Photocatalytic Degradation Of Phenol Using Tio_2 – Activated Carbon Composite From Canarium Ovatum Engl. Nut Shell

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Abstract: The study aimed to determine the potential of composite of TiO_2 immobilized in activated carbon derived from Canarium ovatum Engl. shells through immobilization by boil deposition as an alternative treatment for industrial effluents containing phenol and phenolic compounds. The effect of composite dosage, irradiation time, initial phenol concentration and pH to the percent degradation of phenol were investigated and were ran on Design Expert® under response surface for process optimization. Results showed that composite dosage and initial phenol concentration exhibited no significant effect to the photocatalytic degradation of phenol. On the other hand, degradation increases as solution becomes more acidic. Moreover, at optimum conditions, e.g. 0.1 g composite dosage, 173.95 mins irradiation time, 1000 ppm initial phenol concentration and pH value of 5, the average actual percent phenol degradation is 90.437%.

Index Terms: Activated Carbon, Canarium ovatum Engl, Composite, Phenol, Photocatalytic Degradation, Pili.

1. INTRODUCTION

Wastewater is water containing waste from residential, commercial, and industrial discharge. Large industries, such as refineries, generate wastewater but it is first treated to remove pollutants before discharge [1]. If wastewater is not treated properly, it may cause harm to the environment, animals and humans. Negative effects may include; harm in wildlife population, oxygen depletion of bodies of water, restrictions on recreational water use, restrictions on marine harvesting and contamination of drinking water [2].

Phenol is one of the priority pollutants listed by the US Environmental Protections Agency. Phenol is a colorless, crystalline substance of characteristic odor, soluble in water and organic solvents [3]. It is mainly from industrial effluent discharge released to bodies of water as a result of its manufacture, its use in phenolic resins, organic synthesis, petroleum products, and can be released by combustion of wood and auto exhaust [4].

Separation via Liquid-liquid extraction (LLE) is the traditional method and standard procedure for the recovery of phenol from wastewater. For concentrations of 1000mg/L above, LLE showed 70% - 90% extraction with varying solvents [5]. Since LLE only separates phenol from the water, phenol will take on another form of pollution if not properly handled. Hence, destruction methods, such as photocatalysis, is potentially more favorable in the long run.

Titanium dioxide (TiO_2) has been studied extensively in the field of surface science due to its wide range of application and the expected insights into surface properties. Many studies have been motivated in part by the discovery that titanium dioxide as a photocatalyst with relatively high efficiency for the decomposition of water and degradation of organic species [6]. Photocatalysis has proven to be a promising technology for the degradation of these compounds, being the most commonly used photocatalyst because it is nontoxic, photo-stable, cheap and efficient under ultraviolet irradiation. Whereas most studies focus on the modification and performance of only TiO_2, composites like carbon-TiO_2 has been scarcely explored for photocatalytic degradation of toxic pollutants although it has been shown that the mixture of activated carbon and TiO_2 can have a synergistic effect for the photodegradation of organic pollutants [7]. Canarium ovatum Engl., known in the Philippines as Pili tree, is a hardy rainforest indigenous to the country. The tree bears an edible nut which is protected in a thick and very hard pointed shell, covered in turn with a thick black skin when ripe. The shell houses a single, sweet kernel that is slender with a length and diameter of 6.35 cm and 1.91 cm respectively [8,9]. The nut shell, being a waste material in pili nut processing has not been fully studied [10], hence this study. Through this study, using discarded by-product Canarium ovatum Engl. shells as source of activated carbon used in the TiO_2 – activated carbon composite for the treatment of phenol would pave way in using newer technologies that is potentially more economical and environmentally friendly in waste water treatment. Furthermore, this study will investigate the effect of composite dosage, irradiation time, initial phenol concentration, and pH in the treatment of phenol trough photocatalytic degradation.

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2. METHODOLOGY

2.1. Materials

Chemicals and reagents used in this study were purchased from Aldrich which are laboratory grade unless specified.

