

FENTON OXIDATION DE-CONTAMINATION OF KEROSENE AND GASOLINE CONTAMINATED SURFACE WATER FROM THE OGBE IJOH RIVER: PROCESS OPTIMIZATION AND KINETIC MODELLING

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ABSTRACT

Fenton oxidation decontamination of kerosene and gasoline-contaminated water from the Ogbeloh River was investigated for its effectiveness as an advanced oxidation process (AOP). The optimum conditions at ambient temperature and pH = 3, were 22,500 mg (22.5 g) H₂O₂ and 200 mg FeSO₄ per L of 10% contaminated water treatment. Pseudo-first and second-order kinetic equations were used to test the kinetic model. The result indicated that both the first and second-order kinetics were applicable even though the first order must fit. This indicates that there was a change in the mechanistic pathway during the degradation process. The rate constants of 2.06 X 10⁻² and 2.14 X 10⁻² mg/L.S were obtained for the first-order kinetic plots for the degradation of kerosene and gasoline-contaminated waters respectively. The 90.90 and 94.11% reductions in total petroleum hydrocarbons (TPHs) values for kerosene and gasoline-contaminated water for the six hours of contact time represented significant achievement in remediation. However, some physicochemical parameters of the treated water have negative effects on the overall quality of the water. Thus, there is need for post-treatment to ensure safe discharge or reuse.

Keywords: Degradation, hydroxyl radicals, total petroleum hydrocarbons, reaction kinetics, remediation

INTRODUCTION

Pollution by petroleum hydrocarbons has significant impacts on the ecological system. Water a vital resource that supports and sustains lives on earth, is particularly affected by the release of hydrocarbons into the environment. Hydrocarbons though, naturally presence in the environment, large amount of it in a contaminated environment, which gets into water bodies comes through the activities of man such as: oil exploration and exploitation, pipelines leakages and vandalization, runoff from petroleum contaminated soils, leakages from farm tanks, tankers, trucks, vessels and ships, oil spills, and indiscriminate dumping of petroleum products on water ways. Industrial and municipal waste discharges, fallout of automobile exhaust, and combustion activities carried by runoff and brought down to water bodies constitute other anthropogenic sources of hydrocarbons (Chokor, 2021a). Surface water, particularly river water furnishes valuable resources which include the protection and propagation of aquatic lives (e.g. fishes), recreation, and public water supply etc. (EPA, 2015; Chokor, 2021b;c). Thus, their contaminations represent a danger to man and the ecosystem. The effects of petroleum hydrocarbon exposure to organisms and human health have been variously described by various authors. The disruption in the

activities of various body organs, such as: the pancreas, kidney, liver, blood circulatory system, and ultimately death were noted by Abha and Singh (2012), and Oyinbo et al (2018). Humans health complications like skin irritation and rashes, genotoxicity, respiratory system disorders, cancers of different parts (organs) of the body, deoxyribonucleic acid (DNA) damage, birth defects, childhood leukaemia, infertility and miscarriages in women, have also been linked to petroleum hydrocarbons contamination (Ezekwe and Edoghotu, 2015; Kponee et al., 2015; Asghar et al, 2016, Briggs and Briggs, 2018; Ite et al., 2018; Chokor, 2021a). The severity of the impacts depends on several factors such as: the persistence and bioavailability of specific hydrocarbon, the ability of organisms to accumulate and metabolize various hydrocarbons, the fate of the metabolized products, and the interference of specific hydrocarbons with normal metallic processes (Lee et al., 2015; Chokor, 2022). But generally, impairment of feeding mechanisms, growth and developmental rates, as well as increased susceptibility to diseases and other histopathological disorders are some of the common subtle acute effects that may crop up due to petroleum hydrocarbon exposure (Al-Shwafi 2008; Enuneku et al., 2015). Chronic low-level exposure to hydrocarbons may result in physiological impairment, affects survival, and reduces reproductive success (Enuneku et al., 2015; Lee et al., 2015; Chokor, 2021a).

