



Development of model and subsequent kinetic study on photo-fenton degradation of 5-ethyl-5-phenylhexahydropyrimidine-4,6-dione from pharmaceutical wastewater

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Abstract

Pollution of water bodies with pharmaceutical organic recalcitrant has been a threat to living thing and its environment due to unknown impart and possible damages. This, however necessitate the present study which was focused primarily on the development of model, optimization and kinetic reactivity on the application of Photo-Fenton process on degradation of a barbiturate (5-ethyl-5-phenylhexahydropyrimidine-4,6-dione) in aqueous solution. The principle of this method is based on the *in-situ* generation of hydroxyl radicals from H_2O_2 and reconversion of Fe^{3+} to Fe^{2+} . Influences of major operating parameters on the removal efficiency were investigated using Central Composite Design (CCD) of Response Surface Methodology (RSM). $22\mu l H_2O_2$ and $8.8mg Fe^{2+}$ at pH 3 was found to be the optimum with 97.02% removal within 30minutes reaction time. From the kinetic study, it was observed that as the initial dose decreases to $100mg/L$, 99.77% removal was achieved and at 50 & $75mg/L$, 100% achieved within 10minutes. Both statistical and experimental validations of the Model were verified and found to be in good agreement. Pseudo-first order kinetics reaction rate and half-life were obtained at $0.096min^{-1}$ and 7.22mins respectively at a regression (R^2) of 0.913. Electrical energy per order (EE/O) and cost (Naira) of electrical energy at optimum conditions for this experiment was found to be $1.96kWh/m^3$ and $50.41\text{₦}/m^3$ respectively.

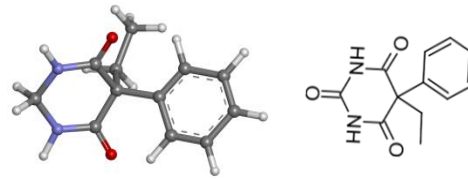
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Introduction

Water is an indispensable part of life. Following to this fate, water reserves have attracted the attention of the most recent past, in regards to the presence of pharmaceuticals. The activities of the pharmaceutical and chemical industries can never be undermined. These organic compounds commonly constitute contaminants as they enter into the environment. Incomplete removal of such compounds during passage through treatment plants has continued to be of concern to researchers (Hallin *et al.*, 1998). The sensitivity of the advanced analytical methods has shown the presence of these compounds in a measurable concentration in wastewater, water sources and drinking water (Henler *et al.*, 2014). Due to the unknown environmental impact and possible damages, pharmaceutical contaminants have raised much attention. Up to date, most of these compounds known as contaminants of emerging concern are not regulated, many of them being recalcitrant towards the traditional urban wastewater treatment methods (Manuel *et al.*, 2019).

5-ethyl-5-phenylhexahydropyrimidine-4,6-dione (Primidone) is the generic form of the brand-name drug Mysoline, which is used to treat and prevent seizures. It belongs to the class of drugs known as anticonvulsants and it works by reducing abnormal electrical activity within the brain. The Food and Drug Administration (FDA) first approved it in 1954 (FDA 2013). Thereby listed in 1999 as a “chemical known to the State to cause cancer” by the Office of Environmental Health Hazard Assessment of the State of California, requiring public notice of potential environmental exposures (OEHHA 2013).

The basis of this listing was an evaluation by the United States National Toxicology Program (NPT 2000). This compound (Fig. 1) has been disclosed as one of the most recalcitrant compounds to conventional biological treatment (Bourgin *et al.*, 2018) which has low potential input, with relatively high detection frequency of 10% (Reh *et al.*, 2013). This indicated a strong persistence in the environment under anoxic aquifer conditions (Has *et al.*, 2012).



$C_{12}H_{14}N_2O_2$ (MW 218.25 $gmol^{-1}$)

Fig. 1. Chemical structure of primidone.

Long exposure of anticonvulsant can lead to occasional side effects on humans, such as sedation, diplopia, feeling of intoxication, gastrointestinal symptoms, loss of libido, folic acid deficiency and other nonspecific effects such as fatigue, listlessness, depression, psychosis, coordination disturbances, tremor and impotence (Brodie and Dichter 1996; Perucca and Gilliam, 2012).