2.2. Preparation of titanium dioxide

Since crude commercial amorphous titanium dioxide shows strong acid reaction, it was washed with 5 M aqueous solution of ammonia to neutralize the reaction. Excess sulphate ion and traces of ammonia was removed with several washings with distilled water. Subsequently, to separate water from the photocatalyst, titanium dioxide was dried at 80 ^{O}C for 24 hours. Lastly, the obtained titanium was ground with mortar and pestle and sieved to get a uniform particle size of 150 µm. H_2SO_4 was added into a little part of the photocatalyst obtained to instantaneously neutralize alkali reactions caused by excess aqueous solution of ammonia. To prevent contact with the atmosphere, it was sealed in an air tight container.

2.3. Preparation of activated carbon

Canarium ovatum Engl. nut were purchased from a local market at Lagonoy, Camarines Sur, PH. Shell was removed from the pulp, testa and kernel, washed with tap water and sun – dried for 72 hours [11]. It was pulverized afterwards and treated with concentrated sulfuric acid (99.7%) in 1:1 ratio to chemically activate the shells. It was soaked for 24 hours and kept at a temperature of 400 ^{O}C using an electric oven (Heraeus UT-6200). The acid was washed off with several runs of distilled water until pH is found to be neutral. To completely dry the shell, it was filtered and oven dried at 150 ^{O}C for three hours. Afterwards, it was ground using mortar and pestle, sieved to obtain a uniform particle size of 300 µm and stored in an air tight container.

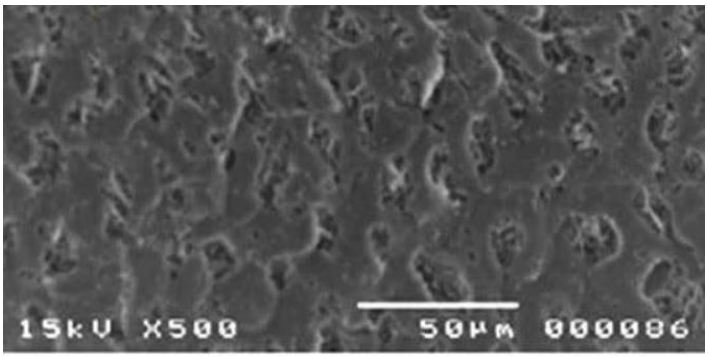

Fig. 1*. SEM micrograph of acid activated Canarium ovatum Engl. Shells activated carbon*

2.4. Composite preparation via boil deposition

100 g of activated carbon (AC) from Canarium ovatum Engl. shells was washed by several runs of deionized water. Afterwards, it was put in a 250 mL erlenmeyer flask and 20 g of titanium dioxide was added. 200 mL of deionized water was added to the mixture and was agitated using magnetic stirrer (Corning – PC 410D) at 150 rpm. Then, it was placed on a hot plate and heated to 120 ^{O}C with constant agitation. It was allowed to boil until all of the water has evaporated. The mixture was rinsed using deionized water and was fully dried at 120 ^{O}C using an electrical oven (Heraeus UT-6200).

2.5. Preparation of synthetic wastewater

Synthetic wastewater stock solution was prepared by dissolving 1000 mg ± 5 mg of phenol in distilled water in 1.0 L volumetric flask [12]. It was stirred at 150 rpm for 15 min to homogenize the solution. Then, it was characterized by determining the temperature, the pH using a pH meter (KL – 009I model) and the absorbance using a UV - VIS spectrophotometer (Spectronic 200). Working solutions were prepared by diluting the stock solution with distilled water to subsequent required concentrations. pH levels were controlled by diluting the solution with 0.1 M NaOH or 0.1 M HCl. Identical aliquots of 25 mL are used as samples to be treated.