The need therefore for hydrocarbon-contaminated water, to be remediated can never be overemphasized. Various remediation techniques have been suggested and are being used in the treatment of water and wastewater (de Abreu Domingos and da Fonseca, 2018; Esmaili and Saremnia, 2018; Campo and Di Bella, 2019; Filatova and Soboleva, 2019; Mohammadi et al., 2020). Biological, physical and or chemical methods are being used for the oxidative destructions and/or removal of organic pollutants in water and wastewater. The cost effectiveness of biological treatment as well as its versatility in handling a wide range of organic pollutants has given it much attention; and its use in remediation far exceeds those of chemical and /or physical methods. However, the long retention time and start-up time of the oxidation process makes it less attractive for the treatment of toxic and refractory organic pollutants (Moussavi et al., 2011). Thermal destructions (incineration) though, simple in principle, had many challenges as regards its operations. Besides, thermal processes are limited in the treatment of aqueous wastes since large quantity of energy is required in heating and vaporising the water mass before specific organic pollutants are destroyed at relatively elevated temperature of not less than 850°C. Chemical oxidation such wet-air oxidation, involving the decomposition of pollutants with atmospheric air or pure oxygen at lower temperature (150 –

370°C.) and 10 -220 bar pressure in the presence of a catalyst has been developed to overcome the above problems; and improved the efficiency of the incineration process. However, the high cost associated with the wet-air oxidation process had caused it to remain an operation only at the preliminary treatment requiring further treatment for the total destruction of organic pollutants. Advanced oxidation processes (AOP) which involve the generation of radicals in situ in sufficient quantity to effect treatment of water is now being looked upon as viable alternatives for the remediation of water and waste water. The specific mechanisms involved in Fenton oxidation process have been variously described by various authors (Babuponnusami and Muthukuma, 2014; Wang et al., 2016; Walling et al., 2021). Some authors (Singh and Tang, 2013; Deng et al., 2015; Medjor et al., 2018) have used Fenton oxidation; an advanced oxidation process for the treatment of hydrocarbons and organic wastes in wastes waters but they measured the remediation efficiency using reduction in chemical oxygen demands (CODs) and total organic carbons (TOC). COD as a collective parameter measures both the oxidizable organics as well as inorganic, including metal ions; while TOC focuses on all forms of organic carbons – both petroleum hydrocarbons and other forms. In this work, Fenton oxidation was used for the treatment of the Ogbe-Ijoh River water contaminated with petroleum hydrocarbons - kerosene and gasoline, using Total Petroleum hydrocarbon (TPHs) measurement as a quantitative evaluation of the extent of petroleum hydrocarbon removal.



Figure.1: Map showing Ogbe Ijoh River and the sampled area

MATERIALS AND METHODS

Sampling area, sample collection and preparation

Water samples were collected from the Ogbe Ijoh River in Warri South West L.G.A of Delta State, Nigeria ($5^{\circ}28' N$ and $5^{\circ} 44' E$) (Fig. 1). Composite sampling were carried out by collecting water samples from the surface of the river at two hourly intervals for over 20 hours period and the flow rate being measured each time interval of collections. Thereafter, a single composite sampling was made by mixing to 10 separate two-hourly samples, using volumes proportional to the flow rate at the time of sampling. The samples were put in pre-cleaned 250 ml capacity amber glass bottles with aluminium-lined screw cap and kept in ice chest at temperature below $4^{\circ}C$ for onward transportation to the laboratory. In the laboratory, a portion of the samples were analysed for physicochemical properties using standard methods as described by Ademoriti (1996), Radojević and Baskin (1999), and Chokor (2021b,c). The other portions were contaminated with 10 percent volumes of kerosene and also of gasoline and thoroughly mixed by

the use of a mechanical shaker to produced 10% contaminations for remediation studies. The hydrocarbons viz; domestic purpose kerosene (DPK) and automotive gasoline used to simulate contaminations, were obtained from the Petroleum Refinery Company (PRC) Warri, Delta State, Nigeria.

Sample Extraction and analysis

The water samples were extracted according to the USEPA methods 1664 (USEPA, 1999). 10 ml of hexane was added to a separating funnel containing 60 ml of unfiltered water sample and this was shaken vigorously for about 5 min. The sample was allowed to stand for 20 minutes until two distinct layers were formed. The upper layer (the extract) was filtered into a beaker through a filter paper containing glass wool and anhydrous sodium sulphate (Na_2SO_4). The process was repeated twice using 10 ml of hexane. The extracts were combined and analysed with UV spectrometer.