Aminat *et al.* (2018) studied about the degradation and sorption of 53 pharmaceuticals present in Urban wastewater treatment plant effluents discharged into simulated estuarine waters and identified primidone as one of the most stable with a persistence index of 100. Many other researchers, has also disclosed the occurrences and fate of primidone in the water bodies (Massmann *et al.*, 2007; Hummel *et al.*, 2006).

Although, attempts has been made by many authors using AOP(s) at very low initial dose (< 50mg/L). Degradation of the emergent contaminants by UV-C, UV-C/ H_2O_2 and neutral Photo-Fenton was carried out by De la Cruz *et al.*, (De *et al.*, 2013). The result obtained in their work shows that direct UV-C photodegradation process is less effective for the removal of the pharmaceuticals while photo-Fenton gives 54% within 10 minutes reaction time ($H_2O_2:Fe(II) - 50:5mg/L$). Dong *et al.* (2015) discussed direct sunlight photodegradation of primidone in ultrapure water (0.5 $\mu g/L$) and in two urban wastewater treatment plant secondary effluents (DOC 6.2 and 8mg/L; primidone initial concentration of 0.119-0.226 $\mu g/L$). Following the researcher, after five days, the amount of primidone degraded by direct photolysis was low (5%), whereas 35-88% was oxidized by the HO^\bullet generated from the photolysis of some organic/inorganic compound present in the secondary effluents. Sasa *et al.* (2015) studied the

degradation of primidone in aqueous solution by photooxidation processes. According to the result of photooxidation experiments, effectiveness of specific photooxidation processes could be arranged $UV/Fe(II) > UV/H_2O_2 > UV$. The optimum condition UV and UV/H_2O_2 was observed at a pH 6.3.

Moreover, data obtain from the literature, though can be used to evaluate the application of Advanced Oxidation processes, but were insufficient to develop statistical model for predicting primidone removal efficiency for industrial wastewater at the point of discharge more especially at very high initial concentration. The need to generate qualitative data for computation and empirical modeling become the aim of the present work. This work is focused on the degradation of 5-ethyl-5-phenylhexahydroprymidine-4,6-dione at high initial dose ($\leq 200\text{mg/L}$). Perhaps, develop regression model for predicting removal efficiency and optimize the operating parameters by Response optimizer. And also to determine and document the principal combination of parameters for the optimal degradation which may also be extended to other heterocyclic nitrogen compounds present in pharmaceutical wastewater.

However, this research oversees the subsequent determination of kinetic parameters such as: half-life, reaction rate constant; quantum yield, electrical energy per order and enable the recommendation of a protocol for satisfactory treatment of wastewaters containing primidone. Also offer an easily effective applicable and affordable procedure for the removal of organic recalcitrants with similar structures and chemical characteristics.

Materials and methods

Photo-Fenton Process ($Fe^{2+}/H_2O_2/UV$)

Classical Fenton Process has the disadvantage of sludge formation due to iron hydroxide precipitation. This actually increases the reaction period. The use of UV light along with Fenton reduces the formation of this sludge by converting the Fe^{3+} formed back to Fe^{2+} , which again reacts to form more hydroxyl radicals. This reduces both the amount of reagents

(H_2O_2 and Fe^{2+}) required and sludge formed. In this work the pH 3 was used in this experiment. Then the required amount of Ferrous Sulphate ($FeSO_4 \cdot 7H_2O$) was added to the solution followed by hydrogen peroxide (50%). The system was kept under constant stirring at 120rpm throughout the experiment. However, the reaction time started as UV- Lamps was switched "ON" for 60 seconds. A 30W (15w x 2) low-pressure mercury lamp with a 254nm wavelength was used for irradiation. The lamp is housed in a metal foiled box. The initial concentration under study was measured 200mgL^{-1} .

Response Surface Methodology (RSM)

Center Composite Design (CCD) of RSM was used to design the experiment and also to run the optimal value. Two variable factors are considered for this design, namely H_2O_2 and Fe^{2+} doses at constant pH, UV and initial Primidone dose for the modeling of the process. And the reaction time for the thirteen run is kept at 30minutes as obtain from preliminary study.

Analytical Procedures

Various concentration in aqueous solution were determined using high performance liquid chromatography, HPLC (Agilent 1200 series) equipped with visual wavelength detector (VWD).

