INFLUENCE OF CALCINATION TEMPERATURE ON CIPROFLOXACIN PHOTODEGRADATION BY VANADIUM PENTOXIDE / GRAPHITIC CARBON NITRIDE PHOTOCATALYST

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Abstract
The employment of vanadium pentoxide (V 2O 5 ) as a photocatalyst has been widely utilized owing to its promising supercapacitor properties for photocatalysis applications under visible light without any alteration. Up to date, there has yet to be a report on the investigation of calcination temperature effect on V 2O 5 and graphitic carbon nitride (g-C 3N 4 ) combination photocatalyst synthesis for ciprofloxacin (CIP) photodegradation. In this study, the V 2O 5 / g-C 3N 4 photocatalyst is synthesized using simple and facile calcination process. The properties of the synthesized V 2O 5 / g-C 3N 4 were evaluated in terms of porosity, surface morphology and composition elements, and its band gap value to well understand its' behaviour and interaction with CIP pollutants. The best synthesis conditions for V 2O 5 / g-C 3N 4 photocatalyst on CIP photodegradation were at 500 °C (500VC) with 90.17 % CIP photodegradation performance. This research has provided a useful future reference in the field of photocatalysis research.

Keywords: Catalysts; Photocatalysis; Porous Materials; Pyrolysis; Ciprofloxacin.

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1.0 INTRODUCTION

Endocrine-disrupting compounds (EDCs) like ciprofloxacin (CIP) are organic chemicals that have altered the endocrine system’s activities and functions [1]–[3]. Human and animal infections are treated with fluoroquinolone antibiotic CIP. CIP can spread antibiotic-resistant bacteria and genes in aquatic ecosystems even at low concentrations. CIP is stable in water because it contains fluorine. Ozone and photocatalysis via advanced oxidation processes (AOPs) are widely used in the organic wastewater industry to address this issue [4], [5].

For energy conservation and environmental protection, finding photocatalysts with band gap energies that overlap visible light is the first task. V 2O 5 , a 2D sheet material that can be used in visible light without alteration, has been intensively researched since 2011 [6], [7]. V 2O 5 nanostructures have a narrow band gap (2.3 eV), wide light response, and stable chemical properties. V 2O 5’s drawbacks include photo corrosion, electron-hole recombination, and low electronic conductivity [8]. Thus, V 2O 5 can be improved by attaching carbon nanostructures like activated carbon (AC) and graphitic carbon (GC). Graphite carbon nitride has high specific surface area, thermal and chemical stability, and an adequate energy band gap (2.7 eV). V 2O 5 and g-C 3N 4 can also form van der Waals heterojunctions [9].

The successful alignment of the conduction band (CB) (0.47 eV) and valence band (VB) (2.73 eV) of V 2O 5 with the CB (-1.2 eV) and VB (1.5 eV) of g-C 3N 4 led to the creation of photocatalyst heterojunctions have been reported [9],[10], [11]. Despite certain defects in the crystalline structure, this heterojunction enhances the efficiency of charge carrier separation, facilitates broad light-harvesting, and exhibits remarkable redox ability. Notably, the combination of V 2O 5 and g-C 3N 4 by calcination may affect their surface area and improve light absorption and charge separation and able to...
degrade CIP pollutants effectively. Different photocatalysts had different best conditions with their targeted pollutants, so researchers have recently focused on the best condition calcination temperature. The surface's morphological and structural parameters show a variety of active response sites for the best photocatalysis process. Thus, the best V_{2}O_{5}/g-C_{3}N_{4} photocatalyst for CIP degradation for calcination temperature parameter in this study and their photocatalysis process mechanism remain unproven.

2.0 METHODOLOGY

2.1 Materials

Melamine and ammonium metavanadate (NH_{4}VO_{3}, Merck, USA) were utilized in the photocatalyst production. Sigma provided the CIP reference standard (United States). Merck provided sodium hydroxide and sulphuric acid for pH correction purposes (United States).

