



KINETIC MODELLING OF THE PHOTOCATALYTIC DEGRADATION OF PHENOL USING TiO_2 – ACTIVATED CARBON COMPOSITE FROM *Canarium ovatum* ENGL. SHELL

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ABSTRACT

Phenol is a toxic pollutant with deteriorating properties to the endocrine and the environment as a whole. Because of this, their removal from wastewater is a global concern. In this study, the kinetic modelling of the photocatalytic degradation of phenol using composite of TiO_2 – activated carbon from *Canarium ovatum* Engl. was investigated. Design Expert® was used in the determination of the effects of composite dosage, irradiation time, initial phenol concentration and pH to the percent phenol degradation. Pseudo - first order was the selected model with the highest R^2 value of 0.9342 amongst the choices being zero order, pseudo – second order, and fractional method. From which, the rate equation is derived to be $-r_A = 0.0125C_A$.

KEYWORDS: *Canarium ovatum* Engl., composite, kinetic model, phenol, photocatalytic degradation.

1. INTRODUCTION

Phenol and phenolic compounds are widely used in the industry and are often component of the wastewater that have become pollutant in water bodies. Effects to the health and to the ecosystem are highly dangerous due to its stability and ability to remain in the environment at longer periods^[1]. Due to this, there has been a great urgent demand to find effective and economical method for the treatment of phenol in wastewater. Nevertheless, methods that are available, adsorption, chemical oxidation and biological digestion, have limitations and flaws^{[1],[2]}.

Advanced oxidative processes (AOP) offers an appealing solution to this dilemma because it can achieve complete oxidation^[3]. One of these processes

is photocatalytic degradation. This process provides advantage over many conventional treatment methods by having faster degradation. Also, contaminants are degraded rather than being transformed into other phases, hence, no additional by – product disposal is required^[4].

In presented work, composite is used in the photocatalytic degradation of phenol. In the composite, anatase titanium dioxide is used as photocatalyst due being catalytically more active than other forms of TiO_2 being rutile and brookite^{[5],[6]}. Activated carbon used in the composite to immobilize the TiO_2 is derived from the shells of *Canarium ovatum* Engl fruits. The tree, being the source of the fruit, is known as pili and is indigenous to the Philippines. The shell,

characterized as thick, hard, and pointed, is a waste by product of pili nut processing. Nevertheless, it has not been fully studied^{[7],[8],[9]}.

The object of the study is to characterize the behavior of photocatalytic degradation of phenol using TiO₂ – activated carbon composite from *Canarium ovatum* Engl shells as kinetic model.

2. METHODOLOGY

2.1 MATERIALS

Reagents used in the photocatalytic degradation of phenol were bought from Aldrich and are laboratory grade. Activated carbon (AC) was prepared from the chemically activated charred shells of *Canarium ovatum* Engl purchased from a local market at Lagonoy, Camarines Sur, Philippines. Anatase titanium dioxide was immobilized in the prepared carbon dioxide to produce the TiO₂ – AC composite through boil deposition method^[10]. Synthetic wastewater was prepared by dissolving and homogenizing phenol in distilled water. pH of the aliquots were controlled using 0.1 M NaOH and 0.1 M HCl aqueous solution^[11].

2.2 PHOTOCATALYTIC DEGRADATION

Treatment of phenol via photocatalytic degradation was carried out in a laboratory scale ultraviolet photocatalytic reactor. 100 mL Aliquots with varying initial phenol concentration (100 ppm, 550 ppm, 1000 ppm) and pH (3, 7, 11) were irradiated at variable time (20 mins, 100 mins, 180 mins) using varying composite dosage (0.10 g, 0.55 g, 1.00 g)^[10]. Experiments were performed with total of 29 runs with parameter values generated though response surface methodology (RSM) by Design Expert[®]. The concentration of phenol was measured by absorbance using UV – Vis spectrophotometer (Spectronic 200) after being withdrawn from the beaker. The percent of phenol degradation was computed using the equation:

$$\text{percent phenol degradation} = \frac{A_o - A_f}{A_o} \bullet 100\% \quad (1)$$

Where A_o and A_f are the liquid phase absorbance of phenol at initial and final (mg/L), respectively.