A mixture of acetonitrile and water (50:50, v/v) was used as the mobile phase. The samples were eluted through the C_{18} column (Zorbax Eclipse XDB C_{18} 150 x 4.6mm 5 μm) at a flow rate of 0.6mL/min. The signal was detected with a detector wavelength of 221nm at an injection volume of 20 μL . A Linear relationship between area of the peak and concentration of the primidone was established by preparing a calibration curve which is used to ascertain the percentage removal.

Result and discussion

Calibration of HPLC

The calibration curve was obtained for concentrations from 1-100mg/L using Microsoft Excel. The curve showed sufficient linearity with an R^2 value of 0.998, as shown in Fig. 2.

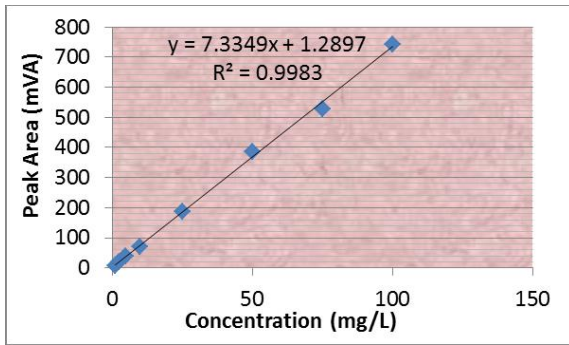


Fig. 2. standard calibration curve.

The percent removal of the process is been calculated using

$$\% \text{ Removal} = \{(C_0 - C_1) / C_0\} * 100 \quad (1)$$

Where C_0 is the initial concentration at time zero, C_1 the concentration at a given time.

RSM Modeling

The RSM model was achieved using two variable factors as H_2O_2 and Fe^{2+} at constant UV irradiation and pH the domain of different parameters used for obtaining the model are as shown in Table 1.

Table 1. Operating Parameters and Ranges selected for the Experiments.

Independent variable	Symbols used	Coded Levels				
		$-\alpha$	-1	0	+1	$+\alpha$
Fe^{2+} (mg/100mL)	X_1	0.0	0.8	4.8	8.8	9.6
H_2O_2 (μ L/100mL)	X_2	6.6	8.0	15.0	22.0	23.4

The different combination of parameters, for CCD by RSM is tabulated in Table 2. Meanwhile a total of thirteen runs were required for the design of experiments. For each of the analysis, the percentage removal was calculated. The model was obtained for both coded and un-coded units. For the coded units, the model obtained is as follows:

$$Y = 67.59 + 19.00X_1 + 8.97X_2$$

$$Y_1 = 67.5 + 19.00[Fe^{2+}] + 8.97[H_2O_2] \quad (2)$$

The importance of the use of the model in un-coded terms is of high esteem in predicting yield.

Final equation in terms of actual factors is:

$$Y_2 = 25.56773 + 4.75051[Fe^{2+}] + 1.28127[H_2O_2] \quad (3)$$

Y_1 and Y_2 is the primidone (%) removal for the coded and the un-coded unit respectively.

Table 2. Experimental responses for photo-Fenton process.

Run Order	$[Fe^{2+}]$ (mg)	$[H_2O_2]$ (μ L)	Peak Area mAU	Concentration (C_1)	% Removal
1.	0.8	8.0	1260.7	171.70	29.30
2.	8.8	8.0	348.7	47.28	80.53
3.	0.8	22.0	1056.5	143.86	40.76
4.	8.8	22.0	54.4	7.24	97.02
5.	0.0	15.0	519.7	70.68	70.90
6.	9.60	15.0	174.6	23.63	90.27
7.	4.8	6.6	904.8	123.73	49.06
8.	4.8	23.4	407.7	55.41	77.19
9.	4.8	15.0	558.9	76.02	68.70
10.	4.8	15.0	558.1	75.91	68.75
11.	4.8	15.0	559.0	76.04	68.69
12.	4.8	15.0	560.0	76.17	68.64
13.	4.8	15.0	556.1	75.64	68.85

Quality of the model

The model F-value of 13.22 implies that the model is significant (Table 3). Values of “Prob> F less than 0.05 indicate the model terms are significant in 95% confident interval. The fact still remains that the X_2 value of 0.0529 prove the competition between interaction of Fe^{2+} and UV radiation on the decomposition of H_2O_2 to its intermediates.

