Investigation of photodegradation of 2,4-Dichlorophenoxyacetic acid on Cu$_2$O/g-C$_3$N$_4$ catalysts

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ABSTRACT
The series x% (wt) Cu$_2$O/g-C$_3$N$_4$ composites were prepared by the conventional impregnation method. These compounds were characterized by different methods such as X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), UV–vis diffuse reflectance spectroscopy (UV-DRS), and Photoluminescence spectroscopy (PL). The results clearly showed the existence of Cu$_2$O and g-C$_3$N$_4$ phases. The photocatalytic activity was estimated by the degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D). The 5% Cu$_2$O/g-C$_3$N$_4$ catalyst showed the highest activity, with the photodegradation yield reached 7.3%. The addition of H$_2$O$_2$ remarkably improved the yield, with 98.5% attained after 1 hour of irradiation.

Introduction
Along with the rapidly development of agriculture, different types of pesticides have been used widely. They are normally organochlorine insecticides such as polychlorinated biphenyl (PCBs), polychlorinated dibenzodioxin (PCDDs). Using an excessive amount of these pesticides in this field leads to soil poisoning and surface water pollution. These compounds are very stable and difficult to degrade in the natural environment. Therefore, their accumulation in the environment causes a threat to the ecosystem and human health [1-3].

There are different physical, chemical, or biological methods to decompose and mineralize these persistent organic pollutants. Among the mentioned methods above, chemical way, concretely photocatalytic decomposition exhibit a high potential. Oxide TiO$_2$ is the most popular photocatalyst due to its low cost, availability, chemical stability, and non-toxicity [4-7]. However, its bandgap energy is 3.2eV, and that means the TiO$_2$ is only activated under ultraviolet light. If sunlight, the most economical energy source, serves to activate catalyst, then this catalytic process is not efficient because the UV intensity in the solar spectrum is relatively low, only ~5%. That is why a lot of research focuses on finding new photocatalysts that can be activated in visible light. Recently, graphitic carbon nitride g-C$_3$N$_4$ has been attracted in the field of photocatalysis due to its good stability and visible light absorption properties ($E_0 = 2.7$ eV) [8].

However, the photocatalytic efficiency of g-$C_3$N$_4$ is still relatively low due to the rapid recombination of produced photoelectron and hole pairs. To overcome this drawback, many composites of g-$C_3$N$_4$ with another oxide, metal, to form Z-scheme photocatalyst type, are investigated [9-11]. In this study, we have synthesized a Z-scheme Cu$_2$O/g-$C_3$N$_4$ catalyst. Its
photocatalytic activity was estimated through the photodegradation of 2,4-D.

**Experimental**

**Catalyst preparation**

The used chemicals were of analytical purity: Melamine C₃H₆N₆ (Merck), Ethanol 99% C₂H₅OH (China), Cu(CH₃COO)₂.H₂O (China), CaCl₂ (China), Cu(CH₃COO)₂.H₂O (China).

The carbon graphitic nitride, g-C₃N₄, was formed when calcining melamine under N₂ flux at 550°C for 3 hours. The x% (wt) CuO/g-C₃N₄ catalysts were synthesized by the following procedure: dissolving the adequate amounts of Cu(CH₃COO)₂.H₂O and g-C₃N₄ salts into a 100ml beaker then covered by paraffin paper. After that, the mixture was stirred at 60°C for one hour, then the paraffin paper was removed and the mixture continuously dried at 60°C to obtain powder; after that, adding a suitable amount of powder A in glucose 0.2M solution adjusted at pH equal to 12 by NaOH 0.1M solution; the final mixture was filtered, washed and dried in oven at 70°C.

**Characterization**

The catalysts were characterized by different methods. The X-ray diffraction (XRD) pattern was measured on X-Ray Diffraction, D8 Bruckner. The Infrared (IR) spectra were determined on FTIR 6300 type A, JASCO. UV-DRS spectra were collected by a Perkin-Elmer Lamda 365 spectrometer equipped with a reflectance sphere using pure calcium sulfate (CaSO₄) powder as a white reflection standard. The photoluminescence (PL) spectra were measured on the HORIBA Jobin Yvon-Fluoromax-4.

