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Highly effective degradation of imidacloprid by H₂O₂/ fullerene decorated P-doped g-C₃N₄ photocatalyst

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Abstract

In this work, P-doped g-C₃N₄ (PCN) was coupled with another conducting material, fullerene (C₆₀). P doping led to an expansion in solar-light-responsive range, prolongation in charge carrier lifetime, facilitation in charge separation, and transportation, while on the other hand, C₆₀ captured electrons from PCN and reduced the recombination of charge carrier. C₆₀/PCN nanocomposites (with different C₆₀ ratios) were successfully synthesized *via* a simple ultrasonic method for imidacloprid (IMI) pesticide degradation. Raman and N₂-adsorption-desorption measurement techniques were implemented to scrutinize structural properties and the successful formation of the nanocomposite. The photocatalytic degradation of IMI signified a loading of 0.04 wt.% amount of C₆₀ as its optimal concentration. Through Brunauer–Emmett–Teller (BET) isotherm, two times larger specific surface area was observed in 0.04 wt.% C₆₀/PCN than PCN. 60 mg/mL and 1 × 10⁻⁴ M were witnessed as an optimal catalyst dose and pesticide concentration at pH 4. Addition of H₂O₂ enhanced photodegradation processes since it also served as a good electron acceptor, which boosted charge carrier separation. Photodegradation results confirmed that 0.04 wt.% C₆₀/PCN/H₂O₂ and 0.04 wt.% C₆₀/PCN nanocomposites exhibited 95 % and 91 % removal efficiency, respectively, which were higher than the percentages exhibited by other tested photocatalysts. A promising mechanism of C₆₀/PCN nanocomposite against IMI degradation was also proposed, validating the role of h⁺, .O₂⁻ and .OH radicals in the photocatalytic process.

Graphical abstract

C₆₀ decorated P-doped g-C₃N₄ exhibited highly effective degradation of imidacloprid using H₂O₂ assisted hydroxyl radical oxidation.

Keywords: P-doped Fullerene; Metal-free photocatalyst; H₂O₂; Imidacloprid; Degradation

1. Introduction

In recent decades, rapid depletion in traditional fossil fuels and water pollution are the major threats hampering the sustainability of living organisms [1]. Agriculture, as an industrial activity, has a significant effect on marine ecological units, because of 70 % (approx.) freshwater use for farming [2,3]. Imidacloprid pesticide (IMI) is creating a danger to all living organisms as a result of its widespread usage, high persistency in surface water, and relatively high solubility (0.58 g/L) [4]. Various wastewater treatment methods have been employed for the removal of pesticides from contaminated water bodies [5].

In this perspective, semiconductor photocatalysis is considered as a sustainable and green approach for environmental remediation [[6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21]]. As a potential photocatalyst, polymeric carbon nitride (g-C₃N₄) has extensively been used for photocatalytic degradation [[22], [23], [24], [25]]. Offering many advantages, such as resource availability, the appropriate bandgap energy (2.7 eV) makes it a noticeable visible-light responsive photocatalyst [[26], [27], [28]]. Furthermore, the facile synthesis approach, non-toxic, and physicochemical firmness are other alluring features of g-C₃N₄ [29]. However, the photodegradation performance of g-C₃N₄ is unsatisfactory as a consequence of limitations, including rapid charge carrier recombination, narrow solar spectrum absorption, and minimal specific surface area [29]. Thus, dopant incorporation and heterojunction formation with suitable semiconductors/support materials are preferable modification strategies to overcome the low photodegradation ability of g-C₃N₄ [30].

Considerably, non-metal doping is a beneficial method to increase solar light absorption in the visible range, tweaking of the g-C₃N₄ bandgap with fastened charge carrier separation [31,32]. Texture and electronic properties of g-C₃N₄ can be modified *via* a non-metal (P, S, C, I, or B) doping, which can be either interstitial or substitutional doping [33,34]. The introduction of an optimal percentage of phosphorus dopant in g-C₃N₄ lattice provides altered electronic properties, reduced bandgap energy, and improved charge carrier separation. In a study, the synthesized phosphorus; P-doped g-C₃N₄ nanosheets *via* 2-aminomethyl phosphonic acid and melamine precursors revealed absorption up to 557 nm in the visible light-receptive region [35]. It was vouchsafed that, most possibly, bay or corner carbon atoms in the g-C₃N₄ framework are substituted by phosphorus heteroatoms and form P—N bonding [36]. In another study, Zhang et al. fabricated P-doped g-C₃N₄ using [Bmim]PF₆ (ionic liquid) and dicyandiamide precursors and obtained high charge carrier separation efficiency [37]. Hexachlorotriphosphazene (HCCP), a phosphorous precursor, was used by Deng and coworkers for phosphorous doping in g-C₃N₄. They reported that P doping increased the mesoporous nature of g-C₃N₄, reduced charge transfer distance from bulk to the interface, and accelerated solar light absorption due to constricting in the sub-bandgap of g-C₃N₄ [38].