Table 3. ANOVA for Response Surface Linear Model.

Source	Sum of Squares	DF	Mean Square	F Value	Prob> F	Significant
Model	3037.647	2	1518.823	13.21599	0.0016	Significant
X_1	2484.212	1	2484.212	21.61628	0.0009	
X_2	553.4347	1	553.4347	4.815691	0.0529	
Residual	1149.232	10	114.9232			
Pure Error	0.02532	4	0.00633			
Cor Total	4186.879	12				

The model is quantified by calculating the usual statistical indicators (Table 4). The “Pred. R-squared” value of 0.4112 is not as close to the “Adj R-squared” value of 0.6706 as one would normally expect. This may indicate a large block effect. This is a ground for possible response transformation and consequent outliers. “Adeq. Precision” value of 10.863 indicates an adequate signal since a ratio greater than four (4) is desirable. That means this model can be used to navigate the design space.

Combined Effect of Variables

From the contour plot of the combined effects (3-D display) of Fe^{2+} and H_2O_2 concentrations (Fig. 3) on primidone degradation discloses the practical values

obtained at every combination point of [H₂O₂] and [Fe²⁺] which can be of use for prediction. The data obtained confirm that the degradation of primidone is significantly enhanced with UV-radiation. When H₂O₂ is used in the presence of UV, more hydroxyl radicals are generated by the photolysis of H₂O₂ (Eqn. 4):

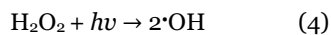
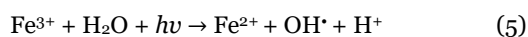


Table 4. Quantification of the Predicted Model.

Statistics	Responses
Std. Dev.	10.72022
Mean	67.58923
C.V.	15.86085
PRESS	2465.27
R-Squared	0.725516
Adj R-Squared	0.670619
Pred R-Squared	0.411192
Adeq Precision	10.86286

The radiation also promotes the conversion of Fe³⁺ back to Fe²⁺, resulting in recycling the reaction processes (Eqn. 5). More importantly, the reconversion of Fe³⁺ to Fe²⁺ results in the reduction of sludge formation.



As the reaction proceeds more hydroxyl radicals are generated which attack the organic compound.

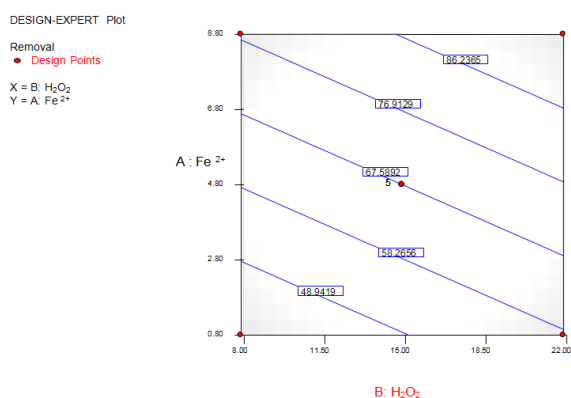


Fig. 3. Contour plot of the combined effects Fe²⁺ and H₂O₂ of Photo-Fenton process on primidone removal.

The pirimidone removal of 97.02% was observed at the H₂O₂ and Fe²⁺ concentrations of 22.0mL/100mL and 8.80mg/100mL respectively. This result is a clear re-enforcement of what was obtained in our previous work on Classical Fenton (Odinma *et al.*, 2021) at same combining ratio. At higher concentrations, the

removal % was reduced due to possibly scavenging effect of H₂O₂ and Fe²⁺ (run nos. 6 and 8 (Table 2)), as earlier observed. From the design point at [Fe²⁺] (8.00mg/100ml) and [H₂O₂] (22.00μL/100mL), the interaction graph (Fig. 4) gives a good account of reactivity of the reactants with the substrate.

The parallell lines predict that there is no direct interaction between Fe²⁺ and H₂O₂ on the substrate. Rather the active intermediates (hydroxyl radical) produced is responsible for the direct interaction on the analyte.