**Photocatalytic procedure**

The photocatalytic activity of the catalysts was evaluated through the photodegradation of 2,4-D, a popular pesticide. The different steps of the test were carried out as follows:

An amount of 0.1g of catalyst was added into 100ml solution of 20ppm of 2,4-D. The mixture was stirred and maintained at room temperature during the experiment. Firstly, the system was left in the dark for 1h to reach adsorption equilibrium. After that, irradiation was carried out with a 500W halogen lamp (at a distance of 30 cm far from the solution’s surface). 5ml of the solution was taken every hour to analyze the 2,4-D concentration by HPLC (Agilent) equipped C18 column. The photodegradation yield was calculated by the formula: H(%) = (C₀-C)/C₀×100%.

**Result and discussion**

**Characterization of the catalysts**

Figure 1 presents the XRD pattern of x% (wt) CuO/g-C₃N₄ (x = 1; 2.5; 5; 10):

![Figure 1: XRD pattern of x% (wt) CuO/g-C₃N₄ (x = 1; 2.5; 5; 10)](https://doi.org/10.51316/jca.2022.056)

From Figure 1, it is evident that the g-C₃N₄ phase was not destroyed during the synthesis process. The diffraction peaks of the g-C₃N₄ phase appear at an angle of 2θ = 27.5°, corresponding to the d₀₀₂ surface, which is a characteristic peak for the layered structure of g-C₃N₄. The typical peaks of the CuO phase were observed in all samples of x% (wt) CuO, except 1% (wt) CuO. The characteristics of 2θ peaks for CuO are of 35.6°, 42.5°, 62°, corresponding to the crystal faces of d₁₁₁, d₂₀₀, d₂₂₀, d₃₁₁, respectively. For the 1%CuO catalyst, the presence of CuO was not detected, probably because of the low content of CuO.

**Infrared spectra of catalysts**

To determine the different functional groups and bonds in the synthesized catalysts, the IR spectra measurements were carried out and presented in figure 2 below.

From the IR spectra, it is noted that the catalysts showed a similar peak group in the range from 1200 to 1800 cm⁻¹ corresponding to the vibrations of the CN, C=N bonds in the hydrazine ring structure of g-C₃N₄. For all samples, the broad absorption band centered at about 3500 cm⁻¹ corresponds to the vibrations of the –

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OH group of physically absorbed water on the catalyst surface. In addition, the results of IR spectroscopy show a small peak of at 620 cm\(^{-1}\) corresponding to the vibration of the Cu-O bond in the Cu\(\text{O}\) phase [11].

To determine the light wavelength activating photocatalytic reaction, the UV-DRS spectra of the catalysts were measured (figure 3a). The plot of Kubelka-Munk function calculated from UV-DRS spectrum results is presented in figure 3b. Based on this result, the bandgap energy was determined and resumed in table 1.

![Figure 2: IR spectra of x% (wt) Cu\(\text{O}\)/g-C\(\text{3N}\) catalyst (x= 1; 2.5; 5; 10)](image)

![Figure 3: UV-DRS spectrum (3a) and of its calculated Kubelka-Munk function (b) of catalyst Cu\(\text{O}\)/g-C\(\text{3N}\)](image)

![Figure 4: PL spectra of g-C\(\text{3N}\) and 5%Cu\(\text{O}\)/g-C\(\text{3N}\)](image)

![Figure 5: Photodegradation of 2,4-D on the catalysts](image)

**Table 1: Band-gap energy of catalysts Cu\(\text{O}\)/g-C\(\text{3N}\)**

<table>
<thead>
<tr>
<th>N(^0)</th>
<th>Catalyst</th>
<th>E(_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1%Cu(\text{O})/g-C(\text{3N})</td>
<td>2.66</td>
</tr>
<tr>
<td>2</td>
<td>2.5%Cu(\text{O})/g-C(\text{3N})</td>
<td>2.60</td>
</tr>
<tr>
<td>3</td>
<td>5%Cu(\text{O})/g-C(\text{3N})</td>
<td>2.47</td>
</tr>
<tr>
<td>4</td>
<td>10%Cu(\text{O})/g-C(\text{3N})</td>
<td>2.25</td>
</tr>
</tbody>
</table>