Among various carbon materials, fullerene (C₆₀) has attracted much interest due to its unique structure, electron acceptable nature, and far-reaching absorbance in a visible light region, which enhances its photo-reactivity [39]. The distinctive structure of C₆₀ delocalizes intramolecular electrons, which have a high affinity (2.65 eV) and electron-withdrawing proficiency [40]. Its outstanding electron captivating nature causes fast separation of photoinduced charge carrier and relatively slothful charge recombination. The coupling of g-C₃N₄ with C₆₀ enhances photoexcited charge carrier separation because C₆₀ serves as a visible light harvester, which improves photon absorption ability of photocatalyst due to its superior conductivity and e⁻ captivating nature [41]. H₂O₂ has been widely used in many research areas as a green and moderately oxidizing agent due to its special applications [42].

H₂O₂ causes the donation and captivation of electrons, which results in the decomposition of H₂O₂ into O₂ and reactive superoxide radical (O₂⁻). However, H₂O₂ decomposes slowly at ambient temperature, which cannot be overlooked; nevertheless, the oxidizing ability of H₂O₂ can be enhanced in the presence of UV light, ultrasound/heat, and other catalysts in order to generate reactive oxygen species to oxidize organic compounds [43].

In this study, we have coupled C₆₀ with phosphorous doped g-C₃N₄ (PCN) through different mass/wt % ratios *via* the sonochemical method. Phosphorous doping was preferred over other non-metal doping because it improved g-C₃N₄ textual properties [44]. Assessment of the potential of the photocatalyst was scrutinized for degrading IMI pesticide in the presence of H₂O₂. H₂O₂-assisted photodegradation results indicated that the synthesized C₆₀/PCN nanocomposites exhibited higher IMI degradation as H₂O₂ caused the production of more •OH radicals by the attraction of photogenerated electrons and augmented photoexcited charge carrier separation. Several characterization techniques were employed for the validation of the synthesized photocatalysts. Eventually, the photodegradation mechanism of the synthesized nanocomposites with and without H₂O₂ has been elaborated in detail.

2. Experimental

2.1. Preparation of C₆₀/phosphorus-doped g-C₃N₄ (C₆₀/PCN) photocatalysts

Graphitic carbon nitride (GCN) and P-doped GCN (PCN) were synthesized *via* a thermal polycondensation route by combining melamine with C₂H₈N₂O through H-bonding to form supramolecules [37,45]. Firstly, melamine powder (3 g) was triturated through mortar and pestle and dissolved in 100 mL deionized water. Afterward, AO (4 g) was mixed in solution, stirred and boiled at 100 °C to attain a clear solution. BmimPF₆ (0.1 g) was then dissolved in the above solution, followed by magnetic stirring for 30 min. The acquired reaction mixture was heated at 100 °C to evaporate entirely. The resultant solid product was grounded in mortar and pestle to acquire a powder form. The obtained product was then placed into a ceramic crucible, covered with a lid and heated at various temperatures in a muffle furnace with a ramping speed of 20 °C/min up to 560 °C for 4 h. The resultant light brown material was cooled at room temperature. The obtained material was crushed into a fine powder and labeled as PCN. A similar method was adopted for the fabrication of the light-yellow g-C₃N₄ (GCN), except for the addition of BmimPF₆.

C₆₀/phosphorous doped g-C₃N₄ (C₆₀/PCN) was prepared using the facile sonochemical method. In a typical synthesis, C₆₀ (0.02 g) and PCN (1 g) were dissolved in 60 mL and 100 mL ethanol, respectively. Afterward, the formed two solutions were ultrasonicated separately for 30 h. After that, both dispersed units were mixed with continual magnetic agitating for 30 min, followed by 30 min of ultrasonication. The obtained reaction mixture was separated by centrifugation and washed with deionized water and ethanol. The solid yield was dried in a hot air oven at 80 °C and crushed into fine powder form to obtain C₆₀/PCN, which was then labeled as C₆₀/PCN nanohybrid. C₆₀/PCN was prepared in different mass ratios of 0.02 wt.% C₆₀/PCN, 0.04 wt.% C₆₀/PCN, and 0.06 wt.% C₆₀/PCN nanocomposite [46] (Scheme 1).