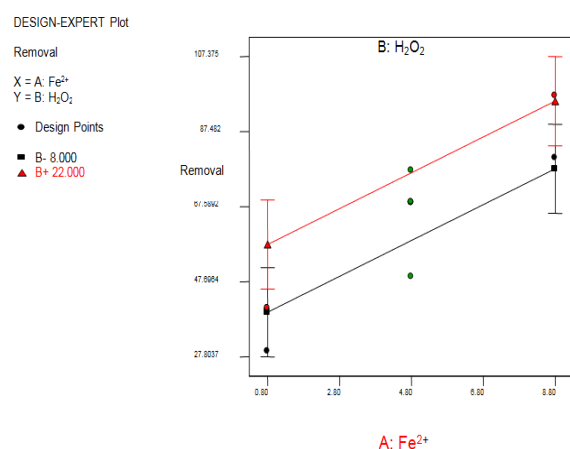


Fig. 4. The interaction plot of [Fe²⁺] and [H₂O₂] on Primidone removal.

One can also conclude quite rightly from the one factor plots (Fig. 5) that as one parameter increases in concentration, primidone removal percent also increases accompanied by the amount of ·OH produced correspondingly within the selected range.

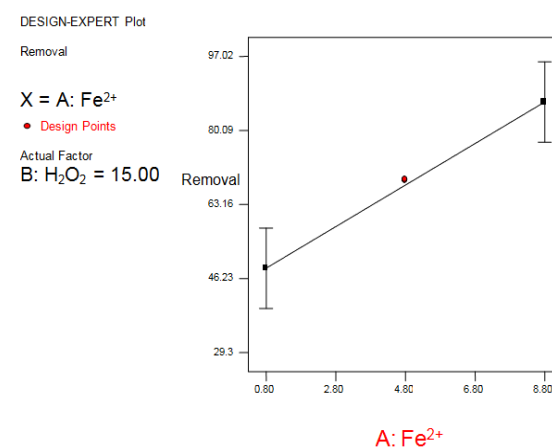


Fig. 5. (a) %Removal against [Fe²⁺] at [H₂O₂] =15.

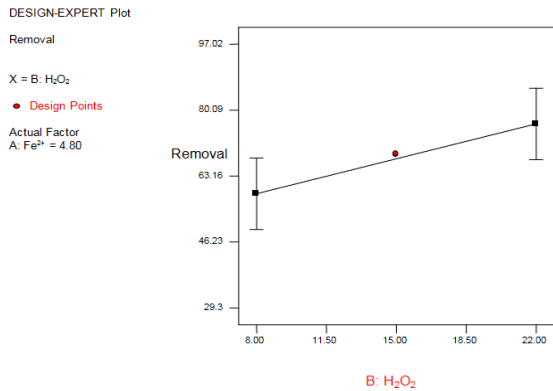


Fig. 5. (b) %Removal against [H₂O₂] at [Fe²⁺] = 4.8.

Validation of the model

Diagnostic case statistics

The diagnostic case statistics were done with RSM to review the statistical validation of the process. The actual and predicted values listed in Table 5 are in agreement except at experimental run 5 where the actual values of 70.9 was high compared to the predicted value of 44.8 and which gave a residual of 26.11 and outlier value of 6.66, greater than 3.50. The reason for this cannot be explained in the present circumstances.

Table 5. Diagnostic Case Statistics validation of Model.

Run	[Fe ²⁺] (mg)	[H ₂ O ₂] (μL)	Actual	Predicted	Student	Cook's	Outlier
Order			Value	Value	Residual	Distance	t
1	0.8	8.0	29.30	39.6183	-10.318	0.36762	-1.2429
2	8.8	8.0	80.53	77.6224	2.90763	0.36762	0.32547
3	0.8	22.0	40.76	57.5561	-16.796	0.36762	-2.3896
4	8.8	22.0	97.02	95.5602	1.45984	0.36762	0.16269
5	0.0	15.0	70.90	44.7868	26.1132	0.28623	6.659*
6	9.6	15.0	90.27	90.3917	-0.1217	0.28623	-0.0127
7	4.8	6.6	49.06	56.8266	-7.7666	0.28623	-0.8452
8	4.8	23.4	77.19	78.3519	-1.1619	0.28623	-0.1218
9	4.8	15.0	68.70	67.5892	1.11077	0.07692	0.10237
10	4.8	15.0	68.75	67.5892	1.16077	0.07692	0.10698
11	4.8	15.0	68.69	67.5892	1.10077	0.07692	0.10145
12	4.8	15.0	68.64	67.5892	1.05077	0.07692	0.09684
13	4.8	15.0	68.85	67.5892	1.26077	0.07692	0.11621

* Case(s) with |Outlier T| > 3.50

Experiment validation

Apart from the statistical analysis, experimental verification of the model is also important. So, the validation of the models was done by conducting experiments at different combinations of independent variables which were not used to formulate the model, but were within the experimental range. It was found that predicted and observed values were in good agreement (Table 6).

