Photodegradation of Reactive Black 5 (RB5) in a Batch Reactor Using Silver Phosphate/titanium Dioxide as Photocatalyst

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Abstract. This study investigates the use of silver phosphate/titanium dioxide for the photocatalytic degradation of reactive black 5 (RB5) in a photocatalytic reactor. This research examined the optimum concentration of silver phosphate for dye degradation and found that the highest reaction rate can be obtained with 27.5 percent silver-phosphate in the catalyst. The effects of pH, catalyst loading, and the initial concentration of the dye in the wastewater were studied sequentially to determine the effects on the degradation of RB5. The highest degradation rates were found at absorption wavelength ≤480nm using blue light. Furthermore, the degradation rate was also found to increase with a higher or lower pH value, at higher catalyst loading, and lower initial dye concentration. This study concludes the potency of the catalyst as a visible-light active photocatalyst for possible industrial wastewater treatment application and the effectiveness of the catalyst produced from in situ deposition method and under visible light irradiation.

1. Introduction
The textile industry is one of the biggest companies that consume water compared with other industrial sectors [1]. The predominant use of chemicals, specifically dyes in processing textile, has also brought serious pressure on improving effluent quality especially when it commonly requires pre-treatment [2]. In the past decades, adsorption technologies have received enormous attention for treating dyes in wastewater due to their numerous advantages [3], despite the high cost of the sophisticated processes of retrieving the adsorbed pollutant. On the other hand, the continuous developments in the use of different microorganisms in biodegradation of dyes such as Penicillium simplicissimum [4], Hypocrea koningii [5], and Irpex lacteus [6], demonstrated that biological treatments remain to low in achieving success rates [7].

Recently, advanced oxidation is one of the evolving processes in wastewater treatment by using hydroxyl radicals that react with the organic pollutants. The hydroxyl radicals can be produced in different ways including ozonation, ultraviolet irradiation of peroxides, and using photocatalysts. Numerous studies have shown the potential of photocatalysis in driving the production of highly oxidizing free radicals [8].

Photodegradation by photocatalysis uses hydroxyl radicals in a semiconductor in order to completely degrade a range of organic molecules [9]. Photocatalysis has become one of the emerging technologies in wastewater treatment when Fujishima and Honda in 1972 discovered the conversion of water molecules into hydrogen and oxygen using titanium dioxide in the presence on UV light.
Heterogeneous photocatalytic oxidation is a powerful technique which can convert a broad spectrum of organic pollutants into harmless substances. Currently, various approaches have been used in enhancing the catalyst characteristics to minimize the bandgap energy required to initiate a reaction. This can be achieved by chemical doping, composite catalyst, and addition of promoters such as peroxides [10]. Studies have also shown that silver doping and silver composites helped to improve the visible light excitation of photocatalysts [11, 12]. With the pioneering efforts on silver-based photocatalysts, further studies are required to fully exhibit their capacity for photocatalytic degradation of dyes.

This work has demonstrated the photocatalytic degradation of reactive black 5 (RB5) using silver phosphate/titanium dioxide nanoparticles under visible light and determined the optimum concentration of the catalyst. The optimum concentration of the catalyst was used to study the effects of various parameters during dye degradation—wavelength of the light source, initial dye concentrations, and initial pH—and the degradation was confirmed by analyzing the chemical oxygen demand (COD). Another goal of this research is to help in the development of an effective, sustainable, and economical solution to treatment of dyes in wastewater in the Philippines.