Optimization of hydrogen peroxide and iron II sulphate concentrations for Fenton treatment process

Concentrations range of 0.00 - 120,000 mg/L were prepared by adding 0.0, 4.5, 6.0, 7.5, 9.0, 10.5, and 12 ml of hydrogen peroxide solutions into seven 100 ml flasks. The flask and content were shaken thoroughly and made up to mark using distilled water. The different masses (0.0, 5.0, 10.0, 20.0, 30.0 & 40.0 mg) of iron (II) sulphate were similarly weighed into six different 100 ml volumetric flasks. To seven 100 ml solutions of kerosene and gasoline simulated water samples were added a constant quantity of $FeSO_4$ (30 mg) and varied amount of 30 ml of 0.0 - 120,000 mg/L H_2O_2 of prepared treatment solution as stated above. It is a well-known fact that the generation of $\cdot OH$ radicals during Fenton reaction is most effective only at acidic pH condition, therefore, the pH was adjusted to 3 using 1M H_2SO_4 at the beginning of the reaction. At the end of the reaction time, the solution pH was adjusted to 10 using 1M solution of NaOH to avoid continuous production of hydroxyl radicals (Singh and Tang, 2013; Deng and Zhao, 2015). The samples were kept stirring to ensure that an even Fenton reaction took place for 30 minutes until extraction and analysis. Kerosene and gasoline in the water layers were extracted using hexane, and the Total Petroleum Hydrocarbons (TPHs) as kerosene and gasoline fractions were determined by UV/visible spectrophotometer at wavelength of 310 nm and 330 nm respectively using standard method (Wang et al., 2011; Akpoveta et al., 2018; Medjor et al., 2018). The optimum concentration of hydrogen peroxide obtained above was used to determine the optimum concentration of iron (II) sulphate. The optimum concentration of H_2O_2 obtained above was held constant while varying the concentrations of $FeSO_4$ used to treat the kerosene and gasoline oil simulated water samples. The solutions were allowed to stand for 30 minutes before extraction and analysis.

Kinetic Studies

The Optimum conditions obtained from the optimization study were applied in the kinetic study of the remediation; where aliquots were taken out at time interval of 0.5, 1, 2, 3, 4, 5, and 6 hours for extraction and analysis.

Quality control

High quality grade n-hexane was used in the extraction of petroleum hydrocarbons from the contaminated surface water; and in preparing working standards for the calibration curves. The dilute

solutions of the hydrocarbons used in the spectrophotometric measurements were homogeneously mixed and found not to associate or dissociate at the time of analysis. Clean and dried quartz cuvettes free from scratches were used. Reagent blanks (analyte-free water + treatment solutions to be analyzed) were

used to correct any absorption of light by n-hexane (Medjor et al., 2018). The analyses were carried out in triplicates and the results are expressed as mean and standard deviation from the mean (\pm).

RESULTS AND DISCUSSION

Table 1: Optimization of Hydrogen peroxide (H_2O_2) concentration in Fenton oxidation of 100 ml of 10% Kerosene and Gasoline contaminated waters

30mL of the different concentrations of H_2O_2 (mg/L)	Kerosene		Gasoline	
	Mean TPHs (mg/L)	% Remediation	Mean TPHs (mg/L)	% Remediation
0.0	4,820.4 \pm 3.40	0.00	5,208.4 \pm 4.50	0.00
45,000.0	2,412.2 \pm 1.93	49.96	2,874.2 \pm 2.53	44.82
60,000.0	2,116.1 \pm 2.36	56.10	2,516.1 \pm 2.36	51.69
75,000.0	1,807.2 \pm 1.70	62.51	2,407.2 \pm 2.42	53.78
90,000.0	2,013.3 \pm 3.80	58.23	2,580.3 \pm 3.11	50.46
105,000.0	1,901.4 \pm 3.02	60.55	1,680.4 \pm 2.71	57.74
120,000.0	2,312.7 \pm 3.21	52.02	2,662.7 \pm 4.81	48.88

Table 2: Optimization of Iron (II) Sulphate ($FeSO_4$) concentration in Fenton oxidation of 100mL of 10% Kerosene and Gasoline contaminated waters