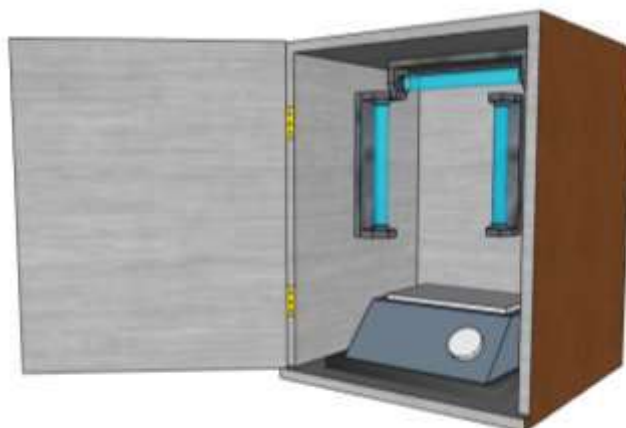


Fig. 1. Illustration of the Laboratory UV Photocatalytic Reactor used in the experimental treatment of synthetic wastewater (Pending IPOPHIL Utility Model Application 2201905034, K. Gasga)

2.3 KINETIC STUDY

Kinetic studies are necessary to optimize different operation condition in degradation process. The kinetics were derived from the model in terms of the actual factors calculated by Design Expert[®]. The kinetics of the photocatalytic degradation of phenol using TiO₂ – AC composite were analyzed using zero order kinetics, pseudo-first order kinetics, pseudo-second order, and fractional life method.

A reaction follows zero order kinetics when the rate of reaction is independent of the concentration of reactants. Zero order kinetics is usually observed at higher concentrations, but was still tested because of the unpredictability of the rate due to the presence of a catalyst. The equation for zero order kinetics is as follows^[12]:

$$-r_a = -\frac{dC_A}{dt} = k \quad (2)$$

Where r_a is the rate of the chemical reaction in concentration over time, dC_A is the differential change with respect to the differential change in time, dt . The rate constant k for zero order kinetics is in concentration per time. Integrating the equation,

$$C_{A0} X_A = kt \quad (3)$$

Where C_{A0} , is the initial concentration of phenol; C_A , is the concentration of phenol at any time, t , X_A , is the percent conversion, which in this case, the percent degradation; and k , which is the reaction constant.

A reaction follows pseudo-first order kinetics when the overall order of the reaction is not equal to 1 but part of the equation is assumed to be constant to simplify the rate equation equivalent to a first-order reaction^[12].

$$-r_A = -\frac{dC_A}{dt} = kC_c^m C_A \tag{4}$$

The catalyst concentration, C_c^m , is constant, so the rate equation is simplified to (5). This is a simplified form of the Langmuir-Hinshelwood kinetic model used to describe surface reactions.

$$-r_A = -\frac{dC_A}{dt} = k_{obs} C_A \tag{5}$$

Integrating,

$$-\ln \frac{C_A}{C_{AO}} = -\ln(1 - X_A) = k_{obs} t \tag{6}$$

Similarly, pseudo-second order kinetics used the same assumption as pseudo-first order kinetics but the rate equation is to be simplified to be of order 2. The rate equation is as follows^[12]:

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = k_{AO}^2 (1 - X_A)^2 \tag{7}$$

Integrating (7),

$$\frac{1}{C_{AO}} \bullet \frac{X_A}{1 - X_A} = kt \tag{8}$$

Fractional life method is used to determine the reaction order, n , by plotting the logarithm of the time, t_f which is the time to reach a certain fraction of the reactant, F , versus the logarithm of the initial concentration. The equation is as follows^[12]:

$$t_f = \frac{F^{1-n} - 1}{k(n-1)} \bullet C_{AO}^{1-n} \tag{9}$$

3. RESULTS AND DISCUSSION 3.1 PHENOL DEGRADATION

Treatment conditions provided by Design Expert[®] was carried out. The parameters were tested and the percent degradation was observed as the result.

