Photocatalytic degradation of phenol using immobilized titania in activated carbon from Canarium ovatum Engl. nut shell

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Abstract. Presented study determined the photocatalytic treatment of phenol in aqueous medium using titania (TiO₂) immobilized in activated carbon derived from charred Canarium ovatum Engl. nut shell through boil deposition method. Composite dosage, irradiation time, initial phenol concentration, and pH were varied to investigate how percent degradation of phenol would respond. The investigation showed that amongst all parameters, only pH has a significant effect to the photocatalytic degradation of phenol, wherein degradation increases as pH value decreases. Moreover, Design Expert® showed that 90.437% phenol degradation will be achieved using optimum values.

1. Introduction
Wastewater is defined as discharged water that contains waste from industrial, commercial, and residential sources. These wastewaters, largely generated by big industries such as refineries, are required by law to be treated to remove pollutants before discharge [1]. If wastewater is not adequately handled, it can affect the ecosystem which includes plants, animals, and humans. Negative consequences may entail damage to ecosystems, nutrient pollution in water sources, prohibitions on outdoor water usage, prohibitions on aquatic agriculture and degradation in 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]. As pollutant, it is generally found on industrial effluent discharge released to bodies of water as a result of its manufacture. Other sources of phenol include organic synthesis, production of phenolic resins and petroleum products, combustion of wood, and automobile 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.

Titania, chemically called titanium dioxide (TiO₂), is known for its wide range of application. It has been widely researched in the area of surface science and is considered to provide insights into surface properties. TiO₂ is classified as a photocatalyst with a fairly high performance of water decomposition and degradation of organic material. [6]. Although most experiments concentrate on the alteration and efficiency of only TiO₂, composites such as carbon-TiO₂ have barely been investigated for
photocatalytic degradation of toxic contaminants. Nevertheless, it has been shown that the combination of activated carbon and TiO$_2$ may have a synergistic impact on photodegradation of organic contaminants. [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 through photocatalytic degradation.

2. Methodology

2.1. 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°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$_2$SO$_4$ 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.

2.2. 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 h [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 h and kept at a temperature of 400°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°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.

![SEM micrograph of acid activated *Canarium ovatum* Engl. shells activated carbon.](image-url)
2.3. 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°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°C using an electrical oven (Heraeus UT-6200).

2.4. Preparation of synthetic wastewater.
Synthetic wastewater stock solution was prepared by dissolving 1000 ± 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 – 009l model) and the absorbance using a UV - VIS spectrophotometer (Spectronic 200). Solutions to be used for treatment 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 HCl or 0.1 M NaOH. Identical aliquots of 25 mL are used as samples to be treated.

2.5. 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. It was then irradiated for different time intervals. Solution irradiation was performed using the laboratory ultraviolet photocatalytic box reactor. The concentration of phenol was measured by calculating the absorption of the samples using the UV-VIS spectrophotometer. (Spectronic 200) after being withdrawn from the beaker at variable time. 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.

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.

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.

| 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         |

Table 1. Model Summary Statistics.
Based on the model summary statistics presented in Table 1, 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.

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 2 (a). As photocatalytic reactions are carried out on the catalytic sheet, the catalyst raises the concentration of a certain phenol solution, so that there are more active reaction sites. Reactive groups produced by light exposure were therefore also increased. As a result, the photocatalytic response rate improved. The increase of the catalytic converter produced ample reactive sites and allowed the reaction to achieve saturation. Continued catalytic increase caused a decrease in light output and a decrease in the rate of oxidation of phenol solution due to the shielding and dispersion effects of the light catalyst. [13]. The composite dosage of 0.1 - 1.0 g for 100 mL aliquot of initial phenol concentrations of 100 – 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 min. 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 min. to achieve above 90% percent degradation. Figure 2 (b) 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].

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. Such experiments have shown that the decrease in the percentage degradation may be attributable to the depletion of active photocatalyst sites by intermediates, thereby producing less adsorption and hydroxyl ion formation sites. 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 2 (c). 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 number 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.

3.3.4. Effect of pH. Industrial wastewater with phenol usually has pH that ranges between 3–11. Shown in Figure 2 (d), The percent degradation decreases slightly as the pH of the solution increases or becomes more basic. This effect was also observed by Udom et. al [15]. The study explained that the surface of photocatalysts is negatively charged, with higher pH (higher alkalinity), phenolate intermediates may be repulsed away from the catalytic surface, thereby preventing the adsorption of contaminant molecules. As a consequence, decreased oxidation of phenol is observed in alkaline environments. At
lower pH, most phenol molecules were observed to be adsorbed on the surface of photocatalysts due to
the unexplained nature of phenol resulting in better 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.

Figure 2. One factor response of (a) percent degradation vs. composite dosage, (b) percent degradation vs. irradiation time, (c) percent degradation vs. initial phenol concentration, and (d) percent degradation vs. pH.
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 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. Design Expert® provided the optimum conditions by considering the constraints given and the values are as follows:

### Table 2. Parameter constraints for optimization.

| Composite dosage | Irradiation time | Initial phenol concentration | pH | Percent phenol degradation |
|------------------|------------------|-----------------------------|----|---------------------------|
| 0.10 g           | 173.95 min       | 1000 ppm                    | 5  | 92.078                    |

### 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 through 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 0.1 - 1.0 g 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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