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

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 250000mg/L H_2O_2 and 300 mg/L $FeSO_4$ 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 $3x10^2$ $mol^{-1}cm^3min^{-1}$.

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 ($15.63x10^6$ 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 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

36 hydrocarbons provides serious problems for many developing countries especially Nigeria. Man

37 has dealt with the cleanup of petroleum products contamination since the first day oil was

38 discovered [10].

39 The development of petroleum industry into new frontiers, the apparent inevitable spillages that

40 occur during routine operations, the records of acute accidents during transportation has called

41 for more studies into oil pollution problems, which has been recognized as the most significant

42 contamination problem encountered in Nigeria [11]. Thereafter, several studies have examined

43 the fate and effect of petroleum in various ecosystems [12,13]. This work is aimed at

44 investigating the effectiveness of Fenton's oxidation in remediating a kerosene contaminated

45 surface water to contribute to the numerous research works meant to create a convincing

46 chemical remediation technique or method that can be employed to treat a water body when

47 there is a case of oil spillage. This work also investigated the optimum conditions and kinetics

48 needed for better performance of the method employed for the treatment of DPK contaminated

49 surface water.

50

51 **Materials and Method**

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

53 temperatures.

54 **Sampling Area and Sample collection**

55 River Bali is located in Bali local government area of Taraba state, Nigeria, with geographical

56 coordinates of $7^o 52'$ $0''$ North, $10^o 58'$ $0''$ East.

57 The water samples were collected by grab sampling method along the bank of river Bali at

58 different locations to make a representative sample. The water which flows through the Bali

59 main bridge is sampled in a thoroughly washed 25 liter container rinsed with distilled water. A

60 standard domestic purpose kerosene (DPK) Samples were obtained from the Nigeria National

61 Petroleum Commission (NNPC) Filling station of Mile-six Jalingo, Taraba state, Nigeria.

62

63 **Samples homogenization**

64 To provide a homogenized water sample and to enhance a thorough mixing of the DPK with the

65 water, the water was thoroughly mixed by the use of mechanical shaker. Pollution was simulated

66 in the laboratory by contaminating $45cm^3$ of the surface water sample with $5cm^3$ domestic

67   purpose kerosene (DPK) in several different containers, stirred with magnetic stirrer to produce

68   10% contamination.

69

Quality control

71   High quality grade n- hexane was used in extracting hydrocarbon from the contaminated surface

72   water in preparing working standards used in constructing calibration curves. The dilute

73   solutions of the analyte employed in the spectrophotometric measurements were homogeneously

74   mixed and found not to associate or dissociate at the time of analysis. Reagent blanks (analyte

75   free water + treatment solutions to be analyzed) were used to correct any absorption of light by

76   n-hexane. Quartz cuvettes free from scratches clean and dried before used [14]

77

Instrument Requirement

79   Different hydrocarbons in water shows absorbance at specific wavelengths. Spectrophotometric

80   measurements gave satisfactory accuracy, sensitivity, reproducibility and linearity at different

81   wavelengths. Stable electricity was ensured by via the use of electric generator and an

82   uninterrupted power supply (UPS) device for reliable performance. In this study, a

83   spectrophotometer was used in preference to a colorimeter to reduce the interference from

84   unwanted chromogenes.

85

Optimization studies

87   Optimization study for the concentrations of H_2O_2, $FeSO_4$, pH, and temperature was carried out

88   to determine the optimum conditions for the treatment of the DPK contaminated surface water.

