Research Article

Photocatalytic Degradation of Diazinon in g-C_3N_4/Fe(III)/Persulfate System under Visible LED Light Irradiation

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Abstract

In the past years, the non-conventional treatment of pesticides in wastewater like photocatalytic degradation has been the focus of the attention of researchers to mitigate its impact on both humans and the environment. In this study, synthesized graphitic carbon nitride (g-C_3N_4) from urea is used in the photocatalytic degradation of diazinon as a photocatalyst with the addition of ferric nitrate ($Fe_3(NO_3)_3$) and potassium persulfate ($K_2S_2O_8$) to enhanced degradation. Graphitic carbon nitride was produced using direct calcination of urea at 550°C for 2 h. The physicochemical properties of the synthesized g-C_3N_4 were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), and X-ray Diffractometer (XRD). The photocatalytic degradation of diazinon was conducted under a g-C_3N_4/Fe(III)/persulfate system using different parameters such as catalyst loading (75, 100, and 125 mg), $Fe_3(NO_3)_3$ (325, 350, and 375 mg L^{-1}), and $K_2S_2O_8$ (275, 300, and 325 mg L^{-1}) resulting to an improved photocatalytic degradation efficiency. The physicochemical results showed a synthesized g-C_3N_4 that exhibits properties that are following the international standards. The results of photocatalytic degradation showed the highest degradation of g-C_3N_4 at 37.3%, under the parametric conditions of 125 mg g-C_3N_4, 325 mg L^{-1} of $Fe_3(NO_3)_3$, and 300 mg L^{-1} of $K_2S_2O_8$. The degradation efficiency was observed to increase as the catalyst load increases, while an increase in degradation efficiency can only be observed up to a certain value using ferric nitrate and persulfate. Overall, this study provided insight on the possible use of urea, as a source of g-C_3N_4 and the use of g-C_3N_4 as a photocatalyst using visible light as a more economic approach and cost-efficient way of handling wastewater.

Keywords: Photocatalytic degradation, Diazinon, Graphitic carbon nitride, Urea, Pyrolysis

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1 Introduction

Diazinon, ($C_{12}H_{21}N_2O_3PS$) is an organophosphorus insecticide that is mainly used in the agriculture industry. Primary environmental concerns with the utilization of diazinon are contamination of bodies of water and poisoning of birds and marine life [1]. It has been categorized by World Health Organization (WHO) as class II or "moderately hazardous" with a toxicity dosage for aquatic life of 350 ng l^{-1} and human of 90–444 mg kg^{-1} [2]. Diazinon was one of the most used pesticides for household and agricultural pest control in the United States. In 2002, it was banned for all residential usages by the United States Environmental Protection Agency (U.S. EPA) and in 2004, all of the outdoor usages leaving its utilization to the agricultural sector only [3]. Before its phase-out of residential use in the United States in 2004, diazinon was commonly found in drinking water sources. In 2001, groundwater contamination of diazinon was detected in the Santa Cruz River Irrigation Scheme (SCRIS) in Laguna, Upper Pampanga River Integrated Irrigation System (UPRIIS) in Nueva Ecija, and Magnuang, Batac in Ilocos Norte through sampling sites [4]. Diazinon is one of the common pesticide residues monitored in food samples from markets in the Philippines and some residues can flow from canals into lakes and until it reaches Manila Bay [5].

In the past, conventional methods such as membrane separation, chemical coagulation, bioremediation and adsorption of removing different kinds of insecticides like diazinon has been extensively studied. Recently, advance oxidation process (AOP) methods in the treatment of persistent organic pollutants (POP's) have shown to be a potential substitute from existing conventional method of treatment. One particular AOP treatment of interest is photocalysis that utilized common metal oxides in the presence of UV lights as applied to the removal or degradation of environmentally detrimental pollutants [6], [7].

Photocatalysis has attracted attention to research and scientist due to its efficiency in the treatment of POP's containing wastewater. However, most of metal oxide photocatalysts are limited to operate in the presence of UV light [8] such as zinc oxide (ZnO) and titanium dioxide (TiO_2) due to their large band gap energy [9].

Because of these limitations, the utilization of graphitic carbon nitride (g-C_3N_4) in the photocatalytic degradation of POP's under visible light has shown a potential alternative. This metal-free semiconductor is environmentally benign characteristics and has low cost, high stability, and responsiveness to visible light. Most of the previous studies focused on treating and decolorizing organic dye, however, it has also shown potentials in treating organic pollutants [7].