Mass of $FeSO_4$ (mg)	Kerosene		Gasoline	
	Mean TPHs (mg/L)	% Remediation	Mean TPHs (mg/L)	% Remediation
0.0	4,820.4 \pm 3.40	0.00	5,208.4 \pm 4.50	0.00
4.0	3,399.8 \pm 2.26	29.47	4,003.2 \pm 3.29	23.14
10.0	3,647.1 \pm 2.00	24.34	3,815.7 \pm 1.50	26.74
20.0	1,757.5 \pm 2.31	63.54	1,680.2 \pm 2.61	67.74
30.0	1,807.2 \pm 3.62	62.51	2,201.1 \pm 3.30	57.74
40.0	3,285.6 \pm 2.51	31.84	3,719.8 \pm 2.45	28.58

kerosene and gasoline contaminated waters were obtained by first keeping constant the concentration of $FeSO_4$ (300 mg/100mL of the contaminated water) and varying that of H_2O_2 (Table 1). The optimum concentration required; producing the maximum remediation (62.51%), that is, the maximum degradation of kerosene contaminated water was 30mL of 75,000 mg H_2O_2 /L (Fig.2). The gasoline contaminated water however, required 30 ml of 105,000mg H_2O_2 /L to yield the optimal percent remediation of 57.74%. Next to this peak was 53.78% remediation produced by 30mL of 75,000mg H_2O_2 /L. Given the closeness of the above two peaks, the 75,000mg/L H_2O_2 was held constant for both kerosene and gasoline contaminated water, and the concentrations of $FeSO_4$ was varied in order to obtain an optimum concentration for the $FeSO_4$ (Table 2). The optimum concentrations for both the 10% kerosene and gasoline contaminated water were found to be 20mg $FeSO_4$ /100mL (Fig. 3). Thus, the optimum conditions for the Fenton oxidation de-contamination of the surface water polluted with 10% kerosene and gasoline contaminated waters at pH 3, and ambient temperature were: 30 ml of 75,000 mg/L H_2O_2 and 20 mg $FeSO_4$ per 100 ml of contaminated water. This translates to 22,500mg (22.5g) H_2O_2 and 200mg $FeSO_4$ per L of 10% contaminated water treatment.

The optimal concentrations of hydrogen peroxide (H_2O_2) and Iron II sulphate ($FeSO_4$) required for the Fenton oxidation of 10%

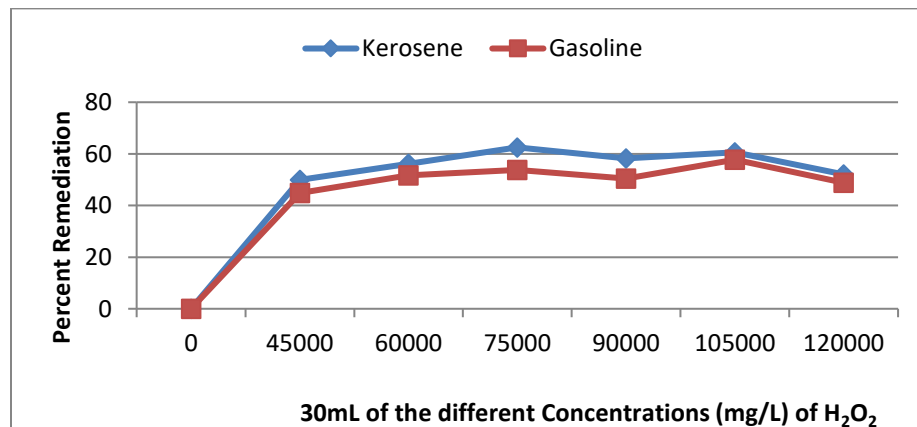


Figure 2: Percent remediation with amount (mg/L) of hydrogen peroxide (H_2O_2) used in the oxidation of