Table 1
Percent Degradation of Phenol at Varying Parameter Values

Run	Comp Dos ^a (A)	Irrad Time ^b (B)	Initial Conc ^c (C)	pH (D)	% Deg ^d
1	0.55	20	550	3	26.970
2	0.10	100	1000	7	64.099
3	1.00	180	550	7	96.226
4	1.00	20	550	7	27.625
5	1.00	100	1000	7	62.185
6	0.55	100	100	3	63.636
7	0.10	180	550	7	92.453
8	0.55	180	100	7	90.909
9	0.55	100	550	7	65.151
10	0.10	100	550	11	63.986
11	0.10	100	550	3	63.727
12	0.55	20	100	7	27.273
13	1.00	100	550	11	61.261
14	0.55	100	550	7	62.093
15	0.10	100	100	7	63.687
16	1.00	100	100	7	62.727
17	0.55	100	550	7	64.117
18	0.55	20	1000	7	27.235
19	0.55	20	550	11	27.415
20	0.55	100	1000	3	64.238
21	0.55	100	550	7	61.164
22	0.55	180	550	11	88.679
23	0.55	180	1000	7	94.040

24	0.55	100	100	11	64.092
25	0.55	180	550	3	94.340
26	0.55	100	550	7	64.161
27	1.00	100	550	3	66.299
28	0.55	100	1000	11	64.163
29	0.10	20	550	7	26.513

^a Composite dosage (g)

^b Irradiation time (min)

^c Initial phenol concentration (ppm)

^d Percent phenol degradation

The photocatalytic degradation of phenol in relation to the composite dosage, irradiation time, initial phenol concentration, and is summarized by a

predictive model in terms of actual factors expressed in (10).

$$\begin{aligned} \% \text{ Degradation} = & 13.99966 + 2.361364A + 0.531544B \quad (10) \\ & - 0.0006C + 0.627122D + 0.018484AB - 0.00118AC \\ & - 0.73554AD + 2.2 \times 10^{-5} BC - 0.00477BD - 7.4 \times 10^{-5} CD \\ & + 1.756071A^2 - 0.00055B^2 + 2.12 \times 10^{-7} C^2 + 0.006761D^2 \end{aligned}$$

Where *A* is the composite dosage (g), *B* is the irradiation time (min), *C* is the initial phenol concentration (ppm), and *D* is the pH.

values for the photocatalytic degradation of phenol presented in Table 2. In which, composite dosage and irradiation time is to be minimized, initial phenol concentration is set within 100 ppm – 1000 ppm, pH is set from 5 – 7, and percent phenol degradation is set to have the maximum value.

3.2 OPTIMAL CONDITIONS FOR DEGRADATION OF PHENOL

From the response provided in Table 1, Design Expert® generated the optimum operating

Table 2

Optimum Parameter Values for Phenol Degradation

Comp Dosa ^a	Irrad time ^b	Initial conc ^c	pH	% Deg ^d
0.1	173.95	1000	5	92.078

provided by Design Expert® shown in (10). Percent degradation is calculated using the optimal conditions presented in Table 1 and variable time.

3.3 KINETIC MODELLING

The kinetic model of the photocatalytic degradation is based on the model on the actual factors

Table 3

Variable Time vs Percent Degradation based on model in terms of actual factors

Time, min	Percent Degradation, X _A
0	0
20	27.66 %
40	37.44 %
60	46.78 %
80	55.67 %
100	64.12 %
120	72.13 %
140	79.70 %
160	86.83 %
180	93.52 %

The x – intercept is the variable time and the y – intercept varies per kinetic model. For zero order, $y = 1/X_A$, pseudo – first order, $y = \ln(1 - X_A)$, and pseudo – second order, $y = (1/C_{AO}) * (X_A/(1-X_A))$

where X_A is the percent degradation equivalent to the percent conversion and C_{AO} is the initial concentration of phenol.

Table 4
Variable Time vs Kinetic Models

Time, min	Zero order $1/X_A$	Pseudo-First order $\ln(1 - X_A)$	Pseudo-Second order $(1/C_{AO}) * (X_A/(1-X_A))$
0	0	0	0
20	0.276613285	0.323811325	0.000382394
40	0.374390168	0.469028374	0.000598452
60	0.467750791	0.630643461	0.000878837
80	0.556695154	0.813497605	0.001255809
100	0.641223257	1.025054968	0.001787284
120	0.721335099	1.277745292	0.002588591
140	0.797030682	1.594700454	0.003926932
160	0.868310005	2.027304639	0.006593723
180	0.935173067	2.736034135	0.014425976

$1/X_A$, which is the inverse of the percent degradation, is plotted against time which gives the following graph shown in Fig. 2. The plot for the zero

order gives a linear equation of $y = 0.0058x$ and R^2 of 0.8831.