2.6. Photocatalytic Treatment

The treatment of the synthetic wastewater was performed using batch system at room temperature. 500 mL beakers containing 100 mL aqueous phenol solution were constantly stirred at 150 rpm using a magnetic stirrer (Corning – PC 410D). An accurate amount of TiO_2 – activated carbon composite was added in the solution at specific pH levels generated by Response Surface Methodology. Then, it was irradiated for different intervals of time. Irradiation of the solutions was performed using laboratory ultraviolet photocatalytic box reactor. The concentration of the phenol was monitored by measuring the absorbance of the samples using UV - VIS spectrophotometer (Spectronic 200) after being withdrawn from the beaker at variable time.

Table 1
Experimental Design

	Factor	Units	- Level	+ Level
A	Composite Dosage	g	0.1	1.0
B	Irradiation Time	Min	20.0	180.0
C	Initial Concentration	ppm	100.0	1,000.0
D	pH		3.0	11.0

The design was performed with a total of 29 experimental runs. Optimization steps of the resulting data from these runs were analyzed with the aid of Design Expert® software as integrated by RSM.

2.7. Analytical method

The percent of phenol degradation was computed using the equation:

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

where A_0 and A_f are the liquid-phase absorbance of phenol at initial and final (mg/L), respectively.

3. RESULTS AND DISCUSSIONS

3.1. Degradation of phenol

Design Expert® was used to provide photocatalytic treatment conditions of the phenol using the TiO_2 – AC composite from Canarium ovatum Engl. shells. The parameters were tested and the percent degradation was observed as the result. Table 2 shows the percent degradation of phenol given the following parameters. From which, Run 3 shows the highest level of percent degradation with the value of 96.226 at 1.00 g composite dosage, 180 min irradiation time, 550 ppm initial concentration and pH of 7. On the other hand, Run 29 shows the least percent degradation with the value of 26.513 at conditions of 0.10 g composite dosage, 20 mins irradiation time 550 ppm initial concentration and pH of 7. It can be assumed from this that phenol degradation favors samples at higher amount of composite dosage and longer irradiation time.

Table 2
Actual Factors and Response Values

Run	Comp Dos[a]	Irrad Time[b]	Initial Conc[c]	pH	% 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

3.2. Modelling

In studying the effects of the composite dosage, irradiation time, initial phenol concentration and pH in the photocatalytic treatment of phenol, Response Surface Methodology using Box Behnken was used. From the given experimental data obtained, Design Expert® generated models and their corresponding statistical values to be able to choose a suited model for the study.

Table 3
Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2
Linear	2.48	0.988723	0.986843	0.983036
2FI	2.65	0.990323	0.984947	0.971089
Quadratic	1.57	0.997373	0.994747	0.988355
Cubic	1.62	0.998796	0.994379	0.94477

Based from the model summary statistics presented in Table 3, the quadratic model is suggested because it has the maximum adjusted R^2 of 0.994747 and predicted R^2 of 0.988355. It gives a difference of 0.0064 which does not exceed the generally accepted level of 0.2. The ANOVA results, shown in Table 4, likewise agree with the model summary, indicating that the model is significant with Model F – value of 379.73 and only 0.01% chance attributed to noise factors. Moreover, Prob > F values were also investigated to know which values are significant, stating that values less than 0.0500 are considered significant while values larger than 0.1000 are considered insignificant. From which, it was deduced that B, which is the irradiation time, and B^2 are significant model terms and Lack of Fit is not significant.

