

Ultraviolet Light (UV)-Induced Photocatalytic Degradation of Diclofenac Using Naturally Derived TiO₂@rGO Composite

Lorenz E. Borromeo^{1*}, Lea P. Bongat², John Patrick S. Nuñez², Kirby F. Mendioro², Jocelyn R. Balisnomo²

¹Department of Environmental and Sanitary Engineering, Technological Institute of the Philippines, Quezon City, Philippines ²Department of Chemical Engineering, Bicol University, Legazpi, Philippines

Email: *lborromeo.ense@tip.edu.ph

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Abstract

Diclofenac (DCF) is a non-steroidal anti-inflammatory drug (NSAID) used to relieve pain in joint-related diseases. It is not completely metabolized after consumption and cannot be easily removed using conventional wastewater treatment. DCF has been detected in water bodies and may pose chronic effects on the endocrines of living organisms even at low-level exposure. Heterogeneous photocatalysis provides an alternative and efficient method of degrading DCF. In this study, the photocatalytic removal of DCF was investigated using the synthesized TiO2@rGO composite. Reduced graphene oxide (rGO) was prepared from graphite powder by modified Hummer's method using Capsicum annuum extract. Titanium dioxide (TiO₂) was then impregnated in rGO via impregnation method. Adsorption and photocatalytic degradation experiments were conducted at room temperature using 100 mL of 10 mg·L⁻¹ DCF solution. The effects of pH, catalyst loading, and UV irradiation time on the removal of DCF were assessed. Results of the parametric study showed that photocatalytic efficiency of TiO2@rGO composite in DCF degradation was directly proportional to the UV irradiation time and catalyst loading. The maximum DCF removal efficiency of 92.75% and nearly 100% was noted at 50 mg catalyst and 120 min irradiation time, respectively. Meanwhile, the maximum removal efficiency of 90.98% was noted at pH value of 6. Using response surface modelling, the optimum operating conditions in terms of maximum percent removal efficiency of DCF were pH at 6.44, irradiation time of 58.13 min, catalyst dosage of 49.98 mg, with 90% removal.

Subject Areas

Chemical and Environmental Engineering, Nanomaterial, Wastewater

Treatment, Heterogeneous Catalysis

Keywords

Diclofenac, Photocatalysis, Optimization, Titania, Wastewater

1. Introduction

Pharmaceutical residues are ubiquitous environmental micropollutants that end up in water and soil environments. Current and conventional biological wastewater treatment technologies are not designed to treat this specific class of pollutants [1]. Diclofenac (DCF) is a prevalent nonsteroidal anti-inflammatory drug (NSAID) commonly used as an analgesic, anti-arthritic, and anti-rheumatic agent. DCF is not completely metabolized after consumption and has been detected in various water bodies [2] [3]. The unmetabolized drug and its residues may pose chronic effects on the endocrine of living organisms even at low-level exposure and accumulation [4]. Several water and wastewater treatment processes such as adsorption, coagulation, ozonation, and membrane processes have been extensively studied to eliminate DCF [5] [6] [7] [8] [9]. However, several major drawbacks of these processes include high operation and maintenance costs, low removal efficiencies, and production of unwanted by-products [10]. Among these aforementioned treatment processes, advanced oxidation process (AOP) is an effective technique for organic pollutants decomposition. AOP involves in-situ production of highly reactive radicals to effect contaminant degradation. Under AOP, heterogeneous photocatalysis is a well-known oxidation process due to its stability, eco-friendly nature, low cost, and energy efficiency [11]. A semiconductor catalyst is usually utilized to generate powerful hydroxyl radicals (•OH) to oxidize and mineralize organic species using ultraviolet light (UV) or solar irradiation. Titanium dioxide (TiO₂) is one of the leading semiconductors used as a catalyst because of its ease of synthesis, non-toxicity, low-cost, and good stability [12]. However, a major flaw of TiO₂ is its rapid recombination rate, which has been evident in some studies [13] [14]. This issue can be addressed by dispersing TiO₂ in carbon support matrices. Graphene oxide (GO), a carbon material, is characterized by unique pore structures, electronic properties, and good adsorptive properties that are ideal for photodegradation [15]. The interaction of TiO₂ and GO narrows down the bandgap of the composite catalyst, thus enhancing the photodegradation of pollutants by slowing down the recombination of electron holes. However, GO demonstrates low conductivity and a low photochemical stability [16]. Conventional reduction of GO can be carried out to address this problem through chemical, electrochemical, and thermal methods. However, these techniques are usually highly toxic, costly, and energy-intensive [17]. These problems in reduction can be addressed by green synthesis utilizing plants, bacteria, fungi, yeasts, or other natural precursors as reducing agents. Plant extracts are more commonly used than microorganisms because of their local availability and ease of handling. Polysaccharides, sugars, and polyphenol contents of the extracts target the oxygen-containing functional groups such as -OH, C=O, C-O-C, and -COOH present in GO [18]. In lieu of this, the researchers aim to develop a composite applied for DCF removal in an aqueous solution via heterogeneous photocatalysis under UV-irradiation utilizing TiO₂ particles dispersed on green-synthesized reduced graphene oxide (rGO) particles. This research study could pave the way to a higher degradation efficiency through the use of a more environment-friendly precursor with little to no known toxicity for photocatalyst synthesis.