2. Materials and methods

2.1. Synthesis of the silver phosphate/titanium dioxide catalyst

The catalyst was synthesized using a modified in situ precipitation/deposition method [13]. Initially, a 10% silver phosphate concentrate was prepared by dispersing 1.598 g of commercial TiO₂ degussa particles in 50 mL of deionized water. Using a Vibrocell sonicator (VCX 500 -500 watts), the slurry was sonicated at 180 kJ for 10 minutes. The TiO₂ solution was mixed with 1.1353 g of AgNO₃ then stirred for 10 minutes. In another beaker, a Na₃PO₄ solution was prepared by dissolving 0.3671 g of pure Na₃PO₄ in 50 mL deionized water. The Na₃PO₄ solution was added dropwise into the TiO₂-AgNO₃ mixture with continuous stirring for 8 hours resulting to a light-yellow suspension. The suspension was then filtered and washed with water and acetone to remove trace amounts of sodium and nitrate ions which adhered to the surface of the precipitate. The precipitate was dried at 70°C. For comparison, different concentrations of the catalyst (10, 20, 22.50, 25, 27.50, 30, 40, and 50%) were prepared by varying the amounts of Na₃PO₄ and AgNO₃ while keeping the amount of TiO₂ constant.

2.2. Photocatalytic degradation of reactive black 5 (RB5)

The photocatalytic degradation of RB5 was observed in a photoreactor equipped an air diffuser (Atec-AR2500) with a discharge of 200 Lhr⁻¹ and a magnetic stirrer. In the photoreactor, a five-meter flexible light emitting diode (LED) strip that emits light within a range of 400-700 nm was positioned around its external surface. The reaction was performed in a fabricated black box while being submerged into a water bath to reduce external light and temperature increase caused by the LED strip. Throughout the experiment, wastewater samples were periodically drawn from the solution and analyzed with a UV/Vis spectrophotometer (Perkin Elmer Spectrophotometer-Lamdba 25) (λmax = 597 nm). The dye concentration was calculated using equation (1) and expressed as % degradation:

\[
\text{% degradation} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)
\]

where C₀ is the initial dye concentration and Cₜ is the final dye concentration in the solution at time t.

To confirm that the degradation was not due to adsorption of RB5, adsorption performance was analyzed in the same setup. Samples were also drawn and analyzed by UV/Vis spectrophotometer (λmax = 598 nm) and the adsorption performance was computed using equation (2), expressed in terms of % adsorption:

\[
\text{% adsorption} = \frac{C_o - C_t}{C_o} \times 100 \quad (2)
\]
To determine the wavelength where degradation of RB5 is best, one representative concentration was selected and subjected to different wavelengths (blue - 475nm, green - 535nm, yellow - 580nm, and red - 685nm). Subsequently, the most effective wavelength was applied to determine the optimum silver phosphate concentration in the catalyst within the range of 10-50%.

2.3. Kinetic studies
The pseudo-first order and the pseudo-second order rate equations were used to evaluate the order of rate of degradation and adsorption activities. The derived pseudo-first-order rate equation for the boundary condition \( t = 0 \) to \( t = t \) and \( C = C_{Ao} \) to \( C = C_A \) is stated as in equation (3):

\[
\ln C_A = \ln C_{Ao} - k_1 t
\]

where \( C_{Ao} \) and \( C_A \) are the dye concentrations (in ppm) at time zero and at any time \( t \), respectively, and \( k_1 \) is the rate constant for first-second-order degradation/adsorption.

2.4. Effect of pH
The degradation of dye in a 30-ppm solution of RB5 with 0.5gL\(^{-1}\) of catalyst (20%) was observed at various pH values (3.0, 5.0, 7.0, 9.0, and 11.0). The pH of the aqueous solution was adjusted using 0.1 M HCl or 0.1 M NaOH buffers. The current and wavelength used was 1.5 amperes and 475nm (blue light), respectively.

2.5. Effect of catalyst load
The solution has an initial concentration of 30ppm of RB5. The catalyst load was varied from 0.5, 1.0, and 1.5 g under the same current (1.5A) and wavelength (475nm).

2.6. Effect of initial dye concentration
The initial concentrations of the dye used were 30, 50, and 100 ppm, maintained for both stages of the experiment with current input at 1.5A and with blue light (475 nm). The mass of catalyst was constant.