89   The same conditions were subsequently used for kinetic studies.

90

Optimum H_2O_2 Concentration

92   About 150mg/L $FeSO_4$ was prepared and kept constant for the sake of the H_2O_2 optimization

93   study. Several solutions of the 10% DPK contaminated surface water taken in ten different

94   conical flasks which were each added 6 mL of 100 mg/L $FeSO_4$ and 30 mL of 50,000 –

95   500,000mg/L H_2O_2 and allowed to undergo remediation for 40 minutes before extraction and

96   analysis. Kerosene in the water layers was extracted using n- hexane. Total Petroleum

97 Hydrocarbon as kerosene was read by UV/Visible spectrophotometer at wavelength of 310 nm.

98 The procedure was repeated for other replicate samples.

99

100 **Optimum $FeSO_4$ Concentration**

101 About 250,000 mgL^{-1} H_2O_2 was observed to be the optimum concentration for the treatment

102 which was used to determined the optimum concentration of iron (II) sulphate. Several solutions

103 of the 10% DPK contaminated surface water taken in eight conical flasks were each added 6 mL

104 of 50-700 mg/L $FeSO_4$ and 30 mL of 250,000mg/L H_2O_2 and allowed to undergo remediation for

105 40 minutes before extraction and analysis using T – 60 UV/Visible spectrophotometer.

106

107 **Optimum pH.**

108 The solution of the 10% DPK contaminated surface water was taken in twelve conical flasks. To

109 each of the several solutions, 6 mL of 300 mg/L FeSO4 and 30 mL of 250,000mg/L H_2O_2 were

110 added. Each of the solutions had their pH values varied between 1.5 to 7.0 pH values by the use

111 of 1M H_2SO_4 and 1M N_aOH for adjustment, pH meter was used for measurement throughout the

112 adjustment and the samples were allowed to run for 40 minutes before extraction and analysis.

113 **Kinetics studies**

114 Optimum conditions obtained from the optimization study were applied in the kinetic study

115 where aliquot was taken out for extraction and analyzed at time interval of 5, 10, 15, 30, 45, 60

116 and 90 minutes [14, 15].

117 **Fenton's Oxidation**

118 The optimum conditions established from the optimization and kinetic studies $6cm^3$ of 300mg/L

119 $FeSO_4$, $30cm^3$ of 250,000mg/L H_2O_2, pH value of 3, were applied to the several solutions of 10%

120 contamination in conical flasks, stirred with magnetic stirrer and kept for a required time until

121 extraction and analysis. TPH concentration was determined by T-60 UV/Visible

122 spectrophotometer at a wavelength of 310 following laboratory method adopted by [16, 14].

123

124

125 **Statistical treatments**

126 Samples were prepared in replicate of three to provide data for statistical treatment. Standard

127 deviation (SDEV), relative standard deviation (RSD) and coefficient of variation (CV)

128 calculations were used to checkmate indeterminate (random) error. Sets of replicate results
129 obtained from the study were found to have measurement uncertainty of less than 2% in terms of
130 their coefficient of variations in all cases.
131 Therefore the results are said to be of high precision. Blank runs were also conducted to reduce
132 the occurrence of determinate errors [14]

133 **Results and Discussion**
134 The efficiency of a remediation technology depends on several factors; pH, type of water, time,
135 concentration of treatment solutions, nature of catalyst and competition between different
136 pollutants [17]. Various experiments were designed to optimize Fenton's oxidation and to
137 investigate the effect of these environmental factors on Fenton's oxidation [18, 19]. The results
138 on the optimization of hydrogen peroxide concentration, iron sulphate concentration, pH, and
139 temperature for DPK contaminated surface water samples treated by Fenton's oxidation are
140 shown below. Optimum concentrations of 250,000 mg/L H_2O_2 and 300 mg/L FeSO4 solutions
141 were obtained for the kerosene contaminated surface water samples with an average 40.84%
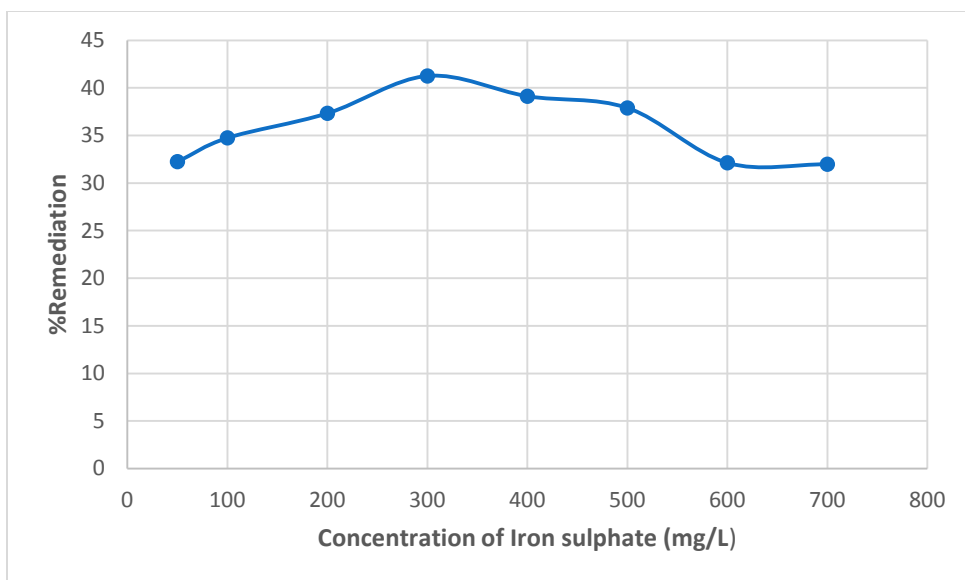142 remediation efficiency. The results are shown in Figs. 1 and 2