Table 6. Experimental Validation of the Model.

Run Order	[Fe ²⁺](mg)	[H ₂ O ₂](μL)	Predicted value	Observed Value
1	9.0	18.00	91.3852	87.5120
2	5.0	20.00	74.9457	70.8461
3	7.0	10.00	71.6340	72.0573

Optimization of the operating parameters

The optimization of the operating parameters was done using response optimizer of design expert. It gives the variation of predicted responses with operating parameters.

The optimum initial H₂O₂ and Fe²⁺ concentrations for primidone removal were predicted to be 22μL/100mL and 8.8mg/100mL, respectively at 95.56% removal response. The optimum value obtained by experimental technique at same initial H₂O₂ and Fe²⁺ concentrations after 30min is 98.63%. The validation of this optimum condition is important in this experiment to fortify the findings and also in quantifying the statistical values.

Kinetics study

This area bridges an important gap in our discussion of chemical reactions happening in the processes to this point. The central idea behind this aspect of the study, kinetics, is that crucial conclusion can be drawn by monitoring the rate at which chemical reactions occur and determining the dependence of this rate on system parameters such as concentrations of reactants. Hence kinetic studies were carried out to study the oxidation of primidone via rate of reaction, reaction constant and half-life.

Effect of H₂O₂ concentration

To study the effect of H₂O₂ concentration on the removal of primidone from water, the pH of the solution was fixed at 3 and concentration of H₂O₂ varied. At each concentration, reaction time was also varied (Fig. 6).

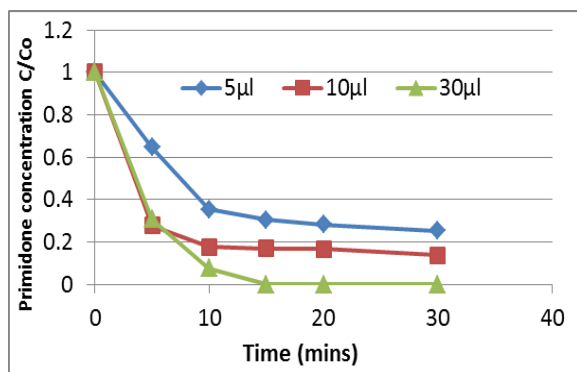
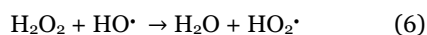


Fig. 6. Effect of initial H₂O₂ concentration on Primidone removal at Fe²⁺ concentration of 8.8mg.

An increase in the rate of removal of primidone was observed when H₂O₂ concentration increased from 5μL to 10μL within the first 5minutes of reaction time. Further increase in H₂O₂ concentration from 10-30 μL did not however show significant improvement in the percentage removal within the same first five (5) minutes reaction time. At 30 μL concentration of H₂O₂, the result obtained shows complete removal within fifteen (15) minutes reaction time and at this time, the reaction responses became so slow for 5 and 10μL of H₂O₂ concentration.

These concentrations (5 and 10μL) of H₂O₂ do not even completely degrade primidone even at 30mins reaction time, considering the amount yet to be removed. It is concluded from these experiment that it is necessary to consider that excess of H₂O₂ reactant is detrimental to removal efficiency (eq. 6).



Effect of Fe²⁺ concentration

The effect of initial Fe²⁺ concentration on primidone removal by photo-Fenton process is shown in Fig. 7. The graph depicts an increase in removal of primidone when Fe²⁺ concentration was increased from 2 - 6mg to be (42.38% - 92.32 %).