2.2. Photodegradation experiment analysis

Photodegradation tests were executed to analyze the removal efficacy of catalysts against IMI in reaction solution underneath visible light illumination. Before the photocatalytic experiment, a suspension of IMI solutions and catalyst was agitated under for a 30-min time interval to establish adsorption-desorption equilibrium. Afterward, the conquered mixture (suspension) was quickly irradiated by a LED lamp (35 W), situated on top of the photoreactor, approx. 25 cm away from suspension. All the photocatalytic tests were accomplished throughout constant stirring (100 rpm). For analysis, 1 mL of suspension was withdrawn and filtered

through a 0.22 μm filter paper for succeeding experiments. The filtered aliquot (2 mL) was inspected at 270 nm spectrophotometrically. Chemical oxygen demand (COD) was estimated *via* a closed reflux procedure. The dissolved carbon dioxide (CO_2) was determined by titration of the sample by NaOH solution exploiting the phenolphthalein indicator [47]. Eq. (1) was used for the determination of removal efficiency: $(1)\% \text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100$. Here, C_0 indicates the initial concentration of sample/COD, and C_t signifies sample/COD concentration at time t . Each photocatalytic experiments were performed in triplicates, ensuring errors of below 5 %, and average readings were recorded. After photodegradation experiments, photocatalyst was centrifuged from the reaction solution and be utilized in recyclability tests. For successive experiments, the recycled catalyst was washed with distilled water and dried out at 60 $^\circ\text{C}$.

2.3. Characterization techniques

Structural information and specific chemical states were explored *via* FTIR analysis studied on Spectrum RX-I spectrometer (Perkin-Elmer) (with KBr disc and X-ray powder diffraction (XRD) patterns study on Panalytical's X'Pert Pro diffractometer with $\text{CuK}\alpha$ -1 (45 kV/100 mA). Optical properties, charge carrier separation, and transportation of nanocomposites were detected at room temperature by UV-Vis diffuse reflectance spectra (DRS/diffuse reflectance spectrometer), photoluminescence (PL) (FLS-920-Edinburgh Instrument) and EIS analysis. A PHI Versa Probe II with AES using 24.63 W Al $\text{K}\alpha$ radiations was exploited for exploring the chemical and elemental composition of 0.04 wt.% C_{60} /PCN nanocomposite through X-ray photoelectron spectroscopy (XPS), and a Coulter SA3100 instrument was utilized for exploring BET surface area *via* Nitrogen adsorption-desorption isotherms. High-performance liquid chromatography analysis was performed by HPLC-Waters with a flow rate of 0.6 mL/min.

3. Result and discussion

3.1. Structural analysis

Powder X-ray diffraction (PXRD) was used to determine the crystal structure of C_{60} /PCN nanocomposites (Fig. 1). GCN exhibited two characteristic peaks at about 13.25° and 27.43° , which were accredited to (100) and (002) planes, respectively. The weak diffraction peak observed at 13.25° (100) was credited to heptazine units, and a sharp peak appeared at 27.43° (002) was assigned to aromatic systems in GCN (JCPDS 87-1526) [48]. In the same way, in PCN, the attained peak at 13.05° was recognized to (100) plane, having a considerable diminution in peak strength compared to GCN (P-doping caused a decrease in crystallinity) [32]. A sharp peak situated at 27.25° was designated to (002) plane, and barely changes were witnessed. Nevertheless, an adverse shift in the peak was detected in (002) plane of PCN from 27.43° to 27.25° owing to a greater dopant radius (*i.e.*, P atom having a 100 pm radius) than substituted C atom having 70 pm radius [49]. For pure C_{60} , diffraction peaks were observed at $2\theta = 10.74^\circ, 17.65^\circ, 20.75^\circ, 21.67^\circ, 27.39^\circ, 28.07^\circ, 30.86^\circ,$ and 32.78° which were indexed to (111), (220), (311), (222), (331), (024), (422) and (333) planes of cubic phase of C_{60} , respectively (JCPDS No. 82-0505) [50]. In the case of C_{60} /PCN, the location and shape of diffraction peaks scarcely changed in comparison to bare GCN and PCN, which signified no effect on the crystal structure of GCN on the addition of C_{60} . Minor diffraction peaks related to C_{60} were observed in C_{60} /PCN nanocomposite owing to low quantity as well as high dispersal of C_{60} in PCN [46].

3.2. Morphological and chemical analysis

Field emission scanning electron microscopy (FESEM) and SEM (Scanning electron microscopy) were performed to analyze the morphology of bare GCN, PCN, Fullerene (C₆₀), and C₆₀/PCN photocatalysts (Fig. 2(a–f)). Modification in the structure of melamine was done by using ammonium oxalate, which led to the formation of MAO supramolecules and increased porosity as well as specific surface area [45]. FESEM micrographs of bare GCN revealed porous and uneven morphology with stacked aggregated nanosheet-like assemblies (Fig. 2a) [32]. FESEM images of PCN exhibited stacked, wrinkled, and slackened nanosheets with more aggregation, porosity, and lumpiness in surface/edges than GCN (Fig. 2b). Fig. 2c displayed SEM images of different shaped C₆₀ nanoparticles with restricted agglomeration forming block particles that facilitated the reunion of C₆₀ nanoparticles [51]. In Fig. 2 (d–f), SEM images of C₆₀/PCN nanohybrids were shown, which revealed irregular anchoring of C₆₀ nanoparticles over PCN nanosheets. As the amount of C₆₀ was increased from 0.02 wt.% to 0.04 wt.%, the surface of PCN became more aggregated, and for 0.06 wt.% C₆₀ was entirely dispersed on PCN nanosheets.