Table 4
ANOVA Response for Quadratic Model

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	13033.33	14	930.9523	379.7297	< 0.0001	significant
A-Comp Dos[a]	0.288143	1	0.288143	0.117532	0.7368	
B-Irrad Time[b]	12911.2	1	12911.2	5266.398	< 0.0001	significant
C-Initial Conc[c]	1.101371	1	1.101371	0.449242	0.5136	
D-pH	7.702243	1	7.702243	3.141697	0.0981	
AB	1.771235	1	1.771235	0.722476	0.4096	
AC	0.227911	1	0.227911	0.092963	0.7649	
AD	7.011692	1	7.011692	2.860026	0.1129	
BC	2.509328	1	2.509328	1.023539	0.3288	
BD	9.317687	1	9.317687	3.800627	0.0716	
CD	0.070481	1	0.070481	0.028749	0.8678	
A^2	0.820245	1	0.820245	0.334573	0.5722	
B^2	80.96527	1	80.96527	33.02523	< 0.0001	significant
C^2	0.01191	1	0.01191	0.004858	0.9454	
D^2	0.075897	1	0.075897	0.030958	0.8629	
Residual	34.32266	14	2.451619			
LOF[e]	23.47709	10	2.347709	0.865868	0.6137	insignificant
Pure Error	10.84557	4	2.711394			
Cor Tot[f]	13067.65	28				

[a] Composite dosage (g)
[b] Irradiation time (min)
[c] Initial phenol concentration (ppm)
[d] Percent phenol degradation

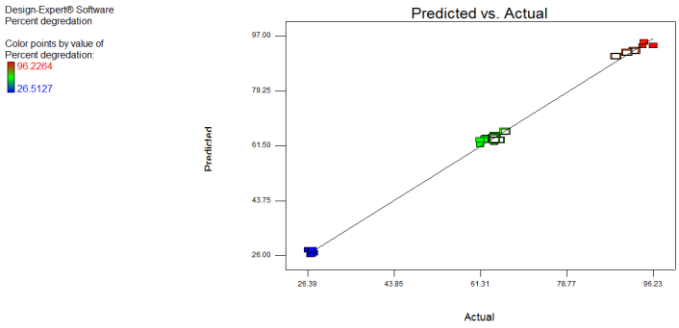

Fig. 2*. Predicted response vs. actual response values*

A graph of predicted values was given based from the model generated versus experimental values is shown in Figure 2. An observation can be obtained that actual data gathered from experimental runs nearly corresponds with the prediction from the quadratic model.

3.3. Responses

3.3.1. Effect of composite dosage

The composite dosage thought to affect the percent degradation of phenol. It was hypothesized that an increase in composite dosage would also increase the percent degradation. However, the results of the study show that the composite dosage have very little or no significant effect on the response, as shown by the almost vertical line in Figure 3.

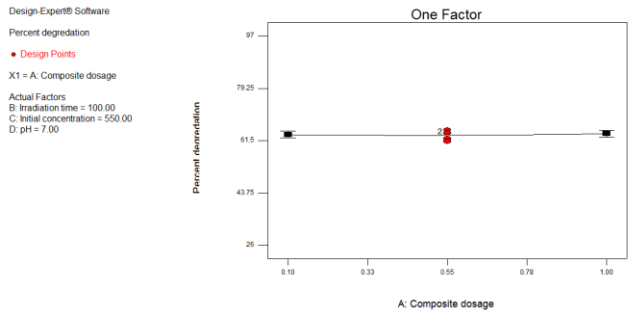

***Fig. 3**. Percent degradation vs. composite dosage*

When photocatalytic reaction is carried out on the catalyst surface, the catalyst increases in the circumstance of a certain concentration of phenol solution, provided more reaction active sites. Therefore, reactive groups generated by illumination had also increased. Consequently, photocatalytic reaction rate increased. Further increase of catalyst provided enough reactive sites and made the reaction reach saturation. Continued increase of the catalyst caused decline of light efficiency and fall of the degradation rate of phenol solution, due to the shielding and scattering effect of catalyst to light [13]. The composite dosage of 0.1 - 1.0 g for 100 mL aliquot of initial phenol concentrations of 100 ppm – 1000 ppm can be said to have made the photocatalytic reaction reach saturation. This is the reason why the dosage has no significant effect on the percent degradation.