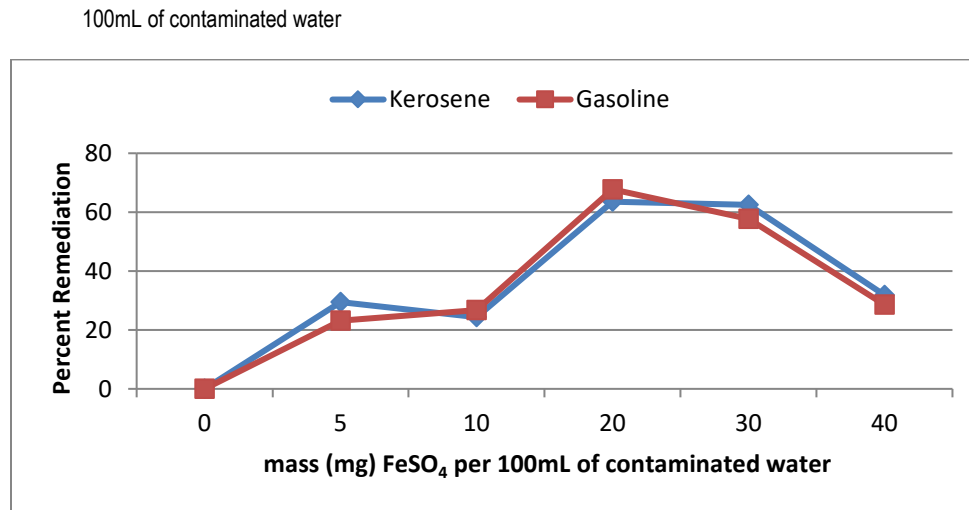


Figure 3: Percent remediation with amount (mg) of Iron II sulphate (FeSO₄) used in the oxidation of 100mL of contaminated water

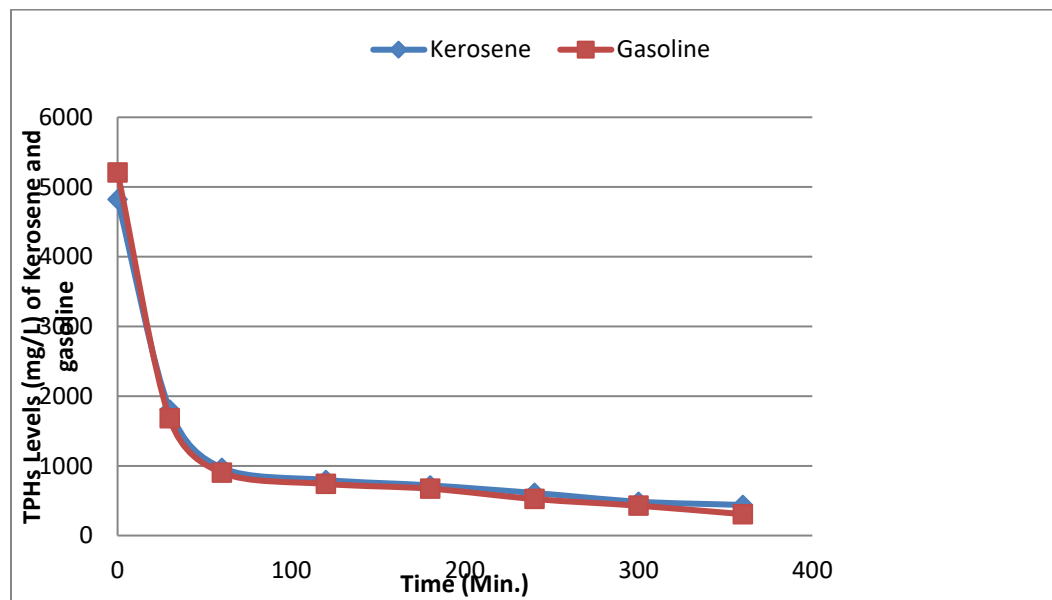


Figure 4: Trend of TPHs (mg/L) degradations with 10% kerosene and gasoline contaminated water by Fenton oxidation

Figure 4 shows the rate of total petroleum hydrocarbon (TPHs) degradations with time in both the 10% kerosene and gasoline contaminated water. The diminishing TPH with time is a strong indication that the reacting species of the treatment solution had a strong interaction with the TPH molecules of the sample medium. The chart showed that for both contaminated waters, there was a very sharp step degradation of the TPHs within the first 60 minutes, followed by slow step degradations afterward. The large number of TPHs available for reaction at the initial stage could be responsible for the initial fast reaction. The reaction becomes slower afterward due to a lesser number of TPHs available for reaction. Several authors have described a two-step stage as characterizing some reactions. Chokor (2017) found a two-step process (a fast first stage followed by a slower second stage) for the adsorption of