TEM and HRTEM descriptions of GCN, PCN, C₆₀, C₆₀/PCN were shown in Fig. 3. Figure S1 displayed the TEM microstructure of GCN and C₆₀ nanoparticles. Images of GCN publicized thin porous nanosheets, and those of C₆₀ exhibited differently sized (spherical to rectangular) shaped nanoparticles. TEM and HRTEM results of PCN disclosed thin sheets with porous nanostructure, as demonstrated in Fig. 3(a–b). TEM and HRTEM micrographs of C₆₀/PCN photocatalysts unveiled the decoration of C₆₀ nanoparticles on PCN surface and authorized nanocomposites formation (Fig. 3(c–h)) [46]. With the increase in the C₆₀ ratio (0.02 wt. %-0.06 wt. %), more C₆₀ nanoparticles were certainly seen on PCN nanosheets (Fig. 3(g–h)). EDAX results also confirmed the presence of phosphorous, carbon, and nitrogen elements in C₆₀/PCN (supplementary data, Figure S2).

Elemental composition and chemical structure of synthesized photocatalysts were investigated by X-ray photoelectron spectroscopy (XPS) (Fig. 4). X-ray photoelectron spectroscopy (XPS) authorizes the occurrence of existed elements. In Fig. 4a, the XPS spectrum of C 1s (Carbon) signposted three peaks at binding energies of 284.48 eV, 287.91 eV, and 290.38 eV. The peaks originated at binding energies of 284.48 eV, 287.91 eV, and 290.38 eV were ascribed to C–C, N–C=N, and C=O bonds, respectively [52]. N 1s XPS spectrum is presented in Fig. 4b. The two sharp peaks at 398.39 eV and 400.15 eV were accredited to sp² N confined in triazine rings (Nitrogen bonded to a carbon atom (C=N–C)) and N–(C)₃, respectively [53]. P 2p XPS analysis was displayed in Fig. 4c, exhibiting two sharp peaks at binding energies of 133.55 eV and 135.48 eV. The peaks that appeared at 133.55 eV was due to the formation of P–N bonds in the GCN framework. It confirmed the substitution of a carbon atom by a phosphorous atom in triazine rings to create P–N bonds [46]. Peak instigated at 135.48 eV binding energies was allotted to the P–O bond, confirming successful doping in GCN structure. XPS spectra of the whole sample (0.04 wt.% C₆₀/PCN) were shown in Fig. 4d. Additionally, FTIR and RAMAN results were discussed in Supplementary data (Figs. S3 and S6).

3.3. UV–vis DRS and electronic bandstructure

UV-Vis diffuse reflectance spectroscopy was used to examine the light-harvesting property of C₆₀/PCN (Fig. 5a). An increase in absorption intensity, as well as redshift, was observed in the absorption edge of PCN and C₆₀/PCN photocatalysts than GCN due to some transitions, *i.e.*, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. It notes that $n \rightarrow \pi^*$ occurred due to N 2p lone pair orbital of GCN and reallocation of electron density as a result of heptazine ring distortion [54].

In Fig. 5a, a noticeable red shift was observed towards the visible-light region in the absorption band for PCN. The phosphorous doping altered the optical property of GCN and reduced its bandgap, which preferred generation of more charge carriers and enhanced photodegradation activity [55]. Phosphorous doping in GCN was also validated by a change in color from light-yellow (GCN) to brown (PCN) (Fig. 5a). Addition of C₆₀ altered the optical capability of PCN, which increases degradation ability [56]. However, a suitable addition of C₆₀ enhanced the surface charge and absorption edge of PCN and, thus, it is necessary to add an appropriate amount of C₆₀. An excessive amount of C₆₀ nanoparticles may certainly inflict a negative effect on the photodegradation activity of PCN owing to its light absorption capacity and induces a considerable restriction on optical absorption of PCN (Fig. 5a).

The bandgap of GCN and PCN photocatalysts was calculated by the Tauc plots method and was observed to be 2.7 and 2.52 eV, respectively. Due to P doping, the bandgap of GCN decreased from 2.7 eV to 2.52 eV in PCN. Bandgap values were estimated *via* recording a graph among $(\alpha h\nu)^n$ vs. $h\nu$ (eV) as displayed in Fig. 5b [57]. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ revealed a straight portion for GCN and PCN photocatalysts which, extrapolated to $\alpha = 0$. The equations applied to calculate bandgap energy follows the Eq. (2) written as:

Here, n has 1/2 and 2 values for permitted direct and indirect electronic transitions and 3/2 and 3 for prohibited direct and indirect ones [29]. Symbol α indicates the absorption coefficient, A denotes constant value, $h\nu$ characterizes photon energy, and E_g designates bandgap energy.