Graphitic carbon nitride, a stable allotrope of carbon nitride photocatalyst family and possesses great photocatalytic activity than the beta carbon nitride [10]. However, g-C_3N_4 has shown to exhibits low efficiency in its photoreactivity thus, limiting its practical applications. Some methods such as doping with metal or non-metal elements and combining with other semiconductors have improved the photocatalytic efficiency of g-C_3N_4 [11], [12]. However, these methods undergo complex preparation processes, expensive, and some can further cause biological toxicity. The presence of ferric ions, Fe(III), can also promote pollutant degradation in organic pollutants such as phenol. Also, the addition of persulfate to the system can further increase the photodegradation efficiency [13].

To the utmost knowledge of the researchers, there has been no study regarding photocatalytic degradation of diazinon using graphitic carbon nitride with the addition of oxidants such as ferric ions and persulfate. This study aimed to conduct a photocatalytic degradation effect of graphitic carbon nitride on recalcitrant organic pollutants such as diazinon and to investigate the effects of the catalyst dosage, pH, Fe(III), and persulfate ($K_2S_2O_8$) on the overall reduction rate.

2 Materials and Methodology

2.1 *Preparation of the raw materials*

Analytical grade urea ($CO(NH_2)_2$) was bought from Shanghai Hushi Laboratorial Equipment Co., Ltd. The main pollutant for the degradation process was Diazinon PESTANAL® 250 mg, analytical standard, which was obtained from Sigma-Aldrich through Belman Laboratories. Analytical grade of Ferric nitrate ($Fe(NO_3)_3$) and persulfate ($K_2S_2O_8$) were bought at Adamson University Chemistry Laboratory.

2.2 *Synthesis and characterization of g-C_3N_4 from urea*

2.2.1 Synthesis of g-C_3N_4 from urea

The g-C_3N_4 was synthesized using the method from Dong *et al*. and Liu *et al*. [9], [10] by putting 10.0 g of urea $CO(NH_2)_2$ into crucibles and subjected under simple heat treatment in an electric furnace (VECSTAR Furnace CM 1300, Derbyshire, England). The operating temperature for the heat treatment was at 550°C with a heating rate of 10°C/min and was maintained for 2 h.

2.2.2 Characterization of synthesized g-C_3N_4

First, the morphology and microstructure of the synthesized g C_3N_4 were obtained using Scanning Electron Microscopy (SEM) (Zeiss EVO MA15, Oberkochen, Germany). Next, X-ray Diffractometer (XRD)-ARL 9900 Pot Flux X-ray Analyzer 2500 W (Thermo Scientific, Massachusetts, USA) was used with 2Θ ranging from 5 to 60°. Finally, fourier transform infrared (FTIR) spectra were recorded using Spectrum Two (Perkin Elmer, Massachusetts, USA) with a KBr pellet and scanned from 400 to 4000 cm^{-1}.

2.3 *Preparation of the aqueous diazinon solution*

The simulated water treated by the photocatalytic degradation process was prepared by mixing 250 mg of diazinon with 1,000 mL distilled water to prepare 250 ppm of stock solution. This was further diluted to 10 ppm by mixing 45 mL of the stock solution with 955 mL distilled water.

2.4 *Photocatalytic degradation of diazinon*

Photocatalytic degradation of diazinon was carried out in a customized photocatalytic reactor equipped with an LED bulb (13 W, $\lambda max = 460$ nm). The solution was maintained at room temperature (25 ± 2°C) aided by a cooling fan inside the reactor. In a 250 mL Pyrex beaker, 100 mL aqueous 10 ppm diazinon is added along with the synthesized graphitic nitrite, ferric nitrate, and persulfate. The system was magnetically stirred in the dark for 30 min to achieve the adsorption-desorption equilibrium before subjecting it to light exposure. The stable suspension was exposed to irradiation in the self-made photocatalytic reactor under constant stirring at 300 rpm for 2 h. After attaining the desired exposure time of 2h, the photodegraded samples were put in a dark bottle to avoid light absorption caused by the environment.

2.5 *Centrifugation and filtration of degraded samples*

The photodegraded sample was then subjected to refrigerated centrifugation using a Hanil Science Industrial Smart R17 Micro Refrigerated Centrifuge at 4°C and 15,000 rpm before being filtered using Samplicity™ Filtration System with a hydrophilic PTFE 0.45µm filter.