2.2 Synthesis of V_{2}O_{5}/g-C_{3}N_{4}

To begin preparing g-C_{3}N_{4}, 15 g of melamine was added to a crucible, which was then covered with aluminium foil and heated in a muffle furnace at 550 °C for 2 hours at a heating rate of 2 °C/min [13]. Meanwhile, pure V_{2}O_{5} was prepared by placing 5 g of NH_{4}VO_{3} in a crucible and thermally treating it in a muffle furnace. For 1 hour, the thermal treatment was carried out at 550 °C at a heating rate of 5 °C/min [12]. About 20 mg of NH_{4}VO_{3} was added to 1000 mg of g-C_{3}N_{4} powder and ground together with an agate mortar for the synthesis of V_{2}O_{5}/g-C_{3}N_{4} photocatalyst. The ground powder was then placed in a covered crucible for calcination. The crucible was placed in a muffle furnace and heated for 3 hours at (450, 500 and 550 °C) at a rate of 5 °C/min.

2.3 Characterization of V_{2}O_{5}/g-C_{3}N_{4}

Scanning electron microscopy (SEM, Hitachi SU8020) depict samples' surface shape and morphologies. Band gap studies were performed using LAMBDA 1050 UV-VIS/NIR spectrophotometer (UV-3600Plus, SHIMADZU). Meanwhile, X-ray Diffraction (XRD) was used to analyze the crystallinity of the photocatalyst using (XRD, Rigaku, SmartLab, USA). Lastly, the Brunauer-Emmett-Teller (BET) method (Thermo Scientific, USA) was employed to analyze the binary photocatalyst V_{2}O_{5}/g-C_{3}N_{4} with regards to its surface area, pore volume, and pore size characteristics.

2.4 CIP Photodegradation

Visible light photocatalytic activity of V_{2}O_{5}/g-C_{3}N_{4} was assessed by CIP reduction. About 0.1 g of the photocatalyst was placed in a 250 mL beaker containing 100 mL of CIP solution 10 ppm at pH 7. First, 60 min of the solution agitation were performed without light to determine the adsorption maximum time of CIP. Then, the mixture was irradiated by a 100 W LED (LED) for 150 min. The concentration of residual CIP was evaluated by UV-Vis Spectrophotometer at 277 nm after 30 minutes of sampling (Perkin Elmer, Lambda 25). The degradation performance in percentage (P) is estimated using the following Eq.1:

\[ P = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \]

Whereby C_{0} and C_{t} are initial and final (at a specific time) concentrations of CIP, respectively.

3.0 RESULTS AND DISCUSSION

3.1 V_{2}O_{5}/g-C_{3}N_{4} Characterization

V_{2}O_{5}/g-C_{3}N_{4} was prepared by simple straightforward calcination process. Figure 1(a) and 1(b) illustrate the initial brownish appearance of V_{2}O_{5} and the yellowish appearance of g-C_{3}N_{4} prior to the calcination process. Following calcination at 500°C for 3 hours, the resulting product took on a slightly brownish-white material, as depicted in Figure 1(c), commonly referred to as 500VC. Following that, characterization analyses were performed. To determine a material's band gap, absorbance spectra were studied with Tauc plots for all samples of V_{2}O_{5}/g-C_{3}N_{4} with different calcination temperatures. As can be seen in Figure 2, the bandgap value of V_{2}O_{5} and g-C_{3}N_{4} alone were found to be 1.95 eV, and 2.71 eV which is consistent with the existing literature [14], [15]. The effects of V_{2}O_{5}/g-C_{3}N_{4} samples at different calcination temperatures of 450, 500 and 550 °C or known as 450VC, 500VC, and 550VC to band gap value are 2.78 eV, 2.64 eV and 2.0 eV respectively. This phenomenon showed that increasing of calcination temperature led to decreasing in band gap value. The calcination process can enhance the crystallinity of the photocatalyst. As the crystallinity improves, the energy levels of the valence and conduction bands become better defined, leading to a more accurate determination of the band gap [16]. Consequently, this refinement can lead to a decrease in the band gap value. After band gap values of all samples have been confirmed in visible light wavelength, the best V_{2}O_{5}/g-C_{3}N_{4} sample which was investigated through CIP degradation performance was taken for next analyses like SEM, XRD and BET together with pure V_{2}O_{5} and g-C_{3}N_{4}. Based on CIP degradation performance, the best calcination temperature of V_{2}O_{5}/g-C_{3}N_{4} sample is 500 °C.