2. Materials and Methods

2.1. Materials

All reagents were analytical grade and used without further purification. The reducing agent for GO was obtained from *Capsicum annuum* using solvent extraction. Diclofenac sodium powder ($C_{14}H_{10}Cl_2NNaO_2$, \geq 98%), phosphoric acid (H_3PO_4 , \geq 95%), potassium permanganate powder (KMnO₄, \geq 99%), liquid hydrogen peroxide (H_2O_2 , \geq 35%), titanium dioxide powder (TiO₂, 100%), graphite powder (C, \geq 99%) and ethanol (C_2H_5OH , \geq 99.5%) were supplied by DKL Laboratory Supplies, Philippines. Concentrated nitric acid (HNO₃, \geq 90%) and sulfuric acid (H_2SO_4 , \geq 95%) were readily available in the laboratory. Prepared hydrochloric acid (HCl, 1 M) and sodium hydroxide (NaOH, 1 M) solutions were used for pH control. All solutions were freshly prepared using deionized water. Moreover, laboratory centrifuge, hot plate with magnetic stirrers, laboratory oven, ultrasonicator, and UV-spectrophotometer were used as equipment to carry out the synthesis, adsorption, and degradation processes.

2.2. Synthesis and Reduction of Graphitic Oxide

GO was synthesized via modified Hummers' method [19]. Concentrated H_2SO_4 and deionized water (in 1:9 volume ratio) were mixed with 1.5 g of graphite powder under constant stirring for 15 min. A constant amount of 6 g of KMnO₄ was slowly added to the acid mixture. It was then heated to 50°C while being magnetically stirred for 12 h. Four (4) milliliters of H_2O_2 were added to the mixture to terminate the oxidation reaction. A color change was noted from purple to dark brown solution [20]. The resulting mixture was centrifuged at 4000 rpm for 15 min. The supernatant solution was then decanted and washed with deionized water to remove any adhered supernatant solution on the GO particles. The washing process was repeated twice to ensure complete separation of the GO from the by-products. The solid material was then oven-dried at 80°C for 4 h. For the reduction process, the synthesized GO was dispersed in 40 mL ethanol to facilitate material exfoliation. The mixture was then ultrasonicated for 20 min. After which, a constant volume of 30 mL extract was added to the ultrasonicated GO solution. The mixture was refluxed at 80°C for 5 h. The successful reduction of GO was indicated by the change in color from brown to black with precipitation [20].

2.3. Synthesis of TiO₂@rGO Composite

The TiO₂-rGO composite was synthesized via wet-impregnation method. Twenty-five (25) grams of the prepared rGO was mixed with 0.5 g of TiO₂ powder in a 50 mL ethanol solution. The mixture was heated and magnetically stirred for 1 hr to allow the reaction to proceed. The solids formed were then filtered using a Whatman filter. The recovered solids were oven-dried and transferred to an air-tight glass container.

2.4. Batch Adsorption Experiments

Batch adsorption experiments were done to evaluate the removal of DCF with the use of TiO_2 and TiO_2 -rGO composite under the absence of UV light. Thirty (30) milligrams of each material were mixed with 100 mL of 10 mg·L⁻¹DCF solution and allowed to adsorb for 60 min. After, samples were filtered using a 0.45 μ m Whatman filter and analyzed for DCF residual concentration using a UV-vis spectrophotometer.

2.5. Photocatalytic Degradation Experiments

The photocatalytic performance of the catalysts was evaluated by exposure under UV-a light irradiation using a 365 nm UV-a lamp positioned at the roof of the photoreactor. The satisfactory suspension of the photocatalyst and the uniformity of the reacting mixture were guaranteed by employing magnetic stirring. The pH of the sample was adjusted by adding 1 M NaOH or 1 M HCl. At varying time intervals, 3 mL of the suspension was sampled and centrifuged at 4000 rpm for 5 min to separate the photocatalyst residue from the solution. The residual DCF concentration on each trial was analyzed using UV-vis spectrophotometer. Removal efficiency (R) was quantified using the Equation (1);

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100$$
 (1)

where *R* (%) represented the DCF removal, C_0 (mg·L⁻¹) and C_t (mg·L⁻¹) were the initial and final concentration of DCF at time *t* min, respectively.