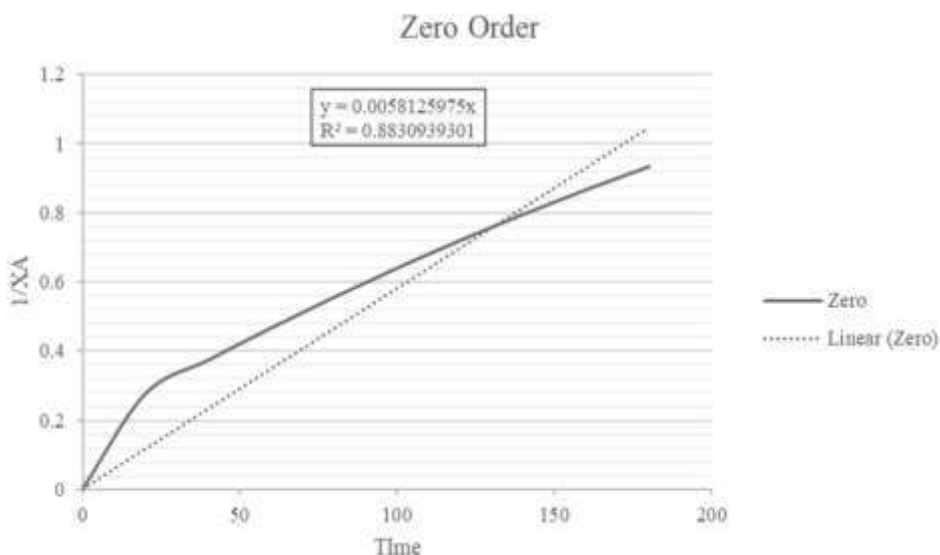


Fig. 2. Plot for zero order

The natural logarithm of $(1 - X_A)$ is plotted against time is shown in Fig. 3. The plot for pseudo – first order presented gave a linear equation of $y =$

$0.0125x$ and $R^2 = 0.934$.

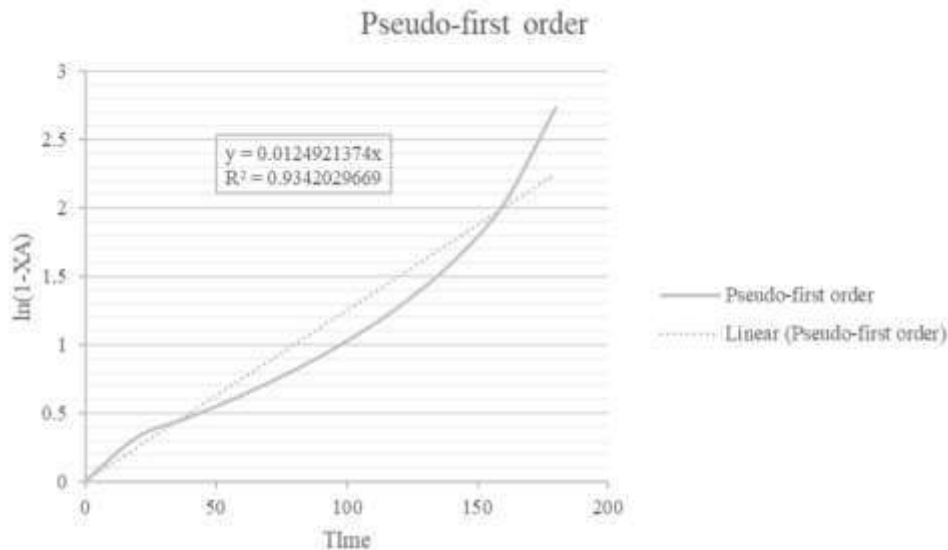


Fig. 3. Plot for pseudo – first order

$(1/C_{AO}) * (X_A / (1 - X_A))$ is plotted against time presented in Fig 3 showing the plot for the pseudo – second order. From which, the graph gave a linear

equation of $y = 0.000043x$ and a low R^2 with value of 0.592 .