2.6 *HPLC analysis*

The photodegraded samples were in the high-performance liquid chromatograph (Flexar™, Perkin Elmer, Massachusetts, USA) with the Chromera software, equipped with a pump (Flexar Binary LC Pump, Perkin Elmer, Massachusetts, USA) and a ultraviolet–visible spectrophotometry detector (Flexar UV/Vis LC Detector, Perkin Elmer, Massachusetts, USA). Identification of the diazinon was done using a Brownlee Analytical C18 column (Perkin Elmer, Massachusetts, USA) with dimensions of 4.6 mm x 150 mm and particle size of 5 µm. The elution was conducted at isocratic method with a mobile phase of 80% CH3CN in water with a flow rate of 0.8 mL-min^{-1} and absorbance detection at 247 nm. Flow gradient was achieved within 5 min with an additional 10 min required to re-establish initial conditions. The diazinon was identified by an average retention time of 0.577 min.

A standard solutions calibration curves were generated with $R^2 = 0.9997$ and the degradation of diazinon were then calculated using the following equation:

$$\text{Degredation} = \frac{C_o - C}{C_o} \times 100$$

where C_o is the initial concentration prior to the photocatalytic degradation, and C is the concentration of the treated sample.

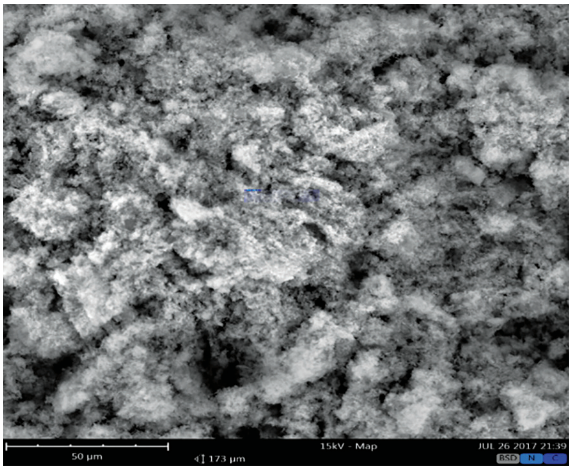

Figure 1: SEM image of synthesized g-C_3N_4.

3 Results and Discussion

3.1 *Characterization of graphitic carbon nitride*

3.1.1 SEM

Shown in Figure 1 is the scanning electron microscope image of the synthesized g-C_3N_4 obtained in this study. The synthesized photocatalyst was identified to have a highly porous structure. This is due to the typical layered morphology of g-C_3N_4 formed during the calcination process [9]. The high porous structure of the g-C_3N_4 is associated to the higher surface area that facilitates an enhance adsorption ability of the target molecules resulting to an improved photocatalytic performance [14].

3.1.2 XRD

Shown in Figure 2 is the XRD pattern of synthesized g-C_3N_4. The stacking structure as confirmed in the XRD results produced two major peaks which occurred at 30.00° and 18.75°, and is similar to the results reported by other studies in the synthesis of g-C_3N_4 catalysts [9], [11]. The strong peak at 30.00° is a characteristic of interplanar stacking peaks of aromatic compounds, which correspond to (002) interlayer stacking [15]. The in-planar repeating unit is shown by the major peak at 18.75° presumably relating to the structural packing motif, such as the hole-to-hole distance of the nitride pores [11].

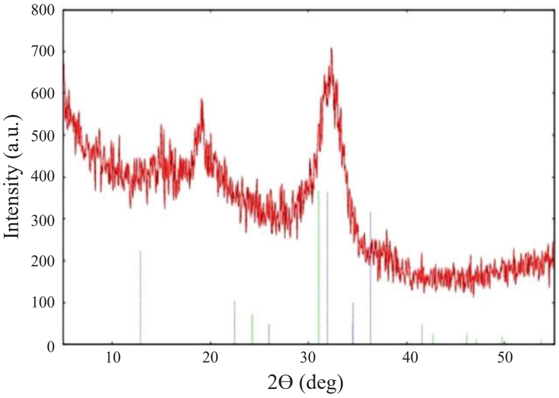

Figure 2: XRD patterns of synthesized g-C_3N_4.