2.6. Optimization

The optimization of photocatalytic degradation under UV-a irradiation was done using central composite design (CCD) method. Three (3) operating parameters were considered namely *catalyst loading*, *pH*, and *UV irradiation time* at constant DCF concentration. The operating parameters together with their factor levels are shown in Table 1. Overall, 19 experimental runs were conducted. The experimental design was executed using Design-Expert[®] software for statis-

tical analysis and data visualization.

3. Results and Discussion

3.1. Effect of Catalyst Loading and pH

It can be observed in **Figure 1** that an increase in catalyst loading increases the degradation of DCF. The maximum DCF removal of 92.75% was noted on 50 mg catalyst dosage. The increase in degradation is possibly due to the increase in the availability of surface catalytic sites and adsorption sites in the composite. Results also showed that $TiO_2@rGO$ composite had the highest adsorptive and photocatalytic removal compared to TiO_2 alone.

As the solution approaches pH < 6 and pH > 6 the percent removal of DCF decreases. As depicted in **Figure 2**, TiO₂@rGO composite exhibited the highest percent removal in photocatalysis. The maximum DCF degradation of 90.98% was obtained in the presence of composite and 76.80% in the TiO₂ catalyst alone at a nearly neutral pH of 6.0, after an irradiation time of 40 min. The pH is known to have a significant effect on the parameters influencing heterogeneous photocatalytic reactions in aqueous systems [21]. Consequently, the interaction of the substrate as well as the intermediates with the *in-situ* generated reactive

Table 1. Operating parameters with their corresponding factor levels.

Factor	Unit	Factor levels					
		- <i>a</i>	-1	0	1	+ <i>a</i>	
Catalyst dosage	mg	6.364	20	40	60	73.636	
pH	-	1.273	4	8	12	14.727	
UV irradiation time	min	6.364	20	40	60	73.636	



Figure 1. Effect of catalyst loading on DCF removal during adsorption and degradation $[DCF] = 10 \text{ mg} \cdot \text{L}^{-1}$; pH = 4; IrT = 40 min.

oxygen species (ROS) also would be affected.

3.2. Effect of UV Irradiation Time

UV irradiation provided a significant leap on the degradation efficiency of DCF as shown in **Figure 3**. The first 60 min showed the performance of adsorption alone and the second half showed the effect of UV irradiation. The removal of DCF was evident by adsorption alone, but with low removal efficiency at a slower



Figure 2. Effect of pH on DCF removal during adsorption and degradation [DCF] = 10 mg·L⁻¹; Catalyst = 30 mg; IrT = 40 min.



Figure 3. Effect of UV irradiation time on DCF removal during adsorption and degradation $[DCF] = 10 \text{ mg} \cdot \text{L}^{-1}$; Catalyst = 30 mg; pH = 4.

rate reaching 20% and 35% for TiO_2 and $TiO_2@rGO$, respectively. The presence of UV irradiation allowed the degradation kinetics to increase, as judged by the steep slope on the graph. Consequently, higher degradation efficiency was achieved reaching nearly 100% removal after subjecting to UV light. The curve flattened after 40 min of irradiation reaching the maximum degradation for the set-up.

The removal performance could be explained by the conduction-band electrons and valence-band holes generated during illumination [14]. Electron-hole pairs prevent the recombination rate which reduces the degradation performance. The electrons react with the dissolved oxygen in the solution to form superoxide while the holes oxidize donor molecules and react with water molecules to form hydroxyl radicals responsible for attacking the DCF [22].

3.3. Statistical Analyses

One-way analysis of variance (ANOVA) was used to determine whether there were any statistically significant differences between the means of three or more independent groups. The summary of p-values is presented in Table 2.

The result showed that there was a significant difference in every operating parameter wherein the corresponding p-values were less than 0.05.

3.4. Optimization

Design Expert[®] software was used to model the degradation of DCF in aqueous solution with varying parameters. The succeeding table summarizes the results of ANOVA analyses for the model, parameters, and interaction of parameters. Terms in consideration with p-values < 0.05 alpha were considered significant in the process. In this case, the model generated was significant which correlated the parameters and the response effectively.

