.* (2004), they reported that the degradation efficiency is unaffected even when the temperature is increased from 10 to 40$^oC$. Above 40$^oC$, efficiency of hydrogen peroxide utilization decreases due to accelerated decomposition of hydrogen peroxide into water and oxygen as observed by Nesheiwat and Swanson, (2000)

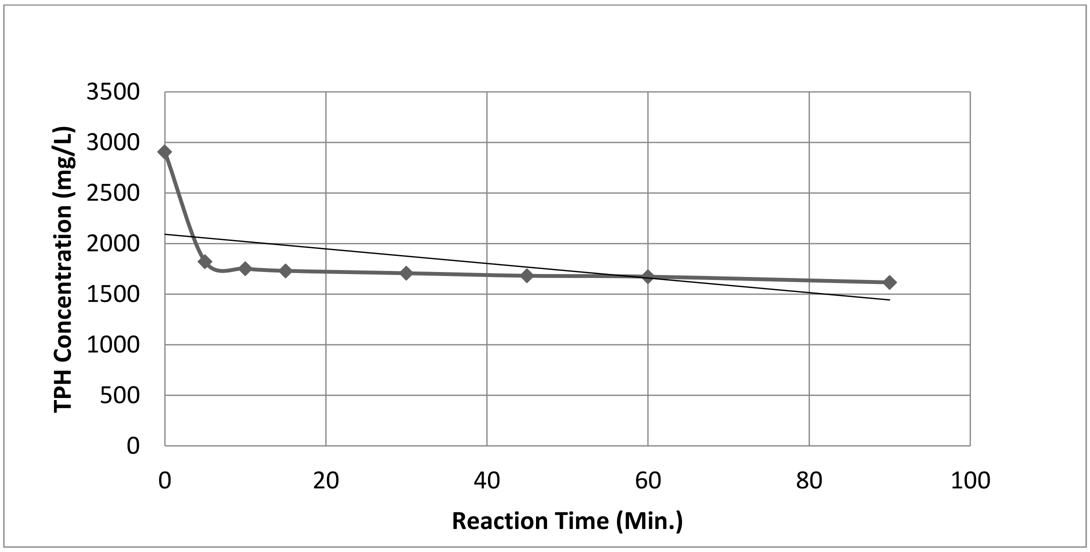


**Figure 5:** TPH left after remediation with different reaction time.

The result obtained from the kinetic study, showed that surface water contaminated with kerosene gave appreciable TPH removal of 43.9% when the reaction was allowed to run for 105 minutes. A plot of percentage remediation against reaction time is illustrated in Figure 6.

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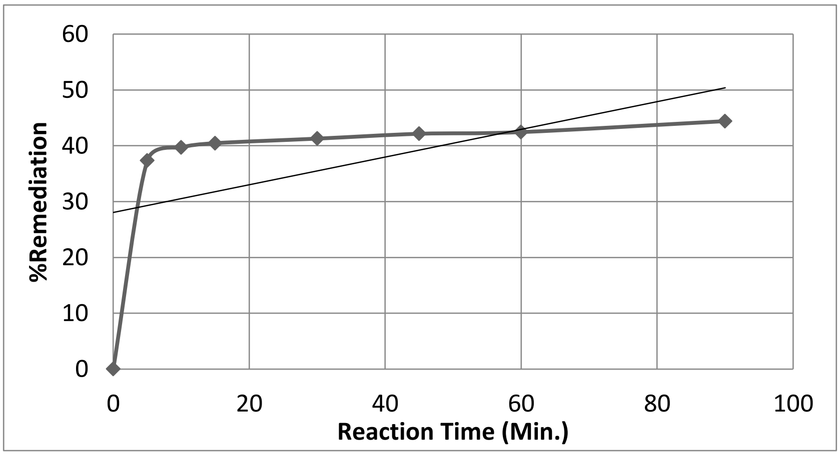


**Figure 6:** Percentage Remediation against Reaction Time

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. A plot of good linearity, shows that the obtained data fits into a Pseudo-first order kinetics.

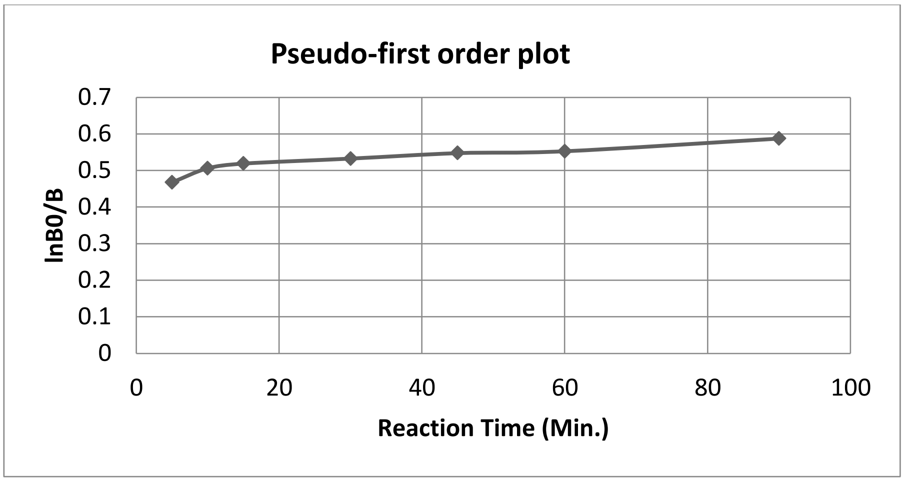


**Figure 7**: Second order reaction kinetics (Pseudo – first order plot).

The rate constant of the Fenton's oxidation used in the remediation of Diesel contaminated surface water samples was obtained from its second order reaction kinetics plot (pseudo-first order plot) as $3x10^2 mol^1 cm^3 min^{-1}$. The half-life of second-order reaction kinetics which is inversely proportional to the initial total petroleum hydrocarbon concentration ($t_{1/2} = 1/k_{[initial\ TPH]}$) was calculated as $1.124 \times 10^{-6}$ minutes which agrees with Shinggu *et al (*2019). The result has shown that the half-life was shorter in the early stage of the reaction when more of the reactant molecules were obtained.

**Conclusion**

The summary of the results obtained from this study have shown that Fenton's oxidation is an efficient and effective technique in remediating diesel contaminated surface water. The study has revealed that various physicochemical factors such 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 research therefore suggests that the environment to be treated must be slightly acidic before treatment. The environment must also not be very acidic as $H^+$ would compete with contaminants for $OH^-$ radicals. Diesel-polluted surface water remediated by Fenton's oxidation may need post-treatment to improve on its potability for industrial, domestic and agricultural applications.

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