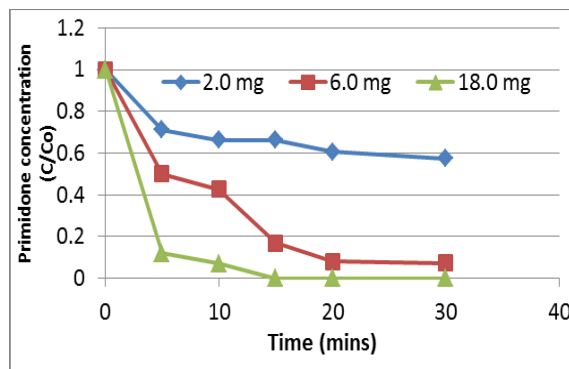


Fig. 7. Effect of initial Fe²⁺ concentration on primidone removal at H₂O₂ concentration of 22μl.

It is necessary to note that only in the case of 18mg of Fe²⁺ concentration was the degradation of primidone able attain one hundred percent removal efficiency at fifteen (15) minutes reaction time. Considering the efficiency and conservation of resources, the concentration of Fe²⁺ at 6mg gives a better result because its removal is quite very close to that of 30mg Fe²⁺ dose within 30minutes reaction time.

Effect of initial dose of primidone

The effect of initial concentration of primidone on the removal efficiency by photo-Fenton process was analysed by conducting experiments in which initial concentration of primidone was varied at fixed (optimal) H₂O₂ and Fe²⁺ concentrations of 22 μL and 8.8mg respectively (Fig. 8)

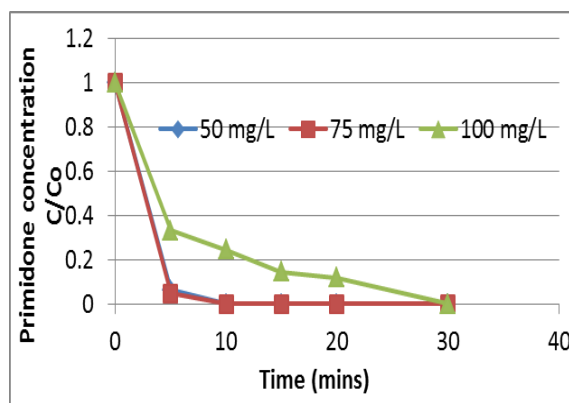


Fig. 8. Effect of initial Primidone concentration on the removal rate.

As expected, the time required for removal of primidone increased with increasing initial primidone concentration. For 50 and 75mg load, the removal

maximum obtained was 98.83±1.4% within 10 minutes of reaction time while 74.65% was achieved at same time for 100mg load. At thirty minutes reaction time, 100mg load virtually attend complete.

Pseudo first order reaction rate determination

The rate of oxidation reaction depends on the concentration of the primidone and the hydroxyl radical concentration. The corresponding rate law expression may thus be generally expressed in the form:

$$R = k[C][OH^*] \quad (7)$$

k is the second order rate constant for the reaction and *C* is the concentration of primidone. In the presence of excess hydroxyl radicals, the rate equation can be written as:

$$d[C] / dt = -k[C] \quad (8)$$

where *k* is pseudo-first order rate constant.

Experiments were conducted to obtain pseudo-first order rate constant, *k'*, and half-life period (*t*_{1/2}).

The pseudo first order rate constant

$$k = \ln(C/C_0)/t$$

$$k = 9.6 \times 10^{-2} \text{mins}^{-1}$$

$$\text{And Half-life, } t_{1/2} = \ln(2)/k = \ln(2)/(9.6 \times 10^{-2} \text{mins}^{-1}) = 7.22 \text{mins.}$$

Quantum yield

In this contest, pseudo-first rate constant of primidone photo-degradation (via Fenton assisted photo-degradation) were used to calculate the quantum yield. The result obtain here is a proposed indicator of the efficiency of a photo chemical assisted reaction. Quantum yield is defined as the number of molecules that reacted during a photo-oxidation reaction divided by the number of photons absorbed (Eqn. 9) (Livingston 2005).

$$\Phi = \frac{\text{number of molecules reacted}}{\text{number of photon absorbed}} \quad (9)$$

or more specifically

$$\Phi = \frac{K}{2.303(I_{0,\lambda} \cdot \epsilon_{D,k} \cdot l)} \quad (10)$$

where Φ is the quantum yield (mol/Einstein) (Table 7); $I_{0,\lambda}$ (Einstein L⁻¹s⁻¹) is the UV light intensity; $\epsilon_{D,k}$ (L mol⁻¹cm⁻¹) is the molar absorptivity at the selected UV wavelength, respectively; and *l* is the cell length (cm)