3.3.2. Effect of irradiation time

The proposed methodology for this study was only allowed for 100 minutes of irradiation but the percent degradation achieved through the pre-experimental runs was only 56%. Due to this, the researcher extended the maximum irradiation time to 180 minutes to achieve above 90% percent degradation. Figure 4 shows relationship between the percent degradation and irradiation time. At 20 mins, the percent degradation of phenol is 27.003, this increases to 92.606 at 180 mins. This direct proportionality can be explained in terms of increased time for the complete utilization of incident photons striking on the catalyst surface. Moreover, more time leads to augmented availability of active sites creating higher adsorption of incident light that can lead to formation of high photoactivated volume in suspension which further increase the efficiency of the system [14].

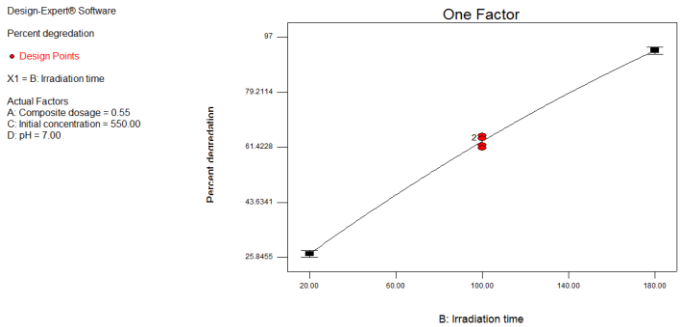

***Fig. 4**. Percent degradation vs. irradiation time*

3.3.3. Effect of initial phenol concentration

It was observed in the studies of S. H. Borji, S. Nasseri, A. H. Mahvi, R. Nabizadeh and A. H. Javadi [15] and Udom et. al. [16] that the percent degradation decreases with increasing initial concentrations of phenol. These studies stated that the decrease in percent degradation could be due to saturation of active sites on the photocatalyst by intermediates, hereby creating fewer sites for adsorption and creation of hydroxyl ions. Contrary to those results, the results of the study show that the initial phenol concentration have very little or no significant effect on the response, as shown by the vertical line in Figure 5. This may be due to the very large surface of the activated carbon in the composite. The large surface area of the activated carbon creates a vast amount of active sites in the composite. The insignificance of the initial concentration denotes that the saturation of the active sites on the composites with the phenol has not been reached given the limited range of phenol concentration. There is always an excess of active site to degrade phenol in the study. Therefore, the rate of reaction for the adsorption of phenol, creation of hydroxyl ions and subsequent degradation, is same throughout, thus, insignificant.

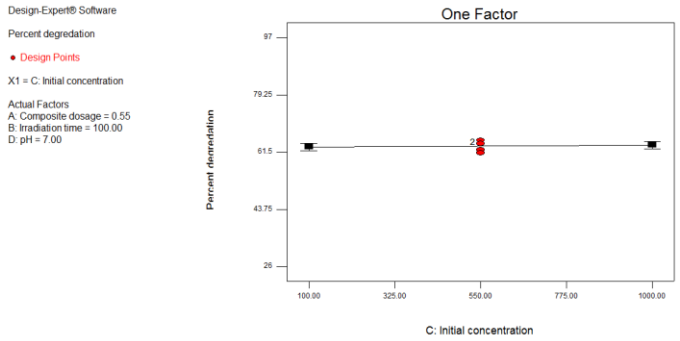

***Fig. 5**. Percent degradation vs. initial phenol concentration*

3.3.4. Effect of pH

Industrial wastewater with phenol usually have pH that ranges between 3 – 11. Shown in Figure 6, The percent degradation decreases slightly as the pH of the solution increases or becomes more basic.