As expected, the combination of two phases, Cu\(\text{O}\) and g-C\(\text{3N}\), decreased the band-gap energy of the catalysts compared with g-C\(\text{3N}\), from E\(_g\) = 2.7 eV of g-C\(\text{3N}\) to 2.25 eV for 10% (wt) Cu\(\text{O}\)/g-C\(\text{3N}\). More content of Cu\(\text{O}\) present in composite, more E\(_g\) reduced. This result confirmed that all catalysts could be activated in the visible light range.

Figure 4 presents Photoluminescence spectra of g-C\(\text{3N}\) and 5%(wt) Cu\(\text{O}\)/g-C\(\text{3N}\). The intensity of 5%(wt) Cu\(\text{O}\)/g-C\(\text{3N}\) is remarkably lower than that of g-C\(\text{3N}\). This result is probably due to preventing the recombination of photogenerated electron-hole pairs in the presence of the Cu\(\text{O}\) phase. This synergistic property could favor the photooxidation of 2,4-D.
Although the yield was quite low, the result showed an improvement in photocatalytic activity when combining g-C3N4 with Cu2O to form a Z-scheme type catalyst [12].

![Figure 5: Photodegradation yield of x% (wt) Cu2O/g-C3N4 versus 2,4D after 4 hour of irradiation](image)

This one is probably due to the transfer of photogenerated electrons on the Cu2O phase onto the conduction band of g-C3N4 and, inversely, photogenerated holes onto the Cu2O valence band as manifested in figure 6. The PL spectra above are according to this hypothesis. The 5% of Cu2O seems to be the most suitable amount for combining with g-C3N4 to reach better photoactivity. This positive synergetic combination was already observed in the researches [13, 14].

![Figure 6: Proposed mechanism of photodegradation 2,4-D on the catalyst Cu2O/g-C3N4](image)

Although the catalyst 5%CuxO/g-C3N4 showed the highest activity however the yield was relatively low, only 7.3%. A stronger oxidant seems to be necessary to better degrades 2,4-D. Hence, 1 ml H2O2 , an well-known strong oxidant was added in the test. The result is exhibited in figure 7.

![Figure 7: Photodegradation of g-C3N4 and 5% (wt) Cu2O/g-C3N4 in the absence and presence of H2O2](image)

From the results in figure 7, after 1 hour of illumination, the photodegradation reaction achieved a yield of 98.5% in the presence of H2O2. This result is better than that of g-C3N4, which is 85.6%. The photo-Fenton process that many studies have mentioned showed a remarkable improvement of photoactivity. The obtained result is likely high potential to treat the 2,4-D pollutant thoroughly in water.

**Conclusion**

The catalysts x% (wt) Cu2O/g-C3N4 were synthesized by the conventional impregnation method. The XRD and IR characterization results showed the clear presence of the Cu2O and g-C3N4 phases. The catalytic activity was evaluated by the 2,4-D photodegradation reaction. The improvement of photocatalytic activity was observed over all the composite catalysts. This confirmed a positive synergetic combination of two phases, Cu2O and g-C3N4. The highest photodegradation of 2,4-D attained 7.3% on the catalyst 5% (wt) Cu2O/g-C3N4 after 5 hours of illumination. This is explained by the lower bandgap energy (Eg=2.2 eV) of Cu2O and the transfer of electron and hole pairs between the two phases, leading to more existence of photogenerated electron-hole pairs. Especially in the presence of 1ml H2O2, 98.5% of 2,4-D was oxidized after 1 hour of irradiation. It is a remarkable result from the point of application view. Optimizing photodegradation of 2,4-D is needed in further studies.

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