3.1.3 FTIR

The FTIR result of the graphitic carbon nitride is shown in Figure 3. The acquired spectrum confirmed the presence of various functional groups of graphitic carbon nitride as compared with the results of Liu *et al*. [10] and Li *et al*. [16]. The strong bond peaks 1243, 1321, and 1633 cm^{-1} fall between the region of 1200 cm^{-1} to 1650 cm^{-1}, which corresponds to the typical stretching modes of CN heterocycles [17]. The spectrum of the product shows broad bands of the stretching and deformation modes of -NH_2 groups at 3202 cm^{-1} [13]. The peak at 810 cm^{-1} belongs to the s-triazine ring modes [18], [19].

3.2 *Photocatalytic degradation*

This study primarily examined the photocatalytic degradation of the organophosphate, diazinon, to evaluate the visible light activity of the photocatalyst g-C_3N_4 with the addition of $Fe_3(NO_3)_3$ and $K_2S_2O_8$ as the oxidants. The concentration of the samples throughout the experiment was quantified by measuring the absorbance using the HPLC analysis method and comparing it to the absorbance of the prepared calibration curve with known concentration.

The photodegradation of diazinon was observed to be negligible in the absence of the catalyst and oxidants. The removal of diazinon was only at 1.3% in the direct photolysis. This indicates that the observed decomposition in the photocatalytic process can be exclusively attributed to the photocatalytic reaction of the catalyst and the oxidants.

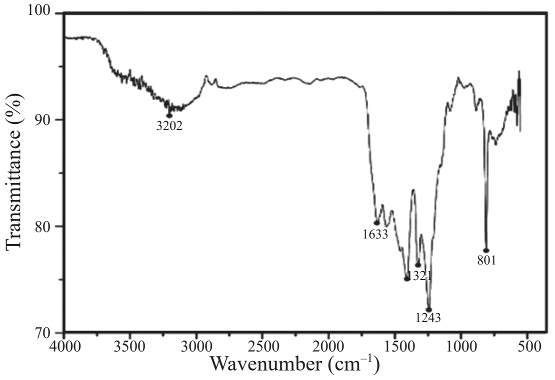

Figure 3: FTIR result of the synthesized g-C_3N_4.

Shown in Table 1, the highest percentage degradation, a value of 37.3%, was yielded by a catalyst load of 125 mg, a ferric nitrate value of 350 mg L^{-1}, and a persulfate value of 300 mg L^{-1}. This lines up with the favorable photocatalytic degradation of diazinon facilitated by the presence of Fe(III) resulting from a light Fenton reaction occurring in the system [13], [20]. Also, the enhanced degradation of diazinon was due to the synergistic effects of the in-situ formation of sulfate radicals ($SO_4{}^{*-}$) that facilitates the possible activation of C_3N_4.

Table 1: Measured values of photocatalytic degradation of diazinon

Photocatalytic Degradation of Diazinon Using g-C_3N_4				
$Fe_3(NO_3)_3$ (mg L^{-1})	**$K_2S_2O_8$ (mg L^{-1})**	**Catalyst g-C_3N_4 Load (mg)**		
		75	**100**	**125**
325	275	16.2%	23.2%	34.0%
	300	17.7%	24.1%	34.8%
	325	17.1%	23.9%	33.4%
350	275	20.9%	26.2%	35%
	300	21.1%	27.2%	37.3%
	325	20.1%	25.7%	36.6%
375	275	15.2%	20.2%	32.7%
	300	16.4%	23.5%	33.7%
	325	15.8%	21.3%	32%

The variation of catalyst load shows that an increase of catalyst, g-C_3N_4, also yields an increase in degradation efficiency. Hence, this factor can have a significant effect on degradation. This can also mean that the catalyst load had not yet reached its limitation point wherein too much adsorption along the photocatalyst surface may occur which leads to a decrease in degradation efficiency [21]–[23].

It can also be noted that while the degradation value increased as the value of the oxidant ferric nitrate increased from 325 mg L^{-1} to 350 mg L^{-1}, the degradation value decreases when it is further increased to 375 mg L^{-1}. The same relationship can be observed within the variations of the oxidant persulfate, when the value of persulfate goes past 300 mg L^{-1}, the degradation percentage starts to decrease. It can be inferred that the photocatalytic degradation increases as the Fe (III) or persulfate concentration increases, but only within a certain range [13]. The decrease of degradation activity beyond this point can be caused by the interference of too many pollutants present with the formation of free radicals resulting in reducing photocatalytic reaction [24], [25]. Due to this, it can be generalized that the variation of the values of the oxidants can affect the degradation of diazinon during the photocatalytic process. Hence, this factor can have a significant effect on degradation.