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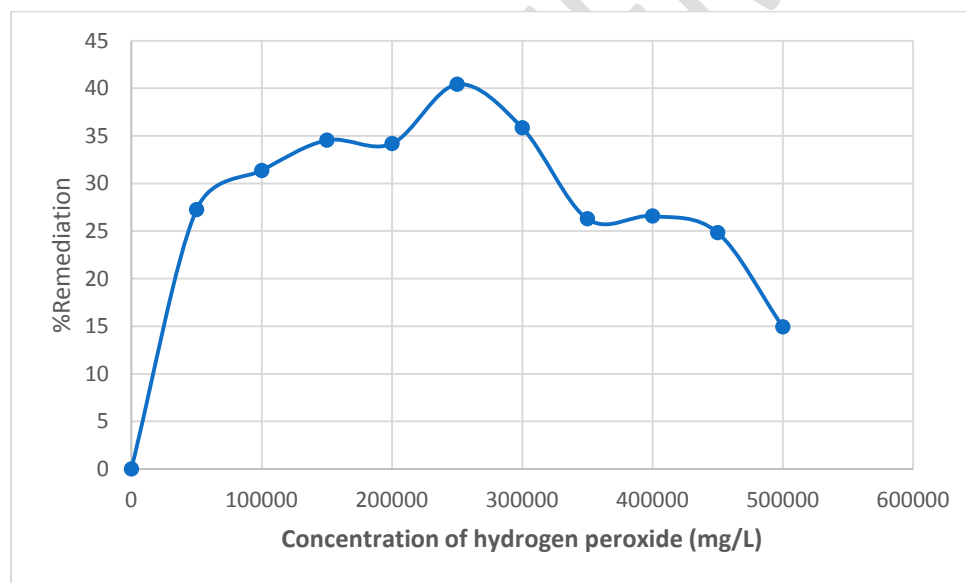
144
145 **Figure 1:** Effect of H_2O_2 concentration on TPH removal efficiency.
146
147

148
149 **Figure 2:** Effect of FeSO$_4$ concentration on TPH removal efficiency.

150
151 Studies found indifferent literatures suggested that the mixture of the hydrogen peroxide and iron

152 (II) sulphate solutions is acidic in nature with an approximate pH value of 4.43, this value was