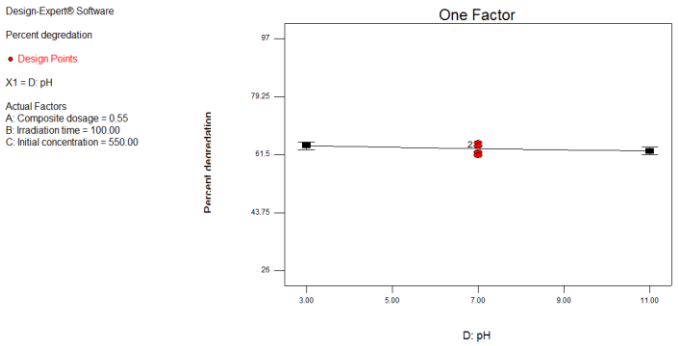

***Fig. 5**. Percent degradation vs. pH*

This effect was also observed by Udom et. al [15]. Their study explained that the surface of photocatalysts are negatively charged, at higher pH (higher alkalinity), phenolate intermediates may be repelled away from the catalyst surface thereby opposing adsorption of contaminant molecules. Thus, lower degradation of phenol is observed in alkaline environments. At lower pH, they observed that most of the phenol molecules are adsorbed on the surface of the photocatalysts due to the undissociated nature of the phenol thereby producing higher photocatalytic efficiency.

3.4. Optimization of parameters

Design Expert® provided the data for the optimization of factors from the actual responses from experimental data. Necessary constraints must be set to obtain the optimum value of the composite dosage, irradiation time, phenol initial concentration, and pH to achieve the highest percent degradation. Composite dosage is targeted to be at minimal since it is best, in economic consideration, to treat phenol solution with the least amount of dosage. Similarly, the irradiation time is set to be at minimum to accommodate more phenol wastewater treatment at a given period of time. The phenol initial concentration is set to range from 100 ppm to 1000 ppm since it is only in the scope of the study. The target value for the pH of the phenol solution is set in range between values of 5 and 7. Also, the lower limit is set to be 5.0 since phenol degradation is more favored at more acidic system. Lastly, the percent degradation is set at target of 99.9 to ensure the highest level of phenol degradation.

Table 5
Parameter constraints for optimization

Factors	Constraints			
	Goal	Lower Limit	Upper Limit	Importance
Comp Dos[a]	minimize	0.1	1.0	3
Irrad time[b]	minimize	20	180	3
Initial conc[c]	is in range	100	1000	3
pH	is in range	5	7	3
% Deg[d]	is target = 99.9	90	100	3

[a] Composite dosage (g)
[b] Irradiation time (min)
[c] Initial phenol concentration (ppm)
[d] Percent phenol degradation

Design Expert® provided the optimum conditions by considering the constraints given and the values are as follows:

Table 6
Parameter constraints for optimization

Comp Dos[a]	Irrad time[b]	Initial conc[c]	pH	% Deg[d]
0.1	173.95	1000	5	92.078

[a] Composite dosage (g)
[b] Irradiation time (min)
[c] Initial phenol concentration (ppm)
[d] Percent phenol degradation

3.5. Test at optimum conditions

To verify if the model generated by Design Expert® adequately explains the behavior of the degradation of phenol, experimental runs were performed using the optimum values presented in Table 6.

Table 7
Predicted vs. actual percent degradation

Predicted % Deg[d]		Actual % Deg[d]	% Error
92.078	Run 1	90.870	1.31 %
	Run 2	89.760	2.52 %
	Run 3	90.680	1.52 %
	Average	90.437	1.78 %

The observed percent degradation recorded yielded and experimental error of 1.78% indicating that the model provided by Design Expert® relates the response variable to the operating parameters.

4. CONCLUSION

Composite made from the immobilization of TiO_2 in activated carbon from Canarium ovatum Engl. shells is effective in the treatment of phenol trough photocatalytic degradation. At optimum conditions generated by Design Expert® under response surface, average percent degradation achieved a value of higher than 90%. For the composite dosage range of 0.1g - 1.0g used for 100 mL aliquot, there is no observed effect on the percent degradation of phenol. The same can be said for the initial phenol concentration. Meanwhile, the percent degradation increases with the increase in irradiation time but decreases with the increase in pH.

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