3.4. Photoluminescence (PL) and Electrochemical impedance spectroscopy (EIS) analysis

Photoinduced charge carrier separation and transmission were explored by photoluminescence (PL) emission and EIS analysis, which have been conferred in supplementary data, and results were depicted in Figure S4 and Figure S5.

3.5. Photodegradation of IMI pesticide *via* as-prepared GCN, PCN and C₆₀/PCN photocatalysts

The photodegradation activity of the synthesized samples for IMI degradation was shown in Fig. 6. The photocatalytic removal efficacy of GCN, PCN and C₆₀/PCN (0.02 wt.%, 0.04 wt.% and 0.06 wt.%) photocatalysts for IMI degradation was detected to be 60 %, 72 %, 78 %, 91 %, and 85 %, respectively, after 9 h visible-light irradiation. Consequently, the observed photo-efficiency rate was highest for 0.04 wt.% C₆₀/PCN. The synthesized nanocomposites and PCN unveiled superior photodegradation ability than GCN (Fig. 6a). Kinetics was measured *via* the Langmuir Hinshelwood model for IMI degradation and Eqs. (3) and (4) were used to calculate IMI photodegradation [34]:

In the above relations, C and C_0 were denoted to IMI concentrations at irradiating time t and at $t = 0$, respectively, and k represents rate constant. The $\ln(C_0/C_t)$ vs. time graphs were shown in Fig. 6b [58]. The k values for GCN, PCN and C₆₀/PCN (0.02 wt.%, 0.04 wt.% and 0.06 wt.%) were calculated as 0.0030 ± 0.0174 , 0.0036 ± 0.0197 , 0.0042 ± 0.0153 , 0.0050 ± 0.0126 and 0.0048 ± 0.0132 h⁻¹, respectively (Fig. 6b). As a result, it was worth saying that P doping lowered the bandgap of GCN, thus, upgraded visible light activity and enhanced the photodegradation efficiency [45]. Similarly, a coupling of C₆₀ with PCN reduced photoexcited charge carrier recombination as C₆₀ acted as a support material as well as a sink, which improved electron conduction and degradation efficiency of 0.04 wt.% C₆₀/PCN. The

upgrading in photodegradation efficiency of photocatalysts was due to effective electron-hole pair separation. This verdict was signposted by PL studies (Figure S4), and discussed in detail in the supplementary data.

Addition of H₂O₂ to reaction solution led to increasing in photodegradation efficiency of photocatalysts. Typically, 65 %, 76 %, 80 %, 95 %, and 87 % of photodegradation efficiency was observed for GCN/H₂O₂, PCN/H₂O₂ and C₆₀/PCN/H₂O₂ (0.02 wt.%, 0.04 wt.% and 0.06 wt.%), photocatalysts, respectively, after 6 h light exposure (Fig. 6c). Consequently, degradation efficacy of 0.04 wt.% C₆₀/PCN/H₂O₂ (95 %) and 0.04 wt.% C₆₀/PCN (91 %) nanocomposites were higher than other photocatalysts. Thus, the IMI degradation efficacy rate (with H₂O₂) followed the order as the kinetics data for IMI degradation is shown in Fig. 6d and reported in Table 1. Among the photocatalytic materials, 0.04 wt.% C₆₀/PCN/H₂O₂ nanocomposite still performed the highest catalytic efficiency in the presence of H₂O₂. A slight improvement had been observed in the presence of H₂O₂, which was attributed to a good electron acceptor of H₂O₂ for enhanced charge carrier separation. Moreover, under dark conditions, IMI was removed through the adsorption process. The adsorption-desorption equilibrium experiment was executed before photodegradation experiments after 30 min stirring in the dark (Fig. 7a). Under the dark condition, the role of H₂O₂ was almost negligible, and the presence of C₆₀ in composite improved the adsorption capacity. From adsorption studies, it was observed that as the amount of C₆₀ in nanocomposite was increased, more adsorption of pollutants occurred. This was due to more active sites provided by C₆₀ nanoparticles for adsorption. The presence of C₆₀ in photocatalyst resulted in an increased surface area of 0.04 wt.% C₆₀/PCN (4.7915 m² g⁻¹), leading to enhanced adsorption capacity (Figure S7 and Table 2).