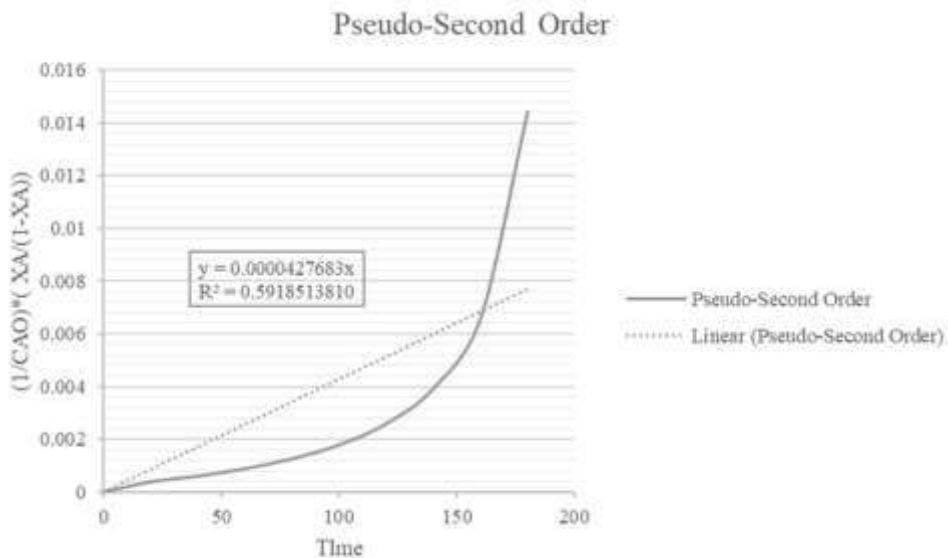


Fig. 4. Plot for pseudo – second order

On the other hand, the kinetic model using the fractional method is calculated separately. Table 5 shows the concentration of phenol with varying time. Table 6 shows the kinetic data required for plotting the

model using fractional method. From which, C_{AO} is the initial concentration of phenol, C_{AF} is the final concentration of phenol, and t_f is the time needed.

Table 5
Concentration of Phenol in Varying Time

Time, min	C _A , M
0	0.010626
20	0.007686
40	0.006647
60	0.005655
80	0.00471
100	0.003812
120	0.002961
140	0.002157
160	0.001399
180	0.000689

Table 6
Data for Plotting Fractional Method

C _{AO} , M	C _{AF} , M	t _f , min	logt _f	logC _{AO}
0.010626	0.0085006	15.55578894	1.191892	1.97364
0.005313	0.0042503	22.2922347	1.348154	2.27467
0.002125	0.0017001	12.07919436	1.082038	2.67261

From Table 6, logt_f is plotted against logC_{AO}. The plot for fractional method shown in Fig. 5 gave a linear equation of $y = 0.1839x + 1.6316$ and $R^2 = 0.2325$. The order is calculated by the slope plus 1; nth order = 1 + 0.1839 ≈ 1.2.

The rate equations from each kinetic model were tabulated and is shown in Table 7. From which, the model with the highest value of R² is chosen.

Table 7
Rate Equations and their Respective R²

Rate Equation	R ²
Zero Order	0.8831
Pseudo-first Order	0.9342
Pseudo-second Order	0.5919
Fractional Method	0.2325

Pseudo - first order kinetics has the highest value of R² being 0.93420 and is chosen as the most appropriate kinetic model of the photocatalytic degradation of phenol using TiO₂ – AC composite from *Canarium ovatum* Engl. shells.

From the linear graph presented in Fig. 3, the rate constant k_{obs} is calculated to be 0.0125 min⁻¹. The rate equation is therefore:

$$-r_A = 0.0125C_A \tag{11}$$

4. CONCLUSION

The kinetic modelling of the photocatalytic degradation of phenol using composite composed of TiO₂ and activated carbon derived from *Canarium ovatum* Engl. shells as presented in this study could be of help to future similar researches and application in economical wastewater treatment. Kinetics was derived using the model based on actual factors provided by Design Expert® as plotted using each kinetic model equation. In which, the degradation is

described to highly behave as a pseudo - first order kinetic with R² value.

CONFLICT ON INTEREST

None

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