heavy metals onto sandy-loam soils in Sapele. Similarly, Mitsika et al (2013) and Covinch et al (2018) found two-step stages for the homogeneous oxidation of real effluent. In this study, a 90.90% reduction (remediation) of TPHs was achieved for the 6 hours of Fenton reagent contact with the kerosene-contaminated water. However, 87.83% of this value corresponding to 79.84% reduction of TPHs was achieved within one (1) hour of contact time. Similarly, the gasoline-contaminated water had within the 6 hrs of contact time, 94.11% of its TPHs degraded; but 87.83% of this value representing 82.66% reduction in initial TPHs concentration was achieved within 1hr of contact time with the Fenton reagent. The reasonable degradation obtained for waters in one hour of contact imply that there may not be need for prolong hours of contacts. Some of the physicochemical properties of the uncontaminated water, after contamination with 10% kerosene and gasoline, and

treatments with Fenton's oxidation shown in Table S1 indicated marked quality improvement compared to the contaminated water. However, the pH, electrical conductivity, and metals content (Cd, Ni, & Pb) were quite high even after treatment; and therefore may

require further treatment before use or discharge to receiving water bodies.

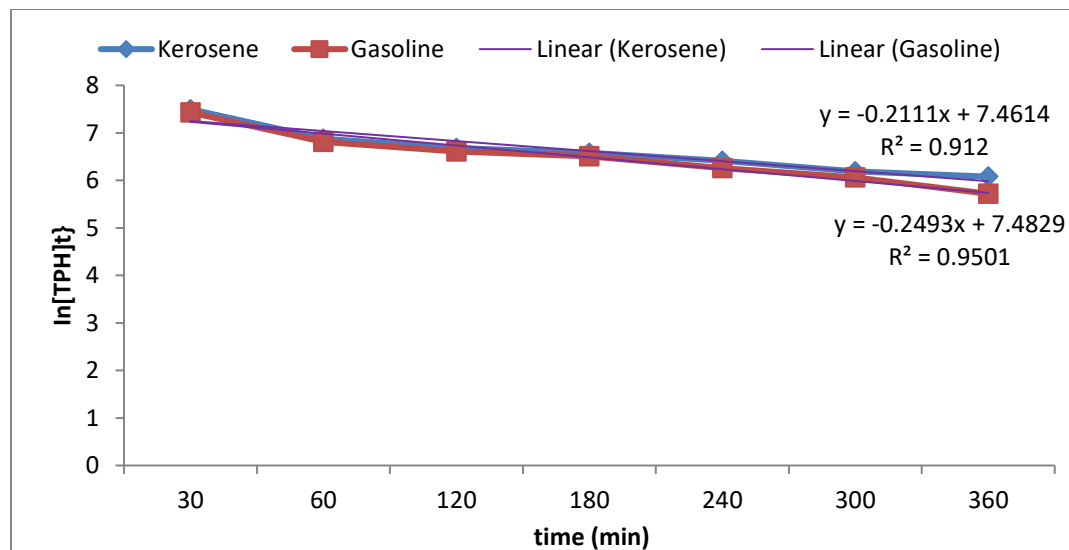


Figure 5: Plot of logarithm of TPHs concentrations ($\ln [TPHs]_t$) against time (min) for the Fenton degradation of kerosene and gasoline contaminated water

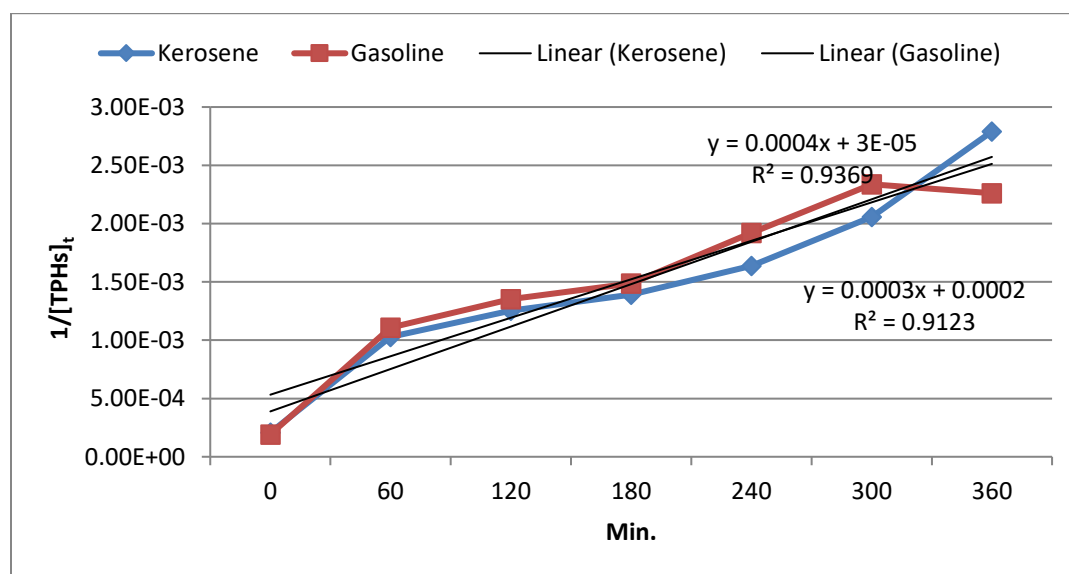
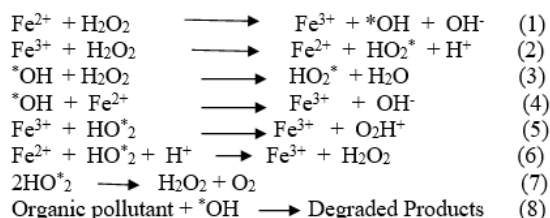