Table 1. Rate constants of imidacloprid (IMI) photo-degradation underneath visible light illumination. Conditions: [IMI] = 1 × 10⁻⁴ mol/dm³; [H₂O₂] = 1.5 × 10⁻⁴ mol/dm³; [Nanocomposite] = 60 mg/100 mL; initial pH value = 4.0; t = 6 h; and intensity of light = 750 lx.

| Photocatalytic system | | Rate constant ± S.D.* (k ₁) h ⁻¹ | R ² ± S.D.* | % Removal efficiency ± S.D.* |
|-----------------------------------------------------------|-----|------------------------------------------------------------|------------------------|------------------------------|
| 0.06 C₆₀/PCN/H₂O₂ | wt% | 0.0056 ± 0.0158 | 0.97 ± 0.0188 | 87 ± 1.92 |
| 0.04 C₆₀/PCN/H₂O₂ | wt% | 0.0060 ± 0.0146 | 0.98 ± 0.0193 | 95 ± 2.10 |
| 0.02 C₆₀/PCN/H₂O₂ | wt% | 0.0053 ± 0.0173 | 0.97 ± 0.0186 | 80 ± 1.89 |
| PCN/H₂O₂ | | 0.0040 ± 0.0228 | 0.96 ± 0.0182 | 76 ± 1.65 |
| GCN/H₂O₂ | | 0.0036 ± 0.0196 | 0.95 ± 0.0180 | 65 ± 1.30 |

Table 2. BET surface areas, pore size and pore volumes of as-synthesized photocatalysts.

| Photocatalysts | BET surface area S _{BET} (m ² g ⁻¹) | Pore size distribution (nm) | Pore volume (cm ³ g ⁻¹) |
|----------------|------------------------------------------------------------------------|-----------------------------|------------------------------------------------|
|----------------|------------------------------------------------------------------------|-----------------------------|------------------------------------------------|

| Photocatalysts | BET surface area | S_{BET} ($\text{m}^2 \text{g}^{-1}$) | Pore size distribution (nm) | Pore volume ($\text{cm}^3 \text{g}^{-1}$) |
|-------------------------------------|------------------|-------------------------------------------------|-----------------------------|---------------------------------------------|
| PCN | | 2.8401 | 24.07095 nm | 0.017091 |
| 0.04 wt% C_{60}/PCN | | 4.7915 | 24.87041 | 0.02979 |

Typically, the pH of a solution, which might indicate the charge on the surface of photocatalyst, plays a substantial role in photodegradation reactions [59]. In this study, IMI degradation kinetics was studied in various pH ranges from 2 to 12 under optimized reaction conditions (Fig. 7b). Higher photodegradation efficiency (91 %) was recorded at pH 4 in 6 h. The decrease in photodegradation efficacy from 78 % to 37 % was observed with pH variation from 6 to 12. At lower pH values, C_{60}/PCN nanocomposite was positively charged since the pH of zero-point charge (pH_{zpc}) was 6, as confirmed by zeta potential analysis (Figure S8). Above pH_{zpc} , the surface of the C_{60}/PCN nanocomposite was negatively charged. With a $\text{p}K_{\text{a}}$ value of 9, IMI did not release H^+ ions into a reaction solution. In acidic medium, IMI is likely to be adsorbed on positively (+) charged surface of PCN due to the existence of electron-rich aromatic rings in the IMI molecule. Under basic conditions, a negatively charged surface was not suitable for the adsorption of IMI. On the other hand, reactions in acidic medium are more capable of organic pollutant degradation as at lower pH values O.H radicals recombination is fixed [60,61]. Therefore, IMI degradation is highest at moderate acidic media (*i.e.*, pH 4).

Experiments were also accomplished for the assessment of optimal concentration H_2O_2 and catalysts dosage. Catalyst dosage effect on the reaction of photocatalysis was explored by varying 0.04 wt.% C_{60}/PCN amount between 10 mg/100 mL and 100 mg/100 mL. There was an increase in degradation efficacy from 65 % to 95 % on increasing catalyst amount from 20 mg/100 mL-60 mg/100 mL (Fig. 7c). After that, a decline in removal efficacy was observed from 95 % to 82 % with a further addition of a catalyst. As the catalyst amount is raised, the numbers of active sites also enhanced, but above 60 mg/mL optimal concentration, excessive light scattering, turbidity, and agglomeration occurred. This caused a reduction in photoactive volume and diminished removal efficiency. Results shown in Fig. 7d vouchsafed that 1.5×10^{-4} M was H_2O_2 ideal concentration at which loftier photo-removal efficacy was attained at pH 4 and 60 mg/mL catalyst dose of 0.04 wt.% C_{60}/PCN . As findings in the previous section over several types of photocatalysts (GCN, PCN, and C_{60}/PCN /(0.02 wt.%, 0.04 wt.% and 0.06 wt.%)), only a slight improvement had been observed in the presence of H_2O_2 . It notes that there is no monotonic relationship between the removal efficiency and the H_2O_2 concentrations.