The data in **Table 3** showed the applicability of the suggested model for the process studied. The best process fit model order was cubic, with the coefficient of determination R^2 of 0.9292, predicted R^2 of 13.3035, and adjusted R^2 of 0.7452 which has the most acceptable fit among all tested models.

$$R(\%) = 68.07 + 23A - 0.4784B + 18.27C - 0.1529AB + 5.05AC + 1.91BC$$

-4.56A² - 8.62B² - 3.44C² - 1.73ABC - 1.81A²B (2)
-6.27A²C - 14.43AB²

Table 2.	p-Values	for the	parametric	study.
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Parameters	Photocatalyst	p-Value	Alpha	Remarks
Catalyst loading	TiO ₂	0.00183	0.05	There is a significant difference
	TiO ₂ @rGO	0.000597	0.05	There is a significant difference
рН	TiO ₂	0.014694	0.05	There is a significant difference
	TiO ₂ @rGO	0.006571	0.05	There is a significant difference
UV irradiation time	TiO ₂	0.006945	0.05	There is a significant difference
	TiO ₂ @rGO	0.003746	0.50	There is a significant difference

The equation described by Equation (2) in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and low levels are coded as -1. The coded factors are useful to determine the relative impact of the factors by comparing the factor coefficients.

The perturbation plot helps to compare the effects of all the factors at a particular point in the design space. Referring to **Figure 4**, a straight-line C and two curved lines A and B intersected from the center point of the experimental region, and from there it measured response in each of the three-dimensional axes.

The contour plots presented in this subsection discuss the effects of the active terms in the model equation on the response values. These correlates only to those non-one-factor terms and other significant factors. The one-factor terms were not included because their involvement in the interactions have a great

Table 3. Fit statistics of the model.

Parameters	Value	Parameter	Value	
Standard deviation	11.13	R ²	0.9292	
Mean	56.13	Adjusted R ²	0.7452	
C.V. %	19.83	Predicted R ²	13.3035	
		Adequate Precision	8.0980	



Deviation from Reference Point (Coded Units)

Figure 4. Perturbation plot.

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effect on the responses.

As observed in **Figure 5**, the satisfactory removal percent, *i.e.*, >80% could be attained at a pH value range of ~6 to 10 and composite dosage at >50 mg employing a constant UV irradiation time of 40 min.

The effect of the interaction between pH and UV irradiation time at constant catalyst is depicted in **Figure 6**. The desired % removal of DCF (red region), *i.e.*, ~80% removal and higher could be achieved at a pH value of 6 - 10 and ~55 min irradiation time or higher. The catalyst performance would be unsatisfactory when the conditions were below the said values.

When both the UV irradiation time and catalyst dosage were considered simultaneously while holding the pH constant at 8.0, the parameter values that would give the most satisfactory degradation performance were >45 min UV irradiation time and ~47 mg catalyst dosage or higher as reflected in **Figure 7**. The irradiation time-composite dosage combination was more sensitive compared to the two previous combinations. Even at a high composite dosage, the degradation would still be low or shorter irradiation time. The case would be the same when the irradiation time is very high, but the catalyst dosage is not that high.

4. Conclusion

%DCF removal (%) **Design-Expert®** Software 12 Factor Coding: Actual %DCF removal (%) Design Points 8.9755 86.3445 10 X1 = A: Composite dosage X2 = B: pH**Actual Factor** C: UV irradiation = 40 60 B: pH 8 5 🔘 70 80 50 6 4 20 30 40 50 60 A: Composite dosage (mg)

TiO₂@rGO composite was successfully synthesized and was identified as a highly





Figure 6. Contour plot for the effect of interactions between pH and UV irradiation time.





efficient photocatalyst under UV-a irradiation for the degradation of DCF in aqueous solution. Almost total elimination of DCF was observed using the engineered composite. The effects of operating parameters namely catalyst dosage, pH, and UV irradiation time were evaluated on the removal of DCF. It was evident that increase in catalyst dosage increased both adsorptive and photocatalytic performance of TiO₂ catalyst and TiO₂@rGO composite due to the availability of both catalytic and adsorptive surface sites. For the effect of pH, the maximum percent removal of DCF was observed at pH = 6 for both TiO₂ catalyst and TiO2@rGO composites during adsorption and photocatalysis. The maximum efficiency at pH = 6 indicated that surface-promoted degradation is less in this case. Also, the degradation efficiency was higher on UV irradiation compared to adsorption. The longer the exposure to UV, the higher the percent removal. Using the central composite design method, the optimum conditions of operating parameters in terms of maximum percent removal efficiency of DCF were pH at 6.44, irradiation time of 58.13 min, and composite dosage of 49.98 mg. By setting the highest importance in % removal of DCF and the three parameters set "in range", the optimum condition showed a 90% removal of DCF.

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Conflicts of Interest

The authors declare no conflicts of interest.

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