Figure6: Plot of inverse of TPHs concentrations ($1/[TPHs]_t$) against time (min) for the Fenton degradation of kerosene and gasoline contaminated water.

Two kinetic models – the pseudo-first, and pseudo-second order equations were applied to investigate the kinetic of remediation process (Fig. 5 & 6). The pseudo rate order plots for the remediation process were tested using the pseudo-first order equation of $\ln[A]_t = -Kt + \ln [A]_0$; and second order equation: $1/[A]_t = Kt + 1/[A]_0$; where \ln is the natural logarithm, and $[A]_0$ and $[A]_t$ are concentrations of A at times $t = 0$ and $t = t$, respectively. It is such that, if the reaction is first order, a plot of $\ln[A]_t$ against time

should give a straight line with slope equals to $-K$, and intercept at $\ln[A]_0$. However if the reaction rate is second order, the plot of $1/[A]_t$ against time will produces a straight line with slope equals to K , and intercept at $1/[A]_0$. The pseudo-first order equations gave straight lines (Fig.5) with R^2 values of 0.912, and 0.950 for kerosene and gasoline contaminated water. This indicated that the remediation kinetic followed a first order. However, the plot of $1/[A]_t$ against t also gave a near straight line (though with lesser values of R^2 ; Fig.6) for both kerosene and gasoline contaminated waters. This

perhaps indicates that at some point in the degradation process, there was a change in mechanism of the reaction. The two (2) steps - fast and slow - processes (Fig. 4) probably involve two different mechanisms. The basic reactions in Fenton oxidation are (Deng and Zhao, 2015; Chok *et al.*, 2020):



The $\cdot\text{OH}$ radical is generated from Eq. 1 through electron transfer. The $\cdot\text{OH}$ produced can however, be scavenged by either of Fenton reagents as shown in Eq. 3 and 4. The fast step may represent a condition when there was initially so much hydroxyl radicals ($\cdot\text{OH}$) generated by the Fenton system to oxidize as much petroleum hydrocarbons that were available (Eq. 1 & 8). The rate at this point, depends only on the amount (concentration) of hydrocarbons (TPHs) in the solution that is; the reaction follows the first order. However, as the reaction proceeds, much $\cdot\text{OH}$ radicals are consumed (Eq. 3 & 4), so that the conversion of hydrocarbons to CO_2 and H_2O (Eq. 8) becomes affected by the number $\cdot\text{OH}$ radicals in solution. At this point, the rate is not just dependent on the concentration of TPHs but also on the amount $\cdot\text{OH}$ generated by the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system; which is a function of equilibrium of the various equations shown above (Eq. 1 – 8). Hence the shift to a second order as evidenced in the slow step process. Covinich *et al* (2018), found a similar two-sequence steps for Fenton-type oxidation of complex industrial effluent. Other workers: Buffle *et al* (2006), Martins *et al* (2010), and Nieto *et al* (2011) have similarly given evidence of "two-steps" kinetic processes involving the decomposition and degradations of waste waters. The fast step process, which involved about 79.84 and 82.66% reduction in TPHs for kerosene and gasoline contaminated water respectively, is, however more of importance. The reaction constant k was respectively 0.211 and 0.249 min^{-1} . These values can be expressed in the usual units of mg/L.S by converting the \ln [TPHs] first to [TPHs] in (mg/L), and then dividing by 60 to convert to seconds. This leaves us with k values of 2.06×10^{-2} , and $2.14 \times 10^{-2} \text{ mg/L.S}$ for the kerosene and gasoline contaminated water.