The SEM images in Figure 3(a)-(c) observed different of morphologies displayed. In Figure 3(a)-(b) showed the morphology of g-C_{3}N_{4} and V_{2}O_{5}, respectively while Figure 3(c) showed 500VC images respectively. It can be seen that appearance of g-C_{3}N_{4} and V_{2}O_{5} in 500VC sample. According to the image of V_{2}O_{5}, it can be seen that irregular flake-shaped like structures [17] and meanwhile g-C_{3}N_{4} showed as interconnected particles in bulk [13]. These two images of g-C_{3}N_{4} and V_{2}O_{5} showed in Figure 3(c) of 500VC sample shows the successful intercalation of these two materials by calcination process [18], [19]. In addition to morphological analyses of SEM, X-ray Diffraction can prove the successful formation of 500VC. In Figure 4(a), the XRD analysis reveals the presence of g-C_{3}N_{4} characterized by two distinct peaks at 27.6°, indicative of (100) in-plane structural units, as illustrated in Figure 4(b) for g-C_{3}N_{4} alone [20]. To confirm the presence of V_{2}O_{5} in Figure 4(a), three
diffraction peaks at 20.3°, 26.1°, and 31.0° are identified, corresponding to the (001), (110), and (301) crystal planes of V$_2$O$_5$. These peaks align with the patterns observed in pure V$_2$O$_5$, as depicted in Figure 4(c) [21]. Notably, in Figure 4(a), the intensity of V$_2$O$_5$ peaks is relatively low, consistent with the quantities of V$_2$O$_5$ precursors compared to g-C$_3$N$_4$ during the sample synthesis. A similar pattern is observed when employing the same ratio of sample combination in XRD analysis, as reported in the literature [12]. As summarized in Table 1, the BET surface areas for V$_2$O$_5$, g-C$_3$N$_4$, 450VC, 500VC, and 550VC were measured at 4.77, 7.70, 16.34, 181.00, and 4.41 m$^2$/g, respectively. Notably, the combined material at 500 °C exhibited a surface area that was 25 times greater than that of g-C$_3$N$_4$ and V$_2$O$_5$ individually. This substantial surface area of 500VC played a pivotal role in the exceptional adsorption of CIP, attributed to the photocatalyst’s surface properties and its efficient utilization of incident light during the photocatalytic degradation of CIP. As can be seen in Table 1, more increasing calcination temperature at 550 °C, the surface areas, pore volumes, and pore diameters decrease due to the crystallization of the g-C$_3$N$_4$ and V$_2$O$_5$ combination and part of pores have been blocked and led to decrease of surface area and porosity [20], [21]. Confirmation from XRD, BET and SEM analyses proved the successful incorporation between g-C$_3$N$_4$ and V$_2$O$_5$.

Table 1 BET surface area and pore structure of samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C$_3$N$_4$</td>
<td>7.70</td>
<td>0.059</td>
<td>30.76</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>4.77</td>
<td>0.024</td>
<td>20.21</td>
</tr>
<tr>
<td>450VC</td>
<td>16.34</td>
<td>0.097</td>
<td>23.81</td>
</tr>
<tr>
<td>500VC</td>
<td>181.00</td>
<td>0.824</td>
<td>18.21</td>
</tr>
<tr>
<td>550VC</td>
<td>4.41</td>
<td>0.011</td>
<td>9.85</td>
</tr>
</tbody>
</table>

3.2 Effect of Calcination Temperature On The CIP Photocatalytic Activity by V$_2$O$_5$ / g-C$_3$N$_4$.

The photocatalytic activity of the photocatalysts was evaluated for the photodegradation of CIP under simulated sunlight. Without the presence of a catalyst, CIP did not degrade through photolysis under the simulated sunlight.
conditions. To ensure adsorption equilibrium, the prepared samples were immersed in the CIP solution for 60 minutes in the absence of light. Figure 5(a) shows that all samples reached adsorption-desorption equilibrium within 45 to 60 minutes. Photoactivity of V2O5 / g-C3N4 was assessed by performing photodegradation of CIP under visible light for all the samples synthesized at 450, 500 and 550 °C or known as 450VC, 500VC and 550VC.