To check the extent of mineralization, CO_2 and COD estimations of degraded IMI were also executed during the photodegradation process, and 80 % of COD removal was perceived in 6 h for 0.04 wt. % C_{60}/PCN / photocatalyst, under visible light irradiation (Fig. 7e and f). The COD removal test was strongly confirmed by the CO_2 assessment test. The CO_2 removal during the process of photodegradation indicated the transformation of IMI into degraded products, *i.e.*, CO_2 and H_2O [59]. Mineralization ability of 0.04 wt.% C_{60}/PCN nanohybrid was more remarkable than other used photocatalysts. The escalation in the removal efficacy of 0.04 wt.% C_{60}/PCN nanohybrid was assigned to the enhanced separation of photo-created charge carrier with raised absorption of visible light than other developed photocatalysts. HPLC analysis was used to find out the formed intermediates products during oxidative

degradation (Fig. 8c) [62]. The steady diminishment of peak intensity, with the manifestation of new peaks in retention times between 25–28 min, was observed, which lastly disappeared after 40 min. Formed byproduct (intermediates) was analyzed by GC–MS analysis, and information regarding byproducts analysis during the degradation process was given in Table 3. Similarly, the proposed degradation pathway mechanism has been explored in Fig. S9.

Table 3. Imidacloprid degradation products determined by GC–MS analysis (intermediates products (TPs), retention time, m/z corresponding [M+H] ions).

| Intermediate Products | Retention time (min) | GC-PCI |
|------------------------------------------------------------------------------------|----------------------|-----------|
| (a) Compound 1: 2-pyrrolidinone | 4.7 | 86 (100) |
| (b) Compound 2: 6-chloronicotinic aldehyde | 5.4 | 142 (100) |
| (c) Compound 6: 6-chloronicotinic acid | 6.8 | 158 (100) |
| (d) Compound 3: 6-chloronicotinamide | 8.3 | 140 (100) |
| (e) Compound 4: (1-(6-chloro-3-pyridylmethyl)imidazolidin-2-one) | 14.6 | 212 (100) |
| (f) Compound 5 (C ₉ H _x CIN _y O _z) | 15.9 | 226 (100) |

3.5.1. Scavenging experiment

In order to find out dominant reactive species during IMI photocatalytic degradation, different scavengers have been used as previously reported in the literature (Fig. 8a and b). In Fig. 8a, we can see that in PCN, Na₂-EDTA, and BZQ led to a significant reduction in IMI degradation rate, whereas IPA possessed a feeble restraining effect on photodegradation rate [63]. The outcomes corroborated that h⁺ and •O₂ – radicals have a substantial role in photodegradation processes than •OH radicals. Results of the scavenging experiment of 0.04 wt.% C₆₀/PCN/H₂O₂ photocatalysts were displayed in Fig. 8b. From the graph, it was perceived that Na₂-EDTA and BZQ scavengers had no influence upon the photodegradation process. Such results confirm negligible role of holes and •O₂⁻ radicals in photodegradation process [64]. However, the addition of IPA decreased photodegradation efficacy of 0.04 wt.% C₆₀/PCN/H₂O₂ system to 16 %, while BZQ and Na₂-EDTA scavengers presented 90 % and 93 % IMI removal, respectively which confirmed the substantial role of •OH radicals in degradation. Subsequently, generated h⁺ and O₂⁻ radicals were the foremost oxidative species in PCN whereas O₂⁻ radical was in 0.04 wt.% C₆₀/PCN/H₂O₂ system.

3.5.2. Proposed mechanism of C₆₀/PCN for degradation of IMI

The potentials of conduction band (CB) and valence band (VB) of PCN were computed *via* the relations given below [32]:(5)EVB=χ-Ee+0.5Eg(6)ECB=EVB-

Here, χ symbolizes electronegativity, E_g means bandgap of photocatalysts, and E° indicates free electron energy. From Eqs. (5)–(6), bandgap and χ value of PCN were calculated as 2.62 eV and 4.71, respectively [45]. The VB edge position of GCN and PCN was calculated to be 2.20 V and 1.62 V, while CB potentials were -0.50 V and -0.90 V, respectively [65]. PCN having an apt bandgap (2.52 eV), quickly absorbs light in the extended solar region and generates photoexcited electron-hole pair. Under visible light illumination, electrons (e^-) present in VB of PCN were excited to CB of PCN, creating holes (h^+) in the VB. Generally, the produced charge carriers quickly recombine and slight number of electrons participated in the photodegradation processes. However, when PCN was coupled with C_{60} to form nanocomposites, photogenerated e^- on the CB of PCN transferred to C_{60} nanoparticles due to their outstanding electronic conductivity which enhanced charge-carriers separation. The transferred electrons get accumulated on C_{60} nanoparticles and reacted with adsorbed O_2 on PCN surface to form superoxide radical ($\cdot O_2^-$) which further participated in the degradation process. However, VB potential was not appropriate for $\cdot OH$ species generation; hence, h^+_{VB} and produced $\cdot O_2^-$ radicals in CB transformed IMI into CO_2 and H_2O (Fig. 9a) [66]. Ultimately, h^+ and $\cdot O_2^-$ radicals were primarily responsible for IMI degradation. Based on this discussion, the degradation mechanism of C_{60}/PCN nanohybrid against IMI degradation was illustrated *via* mechanistic description using Eqs. (7)–(11) [45].