Furthermore, it can be seen that highest percent degradation, however, is achieved with 125 mg of catalyst load which signifies that higher amount of catalyst added in the diazinon photocatalytic degradation results in higher degradation efficiency.

The increasing trend of photocatalytic activity with increasing catalyst loadings could be caused by enough amount of catalyst molecules available for photocatalytic degradation leading to higher excitation of catalyst and oxidation of the pollutant [26]. The set values for catalyst loading for this experiment did not establish a decreasing trend thus the maximum limit point of catalyst loading had not been reached yet. As concluded by Dewidar [27], too much catalyst present in the system could cause a hindered photocatalytic reaction caused by scattering and screening effects wherein the available total surface area of the catalyst for the absorption of light is reduced leading to lower production of free radicals.

3.3 *Statistical treatment*

To essentially confirm the validations of the effects of the varied factors such as catalyst loadings, amount of $Fe_3(NO_3)_3$ and $K_2S_2O_8$ an ANOVA table is presented at Table 2.

Three-Factor ANOVA using Minitab 17 was used in the 27 samples to determine whether the three factors (catalyst loading, amount of $Fe_3(NO_3)_3$ and

Table 2: ANOVA results of the effect the catalyst loadings, amount of $Fe_3(NO_3)_3$ and $K_2S_2O_8$ on the degradation of diazinon

Source	Degree of Freedom	Adjusted Sum of Square	Adjusted Mean Square	F-value	*p*-value
Catalyst Loading (mg)	1	0.00090	0.00090	0.496	9.78×10^{-13}
Amount of Ferric (III) Nitrate (mg)	1	0.00293	0.00293	1.618	0.4845
Amount of Persulfate (mg)	1	0.19817	0.19817	109.297	0.2111
Ferric (III) Nitrate*Persulfate	1	0.00683	0.00683	3.769	0.0596
Ferric (III) Nitrate*Catalyst Loading	1	0.00297	0.00297	1.638	0.2083
Persulfate*Catalyst Loading	1	0.00368	0.00368	2.027	0.1627
Ferric (III) Nitrate*Persulfate*Catalyst	1	0.00533	0.00533	2.939	0.0946
Error	19	1.0257	1.0257		
Significant effect at *p*-value < 0.05					
No Significant Effect at *p*-value > 0.05					

$K_2S_2O_8$) has significant effect on the degradation of diazinon. Shown in Table 2 are the *p*-values of the individual and combined factors and its effects on the degradation of diazinon. Here *p*-value level for the catalyst loading yielded $p = 9.78 \times 10^{-13}$, which denotes that the catalyst loading is a significant factor in the degradation of the diazinon. On the other hand, all other factors and its combination showed a non-significant effect on the degradation of diazinon.

However, the combined presence of $Fe_3(NO_3)_3$ and $K_2S_2O_8$ in degradation of diazinon with a *p*-value of 0.0596 showed a lower value as compared to the combination of three parameters of catalyst loading, $Fe_3(NO_3)_3$ and $K_2S_2O_8$ with a *p*-value of 0.0946. This can be attributed to the synergistic effect of free radical ions of Fe^{+3}/persulfate system in the degradation of diazinon. However, the increasing degradation of diazinon is primarily affected by increasing the amount of catalyst loading present in the wastewater.

4 Conclusions

The synthesized photocatalyst showed a highly porous structure and it is a typical morphology of g-C_3N_4 as confirmed in the SEM. Also, the XRD result showed a synthesized photocatalyst that exhibit XRD pattern similar to a typical g-C_3N_4 reported elsewhere. This was supported by the presence of all functional groups typical of a g-C_3N_4 as confirmed by FTIR spectra.

The highest degradation efficiency of 37.3% was obtained with the set amount of 125 mg of g-C_3N_4, 325 mg L^{-1} of $Fe_3(NO_3)_3$, and 300 mg L^{-1} of $K_2S_2O_8$. The relationship between the measured degradation value and catalyst loading is directly proportional. As the catalyst loading increases, the measured diazinon degradation value also increases.

For future works, it is recommended to try using different catalyst and oxidant systems and varied concentration that will utilize degradation under visible light. Also, a further increase in the catalyst loading is encouraged as it was statistically proven that it has a significant effect and it does not reach the maximum limitation as it gave an increasing trend. Moreover, this research encourages further studies of how the pH and pollutant concentration will work as a parameter for it can give effects on the degradation system.

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