Interestingly, the calcination temperature affected photodegradation activity of V2O5 / g-C3N4 noticeably towards CIP solution as displayed in Figure 5(a). The photodegradation efficiencies of V2O5 / g-C3N4 prepared at 450, 500 and 550 °C were about 43.1%, 90.17% and 71.7% for CIP solution, respectively. The V2O5 / g-C3N4 sample calcined at 500 °C displayed highest CIP photodegradation ability. It was analyzed that increasing calcination temperature from 450 °C to 500 °C led to increasing photodegradation efficiency and following that photocatalytic activity was found to follow a decreasing trend from 500 °C to 550 °C. The increased reaction rate of V2O5 / g-C3N4 calcined at 400 °C to 500 °C could be due to its higher heating temperature led to higher efficiency of absorbing visible light which can lead to better generation of photo-generated electrons causing more efficient separation of charge and hence better photoactivity [20]. Meanwhile, prolonged calcination at very high temperatures may lead to sintering, reduced surface area and decreased photodegradation efficiency like V2O5 / g-C3N4 at 550 °C [16]. When pollutants are present in a less concentrated form, we can assume a pseudo-first-order kinetics model as follows in Eq. (2):

\[ \ln \left( \frac{C_0}{C_t} \right) = k_{app}t \]

where \( k_{app} \) is the apparent rate constant (min\(^{-1}\)), and \( C_0 \) is the initial concentration of pollutants (mg L\(^{-1}\)) and \( C_t \) is the concentration of pollutants at time (mg L\(^{-1}\)). In the process of CIP photodegradation using the photocatalyst that was prepared, the kinetic parameter is assumed to be determined through a pseudo-first-order kinetic model. In this model, the rate constant \( k_{app} \) is determined as the slope of the fitted line depicted in Figure 5(b). The slope of the linear fitted graph shows the calculated \( k_{app} \) values of 0.0026, 0.0032, 0.0052, 0.0082 min\(^{-1}\) for V2O5, g-C3N4, 450VC, 500VC and 550VC respectively. Therefore, the outcome infers that the 500VC nanocomposite has had high reaction rate with 3.28 folds, compared with pure V2O5 and g-C3N4.

3.3 Radical Scavenger Studies

To elucidate the role of various reactive species (e\(^{-}\), h\(^{+}\), superoxide radicals (•O\(_2\)^-) and HO•) in the photodegradation of CIP, multiple quenching experiments were conducted under optimal conditions. In these experiments Silver nitrate (AgNO\(_3\)) and Ethylenediaminetetraacetic acid (EDTA) were used at a concentration of 1 mmol to scavenge e\(^{-}\) and h\(^{+}\), while Benzoquinone (BZQ) and butanol, also at the same concentrations, were employed to quench •O\(_2\)^- and HO• [12], [22]. The impact of each quenching agent on CIP photodegradation is illustrated in Figure 6. As anticipated, the results demonstrate varying degrees of reduction in CIP elimination efficiency in all cases, indicating the involvement of all the aforementioned reactive species in the photodecomposition process. The largest decrease in CIP photodegradation, amounting to 73.64 %, was observed in the presence of butanol, while the smallest decrease of 28.56 % was observed with BZQ. AgNO\(_3\) and EDTA, the scavenger agents, reduced CIP photodecomposition by 45.77 % and 34.54 %, respectively. Consequently, •O\(_2\)^- species were found to contribute the most to CIP photodegradation, followed by positively charged holes (h\(^{+}\))
in the second position. Negatively charged electrons (e⁻) and HO• ranked third and fourth, respectively.

Figure 6. Photocatalytic degradation of CIP in the presence of different scavengers

4.0 CONCLUSION

In conclusion, the synthesis of V₂O₅ / g-C₃N₄ photocatalyst has been investigated with respect to the calcination temperature, aiming to enhance the photocatalytic degradation of ciprofloxacin antibiotics. Through systematic experimentation and analysis, it has been found that the highest performance in degrading ciprofloxacin, achieving approximately 90.17 % degradation, was achieved using a calcination temperature of 500 °C. The successful incorporation of V₂O₅ and g-C₃N₄, confirmed through XRD, SEM, and BET analyses, along with the band gap alteration, where surface area dominantly contributes to the highest photocatalytic degradation of ciprofloxacin. These findings not only advance our knowledge in the field of photocatalysis but also provide a solid foundation for future research in the development of efficient and sustainable photocatalytic systems for water treatment and environmental remediation.

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Conflict of Interest

There are no conflicts present, as stated by the authors.

References