2.7. Characterization of RB5 solution
The dye degradation of RB5 was confirmed by spectral analysis before and after the photocatalytic reactions. At the optimum concentration of the catalyst, the initial and final COD of samples were analyzed with a COD analyzer (Lovibond-RD125). The % degradation was computed by equation (4).

\[
\% \text{ degradation} = \frac{\text{COD}_o - \text{COD}_f}{\text{COD}_o} \times 100
\]

3. Results and discussion

3.1. Effect of light source
The effectiveness of color removal by photocatalytic reactions with TiO\(_2\)-AgNO\(_3\) under visible light after five hours of irradiation were compared (Figure 1) and showed dependence of the RB5 degradation on irradiation source and time. Under these conditions, the catalysts showed the highest performance with blue light followed by green, yellow, and red. The ability of the catalyst to degrade dyes with visible light was due to its wavelength (blue light) that falls within the absorption range. Previous studies show that the AgNO\(_3\) and the TiO\(_2\) have the absorption boundaries around 600 nm [14] and 388 nm [15]. Hence, the energy of light was sufficient to excite electrons and produces holes, which take part in photocatalytic pathway. Beyond these regions, absorption of light is minimal producing less energy.
3.2. Adsorption test and color experiment

Evidences that the dye degradation was not due to adsorption, photolysis, or aeration confirmed that decolorization was caused by the catalyst. In the adsorption test, any concentration from 0-50% did not pose any significant amount of dye absorbed, making the catalyst not an ideal adsorbent for an adsorptive treatment method for wastewater. On the other hand, during photolysis and aeration, it was observed that there was no significant decrease in the concentration of RB5 after exposure to blue LED light and with continuous aeration.

3.3. Photocatalytic performance test

The photocatalytic reactions exposed to blue light showed that the photocatalytic activities were significantly different for each composition of the catalyst (Figure 2). The evidences show improved results when compared with commercial P25-TiO2 catalyst under the same light source. An analysis of the reaction rates using pseudo-first-order kinetics showed that increasing the concentration from 10% to 27.5% increased the rate of the reaction \((k = 0.0027 \text{ to } k = 0.0094)\) and an increase beyond 27.5% caused a decline in the rate of reaction. This decrease in the reaction rate was due to the aggregation of silver phosphate particles [16]. This results to the formation of large aggregates of the compound with a reduced surface area of the catalyst wherein a reduced surface area also reduces the site for adsorption where the reaction starts.

Since the resulting decolorization for 27.5% was the highest among other concentration of silver phosphate, 27.5% catalyst was chosen as the optimum concentration for the degradation of RB5 dye.

Figure 1. Effect of light source in the degradation of RB5 in a solution with natural pH (≈ 5), 30 ppm dye, and 20% catalyst, after 5 hours of irradiation.

Figure 2. Dye degradation under different concentrations of the catalyst.
3.4. Effect of pH
The extreme changes in the pH values of the solution causes an increase in the degradation efficiency (Figure 3). The initial pH of the 30-ppm unmodified RB5 solution is approximately 5.0. The increase in the degradation efficiency can be attributed to the proposed degradation mechanism. Hydrogen ions and hydroxide anions are required to produce hydrogen peroxide or hydroxyl radical, which reacts quickly with the dye molecule. Thus, with an increase or decrease in pH, there is an increase in the available hydroxyl radicals, leading to an increase in the degradation rate. The unchanged dye degradation rates with the pH 5 and pH 7 can be attributed to the neutral or unsatisfactory quantity of free hydronium ion or free hydroxide anion. This observed increase in degradation rate with the extreme change in pH also shows that the reaction between hydroxide ions and the holes is a determining step for the production of hydroxyl radical.

