Restoration of pretreated palm oil mill effluent using TiO$_2$ based photocatalytic system: An optimization study

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Abstract. Phenolic compounds found in pretreated palm oil mill effluent (pre-POME) pose severe threat to aquatic ecosystem and human health due to their build-up in the environment and high toxicity. Thus, the removal of phenolic compounds from pre-POME is necessary to preserve environmental quality and protect human health. In this paper, the optimized degradation of phenolic compound, gallic acid (GA) from pre-POME under visible light assisted TiO$_2$ based photocatalysis is reported. TiO$_2$ nanoparticles (NPs) were synthesized by chemical precipitation technique followed by characterization with X-ray diffraction (XRD), diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis) and field emission scanning electron microscopy (FESEM). The effect of process variables such as loading of TiO$_2$ and H$_2$O$_2$ dose on the degradation of GA from pre-POME was investigated and optimized using response surface methodology (RSM) based on central composite design (CCD). Spherical shaped anatase phase TiO$_2$ NPs with size 45.47 nm and band gap (Eg) of 3.16 eV were obtained. The results demonstrated that both variables, TiO$_2$ loading and H$_2$O$_2$ dosage showed positive effect on GA degradation. The highest removal of GA from pre-POME (71.20%), from 44.85 ppm of initial concentration was observed for the optimal TiO$_2$ loading of 0.88 g/L, H$_2$O$_2$ dosage of 8.5 wt% and 2 h reaction under visible light irradiation. The use of H$_2$O$_2$ combined with TiO$_2$ NPs indicated a great potential for the removal of GA, which has been pointed out as the major phenolic compound in pre-POME.

1. Introduction
The rapid development of oil palm agroindustry in Malaysia has resulted in large quantities of organic waste being discharge into the environment. According to several research studies, pre-POME contains phenolic compounds because 85 to 90% of the palm oil mills in Malaysia employed open ponding system for treatment which is incapable of removing phenolic compounds from POME [1, 2]. The release of waste effluent containing phenolic compounds is escalating environmental pollution. On the other hand, the growing environmental awareness amongst the masses and the desire for a healthy environment demands for improvement in pollution control and clean-up capabilities. Since, phenolic compounds are toxic, carcinogenic and considered priority pollutant, they should be removed...
from pre-POME before the final release into the environment in order to protect human health and preserve environmental quality.

Irrefutably, various physical, chemical and biological treatment methods have been investigated for the removal of phenolic compounds from industrial waste effluent. However, biological treatment using different types of microorganism (MO) is the most widely investigated method for the elimination of phenolic compounds from pre-POME. Tosu et al. investigated the capability of Methylobacterium sp. NP3 and Acinetobacter sp. PK1 for phenolics removal from pre-treated POME. It was found that the acclimatized and immobilized bacteria were capable of removing about 63.4% of 33 ppm initial phenols [2]. Similarly, the ability of Trametes hirsute strain AK 04, was investigated and it was reported that the fungus immobilized on oil palm fiber was able to effectively remove phenols up to 82.2 % of 112 ppm after 8 days of incubation [3]. The results of these investigations were encouraging. Nevertheless, biological treatment suffers from several major drawbacks such as incomplete removal, nutrients and long retention time requirement by MO coupled with difficulty in obtaining their special strains, and the production of secondary pollution in the form of sludge [4].

Photocatalysis using TiO₂ offers a sustainable alternative for the removal of phenolic compounds from pre-POME and has several advantages over the existing treatment techniques. The advantages includes but not limited to higher efficiency, predominant photocatalytic activity, low toxicity, high resistance towards corrosion, low production cost of TiO₂ [5], complete mineralization [6], rapid reaction rates and operation under ambient conditions of pressure and temperature [7]. Despite all the advantages of photocatalysis, the scientific literature is limited regarding the use of this technique for degradation of POME [8]. Only few research groups have investigated photocatalytic oxidation of POME [9, 10]. Nevertheless, these studies were mainly focused on the reduction of chemical oxygen demand. To the best of our knowledge there is no work reported in literature regarding photocatalytic oxidation of phenolic compounds from pre-POME.