153 confirmed and an optimum pH of 2.8-3.0 was obtained and ensured for efficiency of the
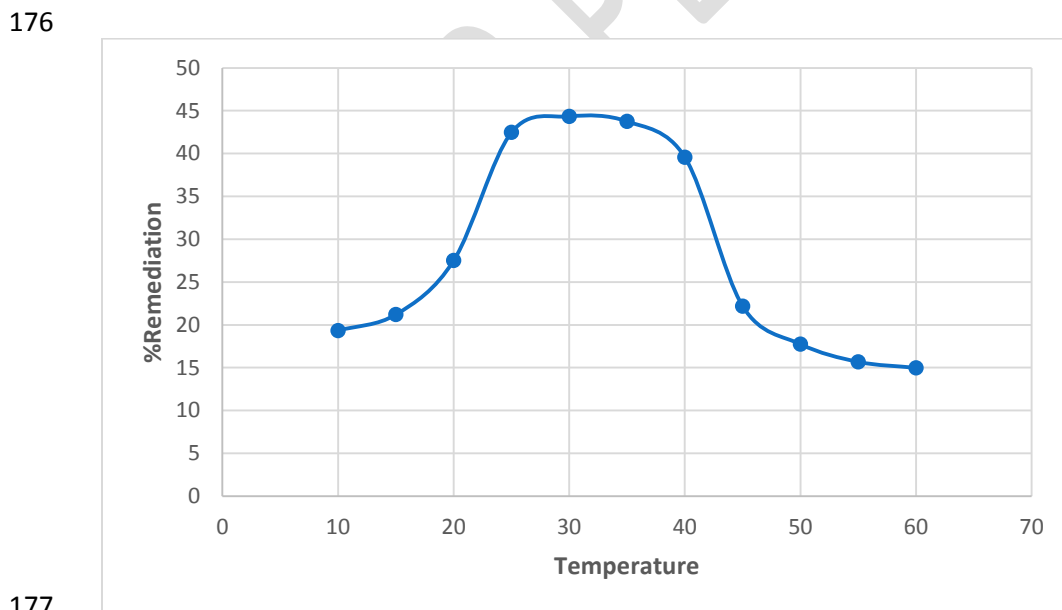
154 Fenton's oxidation [17, 20].

155 The results of the pH test condition demonstrated that the most effective removal was at pH 3

156 with percentage removal of 42.59%. The effect of pH seemed to be less effective in TPH

157 removal at higher pH values. At lower pH values, the removal was quite high (pH: 2 = 35.6%,

158 pH: 2.5 = 37.25%, pH: 3 = 42.59%). With increasing pH, the percentage TPH removal dropped

159 linearly as shown in Fig.3. The drop in efficiency on the basic side is attributed to the transition

160 of iron from a hydrated ferrous ion to a colloidal ferric species [17]. In the latter form, iron

161 catalytically decomposes the H$_2$O$_2$ into oxygen and water, without forming hydroxyl radicals.

162 The drop in efficiency on the acid side is less dramatic given the logarithmic function of pH, and

163 is generally a concern only with high application rates. The result shows that ferrous iron could

164 react with H$_2$O$_2$ efficiently under acidic conditions [21]. Thus pH of 3 is the optimum for the

165 DPK contaminated surface water treated by Fenton oxidation.

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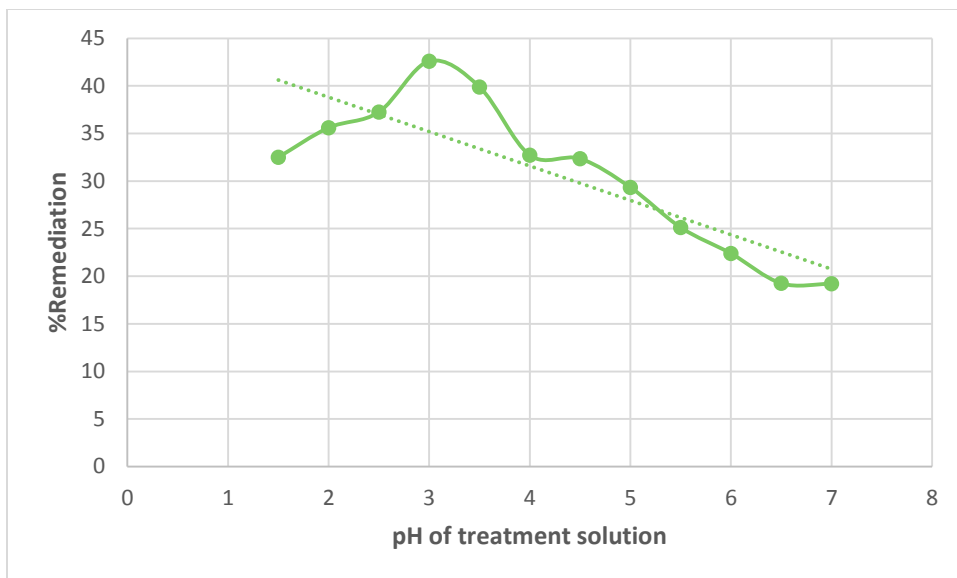
167
168 **Figure 3:** Effect of pH on TPH removal efficiency.
169