The effect of H_2O_2 on the IMI photodegradation process was depicted in Fig. 9b. Under visible light, H_2O_2 reacted with CB electrons (e^-) accumulated on C_{60} surface and VB holes (h^+) of PCN to generate active $\cdot OH$ (Eq. (12)) and $\cdot O_2^-$ species (Eq. (13)), respectively [66]. The produced $\cdot O_2^-$ radicals generated $\cdot OH$ and OH^- by reacting with H^+ ions (Eq. (14)). Generated $\cdot OH$ species, in the end, transformed IMI pesticide into harmless species (Eq. (15)); thus, $\cdot OH$ species are responsible for IMI degradation. H_2O_2 acted as an outstanding charge carrier (electrons and holes) acceptor and thus caused an increase in electron-hole pair separation [43]. On the other hand, C_{60}/PCN was endowed with an excellent electron transportation rate because of the presence of π -conjugation in both PCN and C_{60} . Noting that this structure is very beneficial for H_2O_2 to capture the electrons. Many photocatalysis systems also evidenced advanced photodegradation ability of photocatalysts on the addition of H_2O_2 , and a possible reaction process has been suggested as follows [67]. It was clear from the photocatalytic experiment that the integration of PCN and C_{60} , as well as addition of H_2O_2 , had improved photocatalytic ability of C_{60}/PCN nanocomposite. The proposed mechanism of C_{60}/PCN nanocomposite was presented in Fig. 9, which revealed tremendous photodegradation ability against IMI. All the obtained results were in harmony with previously discussed scavenging results [68]. Moreover, the photocatalytic performance of 0.04 wt.% C_{60}/PCN photocatalyst was examined for ten consecutive runs. After each cycle, fabricated photocatalyst gets isolated from reaction mixture through centrifuging, which was then reused for the next cycles. It was perceived from the outcomes that degradation proficiency of 0.04 wt.% C_{60}/PCN was reduced to 83 % from 95 %, while 62 % and 41 % decrease in removal efficacy was observed for PCN and GCN from 77 % and 59 %, respectively. Moreover, no remarkable change in morphology or chemical differences was perceived after ten cycles in 0.04 wt.% C_{60}/PCN photocatalyst, confirmed by SEM, XRD and FTIR results (Fig. 10a-d) which indicated firmness of photocatalyst throughout degradation processes.

4. Conclusion

In conclusion, GCN, PCN, and C₆₀/PCN photocatalysts were prepared and utilized for IMI pesticide degradation. Phosphorous doping enhanced texture, and electronic properties of GCN and the introduction of C₆₀ with a facile adsorption route made it a visible-light-driven nanocomposite and upgraded its degradation ability. The higher photocatalytic activity of nanocomposite was associated with synergetic effect among PCN and C₆₀, which was considered promising for photoinduced charge (electrons and holes) separation, as C₆₀ performed as a support to accept e⁻. Similarly, H₂O₂ addition enhanced the removal efficacy of photocatalysts by virtue of its good electron captivating nature, which enhanced charge carrier separation. Morphological investigations validated the adornment of C₆₀ particles on PCN. Through UV-DRS, PL and EIS studies optical, photocarriers isolation, and transference properties were explored. The calculated R² value was between 0.95-0.98, which specified pseudo-first-order kinetics throughout the photocatalytic processes. Photodegradation results confirmed the superior degradation ability of photocatalysts in the presence of H₂O₂ than in the absence of H₂O₂. 0.04 wt.% C₆₀/PCN/H₂O₂ system had 95 % removal efficacy while 0.04 wt.% C₆₀/PCN had 91 % removal efficacy against IMI at optimal pH value (*i.e.* 4). Recyclability tests were executed for consecutive 10 cycles to check the recycling efficacy of 0.04 wt.% C₆₀/PCN/H₂O₂ photocatalyst, and the outcomes confirmed no loss of catalyst. Furthermore, radical scavenging tests were performed, which disclosed that hydroxyl radicals ($\cdot\text{OH}$), holes (h⁺), and superoxide radicals ($\cdot\text{O}_2^-$) were leading reactive species for IMI degradation, confirmed by plausible photocatalytic mechanism suggested.

CRedit authorship contribution statement

Anita Sudhaik: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **Pankaj Raizada:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing. **Pardeep Singh:** Conceptualization, Writing - original draft. **Ahmad Hosseini-Bandegharai:** Conceptualization, Writing - original draft. **Vijay Kumar Thakur:** Conceptualization, Writing - original draft. **Van-Huy Nguyen:** Conceptualization, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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