The efficiency of the photocatalytic system can be improved by the optimization of factors affecting photocatalytic degradation. We have known from the work reported by Fisher, that varying one single variable at a time (COST) approach is not an effective way for optimization of process variables [11]. Because, it does not enable the investigation of combined and interaction effects of two or more independent variables. This approach is fine if the goal is to only primarily learn about the system. However, if the goal is the optimization and improvement of a process, then a different approach is required for designing of experiments, where various factors are changed at the same time. RSM can serve this purpose by changing multiple factors at a time and evaluating the interactions of possible influencing factors on desired outcome variable and then the optimum conditions can be achieved more easily [12].

In the present paper, visible light assisted TiO₂ based photocatalytic system for the restoration of pre-POME contaminated with phenolic compounds was investigated and reported. The effect of operating factors such as TiO₂ loading and oxidant (H₂O₂) dosage were investigated and optimized using RSM. The TiO₂ NPs were synthesized by hydrolysing TiCl₄ in water followed by calcination at 300°C. The synthesized TiO₂ NPs were characterized by various analytical techniques such as XRD, FESEM and DR-UV-Vis.

2. Experimental

2.1 Materials and Methods
Titanium(IV) chloride (TiCl₄) (purity: 99.9%), ammonium hydroxide (NH₄OH, 30%), Folin-Ciocalteu’s phenol reagent (99%), sodium carbonate (99.9%), hydrogen peroxide (H₂O₂, 30%) and GA (99%) were bought directly from Merck, Malaysia. Chemical structure of GA is shown in figure 1. All the chemicals were used as received without further purification. Pre-POME samples were collected from the release point of the wastewater treatment plant (WTP) of a local palm oil mill situated in Perak state of Malaysia. It was preserved in cold storage at 4±1°C to avoid biological degradation that would change effluent characteristics. Deionized (DI) water was used throughout the experiments.
2.2 Synthesis and characterization of TiO₂
For detailed synthesis procedure of TiO₂ NPs and the techniques used for its characterization, the previous work is referred [13]. In this paper, the TiO₂ was characterized by XRD as across checking analytical technique to confirm its crystalline phase using a Bruker Advance diffractometer. The XRD data was collected in the 2θ range of 10-80° using a scan rate of 0.05°/s.

2.3 Photodegradation
A Pyrex® quartz reactor (100 mm long, 50 mm diameter) was used for carrying out photocatalytic reactions. Photocatalytic reactions were carried out to assess the photocatalytic activity of the as-synthesized photocatalysts under visible light illumination. An accurately weighed TiO₂ photocatalyst (0.1-1 g/L) was evenly dispersed into 50 mL of pre-POME with initial GA concentration of 44.85 ppm. Then, H₂O₂ (3%, 6% and 9%) was added to pre-POME. The suspension was stirred for 30 min in the dark to attain adsorption-desorption equilibrium. Subsequently, the reaction was initiated with visible light (halogen lamp, 500W). For comparison purpose reactions were also performed without light (adsorption) and with light (photolysis). All the reactions were carried out under constant magnetic stirring to ensure the uniform dispersion of TiO₂. An aliquot, 10 mL of pre-POME was taken out from the reactor after 120 min of reaction. Prior to analysis the nanoparticles were removed from the treated POME samples. The degradation efficiency, (X %), for each treated POME sample was calculated using equation (1):

\[
X\% = \frac{C_i - C_f}{C_i} \times 100 \%
\]

Where X% represents the percentage of GA degraded, the initial and final concentration of GA after 120 min of the reaction were denoted by (Cᵢ) and Cᵢ, respectively.

2.4 Analytical method
Folin-Cecocaleau method as described by [14] with a slight modification was followed for the determination of GA concentration in pre-POME. First, the solid residues were removed from pre-POME sample by centrifugation at 7000 rpm for 10 min. Then, 0.5 mL of pre-POME’s sample (5-fold diluted) was mixed with 1 mL of Folin-Cecocaleau phenol reagent (four-fold diluted). Afterwards, 1 mL of 200 g/L sodium carbonate was added to the sample after being kept for 5 min. Finally, the absorbance was measured at 765 nm using spectrometer SpectroVis Plus® instrument. The concentration of GA in pre-POME was calculated from standard calibration curve of GA.