170 Optimum temperature range of $25 - 30^0C$ was obtained, this is in agreement with other studies
171 found in literature. The rate of reaction with Fenton's reagent increases with increase in
172 temperature, with the effect more pronounced at the range of 25 to 30^0C. However, as the
173 temperatures increase above 40^0C, the efficiency of Fenton's oxidation declines. This is due to
174 the accelerated decomposition of H_2O_2 into water and oxygen [17, 22]. This discussion is
175 illustrated in Figs. 4 below

176

177
178 **Figure 4:** Effect of temperature on TPH removal efficiency.
179

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 60mins 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.
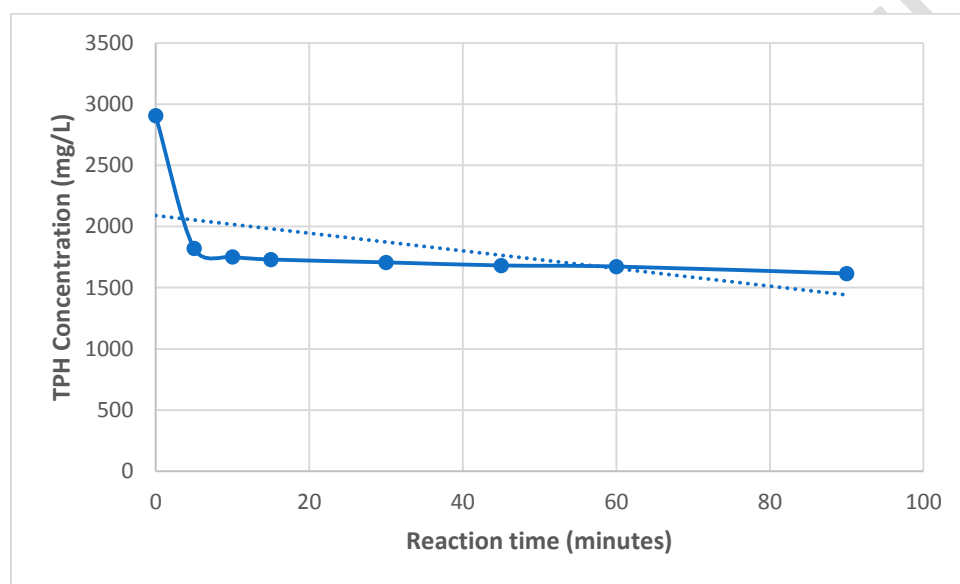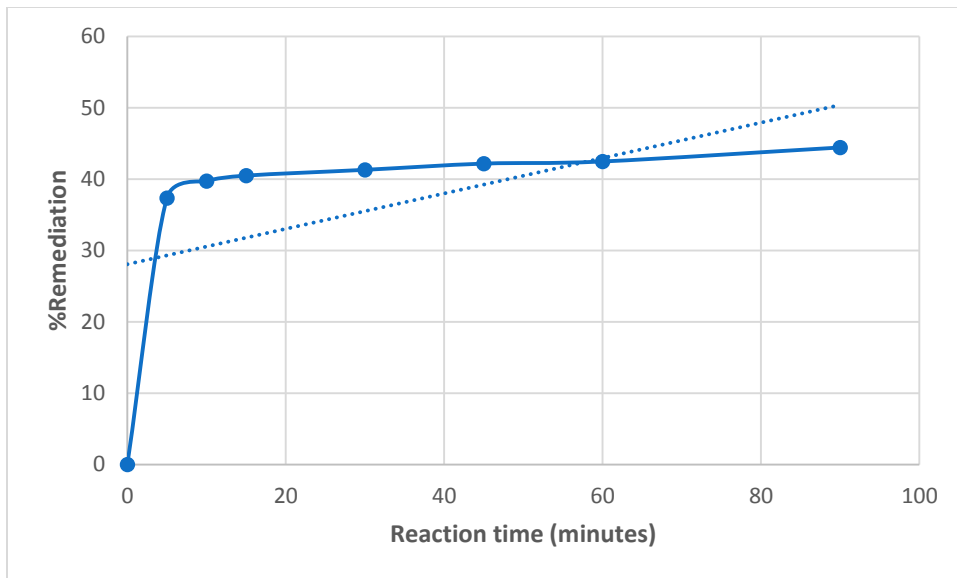