![Figure 3. Effects of varying pH values on the degradation of RB5 using 30-ppm dye at 500-ppm loading of 27.5% silver phosphate/titanium dioxide catalyst load.](image)

3.5. Effect of catalyst loading
After 5 hours of treatment using different catalyst loads of 0.5, 1.0, and 1.5 grams using 30-ppm dye concentration at natural pH of RB5, the degradation of RB5 showed an increasing rate and total degradation with increasing catalyst load (Figure 4). However, the maximum dye degradation was only found between 83-85% regardless of the catalyst loading. This is because of the presence of stable, yet, incompletely degraded organic molecules from the RB5 molecule. The different rates per loading can be attributed to the adsorption of the dye molecule on the surface of the catalyst before degradation can happen. In other words, an increase catalyst loading will increase the surface area on which more dye molecules can be adsorbed.
3.6. Effect of initial dye concentration
Meanwhile, in terms of initial dye concentration, the initial concentration of dye increases along with the amount of dye degraded (Figure 5). However, the percent degradation with respect to time decreases as the initial dye concentration increases. This means that as the initial concentration increases, the quality of effluent decreases. Although there was great amount of dye being degraded, there was still a huge amount of dye left in the solution because of the reason that there was greater amount of dye to be degraded. And it takes longer time, additional catalyst loading, or increase in the intensity of light. A sharp decrease in percent degraded was observed at an initial concentration beyond 50-ppm. On the other hand, initial concentration of 100-ppm results in 20% decrease of the effectiveness of degradation.

3.7. Characterization of the RB5 solution
The analysis of the chemical oxygen demand showed a decrease from an initial 53.76ppm, at time 0, to 36.67-ppm, at time 300, reflecting a percentage degradation of 31.80%. Degradation and COD cannot be assumed equal based on the analysis since COD analysis is used to measure the amount of the carbon being converted into carbon dioxide. On the other hand, the decolorization of RB5 only needs to break the conjugation of RB5, which can be read using UV-Vis spectrophotometer. A further study to correlate degradation and decolorization must be conducted.

Meanwhile, the UV-Vis spectroscopy of the dye solution before and after the photocatalytic reaction confirms the degradation of RB5 into much simpler organic molecules. The maximum absorption peak of the initial dye solution at $\lambda_{\text{max}} = 595\text{nm}$ before reaction shifted to $\lambda_{\text{max}} = 323\text{nm}$ after 300 minutes of

Figure 4. Effect of catalyst loading in RB5 degradation using 30ppm dye at natural pH on RB5 degradation.

Figure 5. Effect of initial dye concentration in RB5 degradation using pH using 500-ppm of 27.5% silver phosphate/titanium dioxide catalyst load at natural pH level.
degradation with lower absorption value. This indicates the disruption of conjugated pi system of the RB5 molecule. However, to fully elucidate the molecule/s formed in the degradation, further characterization of end solution must be conducted.

4. Conclusions and Recommendations
This study showed the effective photodegradation of the industrially used azo dye, RB5, using a synthesized photocatalyst, TiO$_2$-AgNO$_3$ under visible light irradiation. The results of the experiment showed that the photocatalyst can be effectively irradiated under visible light, but only up to its absorptive range of 480nm, which is blue LED light. The study showed that 27.5% silver phosphate is the optimum concentration of the composite catalyst, having an average degradation of 87-83%. The study also showed that the rate of degradation is affected by the initial pH, catalyst loading, and initial dye concentration. In terms of the effect of the initial pH, the catalyst performs better in both higher and lower pH, since both hydronium and hydroxide ion are abundant and are precursors in the formation of hydroxide radical. A higher catalyst loading increases dye degradation rate in contrary with the effect of a higher initial dye concentration. From all these evidences, TiO$_2$-AgNO$_3$ produced from in situ deposition method is an effective photocatalyst for the oxidation of industrial dyes under visible light irradiation. Moreover, it highly recommended for further studies to establish the relationship between dye degradation and dye decolorization, and characterization of the surface properties of the photocatalyst.

5. References
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