2.5 Experimental design
RSM based on CCD, composed of a factorial model, star points and three replicated central points was used for designing photocatalytic experiments. The experimental design for three-level variables was applied on the response surface function. Two important process factors such as TiO₂ loading and oxidant (H₂O₂) dosage were considered. The actual and coded values for these variables are given in table 1. TiO₂ loading was varied from 0.1 g/L – 1.0 g/L and H₂O₂ dose was in the range of 3-9 wt%. The range over which the variables will be varied was previously identified by the researchers [15] as being appropriate to truly show a difference in the degradation. This is because the data will be fitted to a linear model. The procedure consist of change in variable from low to high, identifying the
experimental conditions for improving photocatalytic degradation of GA by carrying out only a few experiments. A total of 11 experiments were generated using the following expression: \(2^n + 2n + 3\), where 2 denotes the number of levels, n represents the number of factors, 2n denotes the star points, and finally three central points were added in order to validate the model statistically. Percent degradation of GA under visible light irradiation for 120 min was chosen as response variable. The independent and response variables were fitted into a linear model given in equation (2) to reach optimization.

\[
Y = \beta_0 + \sum \beta_j X_j + \sum \beta_{ij} X_i X_j + \varepsilon
\]  

(2)

The data was analyzed using Design Expert v.10.0.0 software (Stat-Eas Inc., USA) in order to get the associated polynomial for the photocatalytic system and to build the response surface plot. The statistical validation of the mathematical model was accomplished by Analysis Of Variance (ANOVA-Test) using the same software. The model was also validated by comparing experimental results with predicted values.

Table 1. The actual and coded values of the independent process variables.

| Independent variables | Symbols | Coded values |
|-----------------------|---------|--------------|
| TiO\(_2\) loading (g/L) | A       | -1 0.1 0.5 1.0 |
| H\(_2\)O\(_2\) dose (wt\%) | B       | 3.0 6.0 9.0  |

3. Results and discussion

3.1 Characterization of TiO\(_2\)

The anatase crystalline structure of the TiO\(_2\) synthesized by precipitation technique and calcined at 300 °C was confirmed by XRD. Figure 2 shows the x-ray diffractogram of the TiO\(_2\) NPs. The x-ray diffraction peaks observed corresponding to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes at \(2\theta = 25.3^\circ, 38^\circ, 48.22^\circ, 54.17^\circ, 55.24^\circ, 63.05^\circ, 68.97^\circ, 70.58^\circ\) and \(75.38^\circ\), respectively. The presence of the main and sharp diffraction peaks of the anatase crystalline phase are in agreement with JCPDS data (card no. 21.1272). Since, the XRD was employed as a cross checking analytical method to identify and confirm the crystalline structure of the TiO\(_2\), the XRD diffraction peaks corresponding to anatase crystalline structure were found consistent with Raman results reported in our previous work [13]. Sharp diffraction peaks at \(2\theta = 25.3^\circ\) in XRD diffractogram, indicates higher crystallinity of TiO\(_2\). High crystallinity is desirable because it can minimize electron hole pair recombination during photoreaction [16]. The crystallite size of the synthesized TiO\(_2\) NPs was 45.47 nm and it was determined from the full width at half maximum (FWHM) of the (101) anatase peak at \(2\theta = 25.3^\circ\) using Scherrer’s formula as shown in equation (3):

\[
D = \frac{k\lambda}{w\cos\theta}
\]  

(3)

Where, k is the shape factor (~0.9), \(\lambda\) the x-ray wavelength (0.15418 nm), w is the full width at half maximum and \(\theta\) is the diffraction angle.