Figure 5: TPH left after remediation with different reaction time.

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
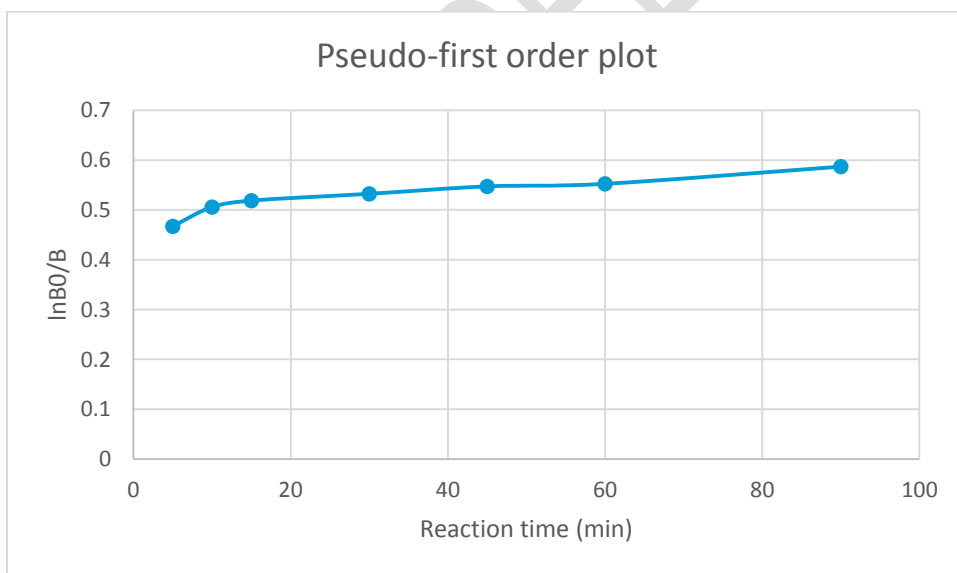
Figure 6: Percentage remediation against reaction time

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

212   order plot) as 3×10^2 $mol^1cm^3min^{-1}$. The half-life of second-order reaction kinetics which is

213   inversely proportional to the initial total petroleum hydrocarbon concentration ($t_{1/2}=1/k_{[initial\ TPH]}$)

214   was calculated as 1.146×10^{-6} minutes. This shows that the half-life was shorter in the early stage

215   of the reaction when more of the reactant molecules were present.

Conclusion

217   The results obtained from this have shown that Fenton's oxidation is an efficient technique in

218   remediating DPK contaminated surface water. The study has revealed that various factors such

219   pH, type of water, type of hydrocarbon, H_2O_2 concentration, $FeSO_4$ concentration, temperature

220   and reaction time can affect the efficiency of Fenton's oxidation.

221   Fenton's oxidation was found to be more effective in acidic environment than in basic

222   environment. This suggest that the environment to be treated must be slightly acidic before

223   treatment. The environment must also not be too acidic as H^+ would compete with contaminants

224   for OH radicals.

225   DPK polluted surface water remediated by Fenton's oxidation may need post-treatment to

226   improve on its portability for domestic and agricultural uses.

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