(Livingston, 2005). In this study, the photon flow was obtained 0.03823 Einstein min⁻¹ (Eqn. 11) (Thomas 2003), light intensity of 0.382 Einstein L⁻¹min⁻¹ as calculated (Eqn. 12) and the cell length was 18 cm for this study. The molar extinction coefficients *e* of primidone at 254nm is 220 L mol⁻¹cm⁻¹ (Real *et al.*, 2009).

Table 7. Pseudo First-order reaction rate *K*, Regression coefficient R², and Quantum yield.

SN	Primidone (mg/L)	Fe ²⁺ (mg)	H ₂ O ₂ (μL)	K (min ⁻¹)	R ²	Φ (μmol/Einstein)
1	100	8.8	5	0.043	0.79	12.3
2	100	8.8	10	0.051	0.62	14.6
3	100	8.8	30	0.292	0.982	83.8
1	100	2	22	0.015	0.73	4.31
2	100	6	22	0.088	0.90	25.3
3	100	18	22	0.276	0.95	79.2
1	50	8.8	22	0.444	0.99	127.0
2	75	8.8	22	0.424	0.968	122.0
3	100	8.8	22	0.132	0.928	37.9

$$\text{Photon flow} = (501.567 \text{ mol W}^{-1}\text{m}^{-1} \text{ min}^{-1}) \times (P^{\text{lamp}} \text{ W}) \times (\lambda \text{ m}) \quad (11)$$

Where *P*^{lamp} is the power of lamp in Watts, λ is wave length in meters.

$$\text{Light intensity} = (\text{photon flow}) / (\text{UV exposed vol. of sample in liters}) \quad (12)$$

Table 7 re-enforced the work done by Real *et al.*, (2009) that as primidone concentration increases, degradation rates decrease. This could be attributed either to its relatively high UV absorbance at 254nm or to the presence of by-products of primidone that competed for active species in the process.

Determination of electrical energy per order

The energy consumption was determined at the reaction combination of variable where optimum conditions are observed, using the mathematical expression of electrical energy per order (EE/O) (Asaithambi *et al.*, 2015).

$$EE/O = \frac{P_{el} \times t \times 1000}{V \times 60 \times \ln(C_0/C)} \quad (13)$$

EE/O is the electrical energy per order (kWh/m³ order⁻¹), *P*_{el} is the electrical power input (kW), *t* is the irradiation time (min.), *V* is the volume of effluent used (L), *C*₀ and *C* are the initial and final effluent concentrations (mg/L).

The degradation of primidone was investigated using the pseudo-first-order kinetic model as discussed in section 3.5.4.

$$\text{Log}(C_0/C) = kt \quad (14)$$

Combining eqns. 13 and 14 gives an equation for the electrical energy in the form independent of the initial concentration (eqn. 15):

$$EE/O = \frac{38.4x P_{el}}{Vxk} \quad (15)$$

This gave EE/O of 1.96kWh/m³ and the cost of electrical energy of 50.41 ₦ m⁻³ (eqn. 16) at the rate cost of electrical energy of twenty-five naira, seventy-three kobo per kilo-Watt hour (₦25.73/kWh) which was the average cost of electrical energy in Nigeria as at the period when the cost analysis was carried out using the expression:

$$\text{Cost of electrical energy} = [(\text{cost of electricity/kWh}) \times (EE/O (\text{kWh/m}^3))] \quad (16)$$

Conclusion

The results of the study revealed the capacity of using photo-Fenton process for the removal primidone from wastewater. The optimum condition for effective removal was found to 22μL of H₂O₂ and 8.8mg of Fe²⁺ at pH 3. Removal rate efficiency increases with an increase in initial H₂O₂ and Fe²⁺ dose. The pseudo-first order reaction constants obtained for the processes at optimized condition is 0.096min⁻¹, and the half-life at optimal condition is 7.22mins. However, quantum yield was also obtained within the optimum points of the variable factors. Thus, it can be concluded that the adopted model can be used to navigate the design space.

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