In addition, the electronic and optical properties of the as-prepared TiO\(_2\) were determined using DR-UV-Vis. The spectrum obtained in the wavelength from 200 to 800 nm at room temperature, the photocatalyst revealed strong absorption in the UV region (<380 nm) as given in figure 3. The band gap energy was determined using Tauc’s method, where \((a\nu^2)\) was plotted against \(\nu\) and the linear part of the curve at \(a=0\) was extrapolated to x-Axis as shown in figure 3 (inset). The typical band gap energy (3.2 eV) is previously reported for pure anatase TiO\(_2\) [17]. The band gap energy of the synthesized TiO\(_2\) was 3.16 eV, which is lower than the band gap energy for pure anatase phase of P25. The TiO\(_2\) with narrow band gap can be used for practical application especially in wastewater treatment as this can minimise energy consumption thus reducing the capital cost of the treatment [18].
Since, the synthesized TiO$_2$ showed narrow band gap and was used for the restoration of pretreated POME loaded with phenolic compounds.

FESEM images of the synthesized TiO$_2$ NPs were taken at 100 kX magnification to study its surface morphology. A representative image of TiO$_2$ synthesized by precipitation and calcined at 300 °C is shown in figure 4. The TiO$_2$ were spherical shaped in the form nano-clusters. No agglomeration of the nanoparticle was evident from the images of the synthesized TiO$_2$.

![Figure 2](image1.png)  
**Figure 2.** XRD diffractogram of the synthesized TiO$_2$ NPs.

![Figure 3](image2.png)  
**Figure 3.** DR-UV-Vis spectra and Tauc’s plot (inset) of the synthesized TiO$_2$ NPs [13].

![Figure 4](image3.png)  
**Figure 4.** FESEM image of the synthesized TiO$_2$ NPs [13].

3.2 Preliminary photocatalytic evaluation
The photocatalytic activity of the synthesized TiO$_2$ NPs for the degradation of GA in pre-POME matrix was determined by conducting some preliminary experiments. The degradation profile of GA concentration in pre-POME matrix under non-optimized conditions is presented in figure 5.
Experiments carried out in the dark and presence of TiO$_2$ show that the adsorption of GA on the surface of the photocatalyst is negligible. Conversely, as expected when the pre-POME solution was irradiated using visible light in the absence of a photocatalyst, insignificant photolysis was observed, because gallic acid does not absorb the light at the wave length emitted by the halogen lamp [19]. A notable improvement in GA degradation was observed in the presence of the TiO$_2$, indicating a sizeable photoactivity of the material. The degradation value reached 26% at a catalyst dose of 0.5 g/L after 120 min of reaction time. The as-synthesized TiO$_2$ was suited for photocatalytic application and was used for further optimization study.

![Graph](image.png)

**Figure 5.** Profile of GA degradation by photolysis, adsorption and TiO$_2$ photocatalysis (44.85 ppm of GA).

### 3.3 Statistical analysis and optimization

In the visible light photocatalytic system, the degradation of GA was measured as an outcome under different set of experimental conditions. The obtained experimental results were statistically analysed to identify the significant factors and validate the mathematical model. The experimental outcome ($Y_{\text{exp}}$) and predicted ($Y_{\text{pred}}$) values of GA degradation are presented in table 2.

An empirical model showing the relationship between photocatalytic degradation of GA and independent variables are shown in equation (4). A polynomial equation consisting of five coefficients was obtained from the ANOVA table.

$$Y = 63.38 + 3.66A + 4.06B - 1.61AB + 0.12A^2 + 0.85B^2$$  \hspace{1cm} (4)

Where, $Y$ represents the photocatalytic degradation efficiency, $A$ and $B$ denoting the coded values of TiO$_2$ loading and H$_2$O$_2$ dosage, respectively.