Conclusion

The Fenton oxidation, one of the advanced oxidation processes (AOP) demonstrated high efficiency towards the degradations of petroleum hydrocarbons in 10% kerosene and gasoline contaminated water of the Ogbe Ijoh River. The percentage removal of hydrocarbons in terms of total petroleum hydrocarbons (TPHs) under optimum conditions were 90.90 and 94.11% for kerosene and gasoline contaminated water respectively in six hours of contact time. A reasonable value of percent reduction was however, met within one(1) hour of contact time signifying that prolonged treatment time may not be necessary. The generation of secondary pollutants in water by the Fenton process however, calls for post-treatment measures before reuse or discharge into natural water bodies.

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Supplementary Information

Table S 1: Some physicochemical properties of the Ogbe Ijoh surface water, after contaminations with 10% kerosene and gasoline and treatments with Fenton's reagent

parameters	Surface water	Contaminated water		Remediated water		Standards
		10% Kerosene	10% Gasoline	10% Kerosene	10% Gasoline	
pH	6.90±0.02	7.93±0.15	10.70±0.30	8.60±0.06	10.50±0.05	6.5–8.5 ^a
Turbidity (NTU)	48.27±0.15	561.8±0.49	588.6±0.50	14.17±0.12	12.24±0.15	5 ^a

DO (mg/L)	7.20± 1.03	4.10± 0.45	3.40± 0.27	5.70± 0.10	6.20± 0.17	
BODs (mg/L)	4.65± 0.15	6.50± 0.21	7.40± 0.20	5.80± 0.06	7.50± 0.25	
CODs (mg/L)	17.27 ±0.00	27.00 ±0.2	31.50 ±0.22	6.70± 0.10	6.80± 1.15	
TPHs (mg/L)	0.437 ±0.07	4820. 4±3.4 0	5208. 4±4.5 0	438.6 ±3.50	306.7 ±5.10	0.3
TDS (mg/L)	62.54 ±1.53	104.0 0±0.2 7	106.1 0±0.3 5	20.35 ±0.06	22.60 ±0.25	500 ^a
TSS (mg/L)	1.56± 0.04	1.70± 0.30	1.71± 0.36	1.60± 0.10	1.64± 0.14	
Cl (mg/L)	117.2 5±0.0	142.2 6±0.3 3	182.3 0±0.3 4	142.2 0±0.3 4	120.3 0±0.1 9	250 ^a
Cond. (µs/cm)	163.1 0±0.1 0	147.3 0±0.4 0	133.0 0±0.5 0	956.1 7±0.1 2	1045. 10±0. 55	100 0 ^a
Phosphates	0.38± 0.11	0.53± 0.02	0.52± 0.08	0.66± 0.03	0.68±. 04	
NH ₃ (mg/L)	0.67± 0.01	0.33± 0.01	0.26± 0.02	0.08± 0.01	0.04± 0.02	
NO ₃ ⁻ (mg/L)	6.00± 0.28	11.00 ±0.27	15.50 ±0.30	8.00± 0.16	8.00± 0.15	50 ^{ab}
T. Alkalinity (mg/L CaCO ₃)	118.6 7±0.1 5	102.5 ±0.71	116.4 8±1.2 4	21.64 ±4.00	23.20 ±1.30	30 - 500
Cd (mg/L)	0.13± 0.001	0.13± 0.01	0.14± 0.03	0.11± 0.01	0.13± 0.01	0.00 3 ^{ab}
Cr (mg/L)	0.09± 0.01	0.11± 0.01	0.13± 0.01	0.11± 0.01	0.13± 0.01	0.05 ab
Ni (mg/L)	0.31± 0.01	0.39± 0.01	0.30± 0.01	0.04± 0.02	0.44± 0.02	
Pb (mg/L)	0.07± 0.01	0.09± 0.01	0.04± 0.03	0.09± 0.01	0.14± 0.02	0.01 ab
V (mg/L)	0.01± 0.01	0.02± 0.01	0.04± 0.02	0.01± 0.00	0.03± 0.01	

a = Nigerian Standard for Drinking Water Quality (NSDWQ), b = World Health Organization (WHO) guidelines for drinking water quality