Negative and positive sign following the terms in the equation symbolises the synergistic or antagonistic effects of parameters on photocatalytic degradation of GA [20]. The empirical model was validated by performing ANOVA for regression test. According to results, there was no significant difference between the variance of the regression and residuals ($p = 0.0028$), whereas, there was no significant difference between the variance of lack of fit and pure error ($p = 0.3097$). The comparison of experimental results and predicted results are good agreement and showing the significance of the model. The p-value lower than 0.05 and higher than 0.05 verified the significance and insignificance of the variables, respectively. The results showed that the photocatalytic degradation of GA was positively affected by TiO$_2$ loading (A) and H$_2$O$_2$ dose (B) showing p-values of 0.0022 and 0.0006, respectively. The higher terms $A^2$, $B^2$ and $AB$ with p-values more than 0.05 showed insignificant effects.
Table 2. CCD matrix in coded units, experimental results and predicted values from empirical model for photocatalytic degradation of GA.

| Run | A  | B  | Degradation (%) |
|-----|----|----|------------------|
|     |    |    | $Y_{\text{exp}}$ | $Y_{\text{pred}}$ |
| 1   | 0  | +1 | 69.52            | 69.03             |
| 2   | 0  | 0  | 62.59            | 63.38             |
| 3   | +1 | -1 | 65.13            | 64.82             |
| 4   | +1 | 0  | 67.65            | 67.16             |
| 5   | 0  | 0  | 63.87            | 63.38             |
| 6   | +1 | +1 | 70.42            | 71.20             |
| 7   | 0  | -1 | 57.74            | 59.43             |
| 8   | -1 | +1 | 67.39            | 67.09             |
| 9   | 0  | 0  | 64.89            | 63.38             |
| 10  | -1 | -1 | 55.68            | 54.28             |
| 11  | -1 | 0  | 58.15            | 59.84             |

To identify the optimum values for the factors affecting photocatalytic process, an experimental design was created considering the TiO$_2$ loading and H$_2$O$_2$ dose. The variables were varied according to the design of experiments to identify the conditions most favourable for GA degradation. Figure 6 (a and b) show the response surface plot and contour plot, respectively.

Figure 6. Response surface plot (a) and contour plot (b) of optimized conditions for degradation of GA from pre-POME.

Based on the results, the optimized reaction conditions were located at 0.88 g/L TiO$_2$ loading and 8.5 wt% of H$_2$O$_2$ dose. Further experiments were performed under the optimized conditions, obtaining 71.20% of GA degradation in 120 min of visible light radiation, showing a considerable enhancement as compared to preliminary studies where only 26% GA degradation was achieved in 120 min. The use of H$_2$O$_2$ in combination with TiO$_2$ enhanced the photocatalytic degradation of GA which is
consistent with previous studies [21, 22]. The improvement in photocatalytic degradation of the target contaminant can be attributed to formation of additional amount of hydroxyl radicals produced by H2O2, which are vital for attacking the pollutant and preventing the recombination of electron hole pair [23]. In comparison with previous photocatalytic study, Luna et al. obtained about 63% of GA degradation from aqueous suspension using 40 wt% CuO loaded on TiO2 under visible light irradiation [24]. The GA removal efficiency obtained by Luna et al. using CuO-TiO2 was higher than the current study where only 26% of GA removal was achieved using TiO2 without H2O2. This could be ascribed to the significant narrowing of band gap (Eg = 3.10 eV) of TiO2 by loading CuO onto it [24]. However, the achievement of 71.20% GA removal efficiency by augmenting TiO2 with the addition of H2O2 in the current study was higher than those previously reported, which is also an indication that H2O2 played a dual role. First, it produces more hydroxyl radical and second, it prevents the recombination of charge carriers.

4. Conclusion
Anatase phase TiO2 NPs of crystallite size of 45.47 nm with spherical shape and band gap energy of 3.16 eV were synthesized by a simple chemical precipitation method using TiCl4 as precursor. The synthesized TiO2 NPs exhibited considerably high photoactivity for degradation of phenolic compound, GA from pre-POME. The optimization of the process variables such as photocatalyst loading and hydrogen peroxide was achieved. It was identified that factors affecting photocatalytic degradation such as TiO2 loading and oxidant (H2O2) dosage showed positive effect on GA degradation from pre-POME matrix. Under the optimal loading (0.88 g/L) of TiO2 and 8.5 wt% of H2O2 dose 71.20% of GA was removed from pre-POME under visible light irradiation in 120 min of reaction.

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