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## Highly effective degradation of imidacloprid by H<sub>2</sub>O<sub>2</sub>/ fullerene decorated P-doped g-C<sub>3</sub>N<sub>4</sub> photocatalyst

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### Abstract

In this work, P-doped g-C<sub>3</sub>N<sub>4</sub> (PCN) was coupled with another conducting material, fullerene (C<sub>60</sub>). 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, C<sub>60</sub> captured electrons from PCN and reduced the recombination of charge carrier. C<sub>60</sub>/PCN nanocomposites (with different C<sub>60</sub> ratios) were successfully synthesized *via* a simple ultrasonic method for imidacloprid (IMI) pesticide degradation. Raman and N<sub>2</sub>-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 C<sub>60</sub> as its optimal concentration. Through Brunauer–Emmett–Teller (BET) isotherm, two times larger specific surface area was observed in 0.04 wt.% C<sub>60</sub>/PCN than PCN. 60 mg/mL and 1 × 10<sup>-4</sup> M were witnessed as an optimal catalyst dose and pesticide concentration at pH 4. Addition of H<sub>2</sub>O<sub>2</sub> enhanced photodegradation processes since it also served as a good electron acceptor, which boosted charge carrier separation. Photodegradation results confirmed that 0.04 wt.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> and 0.04 wt.% C<sub>60</sub>/PCN nanocomposites exhibited 95 % and 91 % removal efficiency, respectively, which were higher than the percentages exhibited by other tested photocatalysts. A promising mechanism of C<sub>60</sub>/PCN nanocomposite against IMI degradation was also proposed, validating the role of h<sup>+</sup>, .O<sub>2</sub><sup>-</sup> and .OH radicals in the photocatalytic process.

### Graphical abstract

C<sub>60</sub> decorated P-doped g-C<sub>3</sub>N<sub>4</sub> exhibited highly effective degradation of imidacloprid using H<sub>2</sub>O<sub>2</sub> assisted hydroxyl radical oxidation.

**Keywords:** P-doped Fullerene; Metal-free photocatalyst; H<sub>2</sub>O<sub>2</sub>; 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-C<sub>3</sub>N<sub>4</sub>) 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-C<sub>3</sub>N<sub>4</sub> [29]. However, the photodegradation performance of g-C<sub>3</sub>N<sub>4</sub> 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-C<sub>3</sub>N<sub>4</sub> [30].

Considerably, non-metal doping is a beneficial method to increase solar light absorption in the visible range, tweaking of the g-C<sub>3</sub>N<sub>4</sub> bandgap with fastened charge carrier separation [31,32]. Texture and electronic properties of g-C<sub>3</sub>N<sub>4</sub> 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-C<sub>3</sub>N<sub>4</sub> lattice provides altered electronic properties, reduced bandgap energy, and improved charge carrier separation. In a study, the synthesized phosphorus; P-doped g-C<sub>3</sub>N<sub>4</sub> 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-C<sub>3</sub>N<sub>4</sub> framework are substituted by phosphorus heteroatoms and form P—N bonding [36]. In another study, Zhang et al. fabricated P-doped g-C<sub>3</sub>N<sub>4</sub> using [Bmim]PF<sub>6</sub> (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-C<sub>3</sub>N<sub>4</sub>. They reported that P doping increased the mesoporous nature of g-C<sub>3</sub>N<sub>4</sub>, reduced charge transfer distance from bulk to the interface, and accelerated solar light absorption due to constricting in the sub-bandgap of g-C<sub>3</sub>N<sub>4</sub> [38].

Among various carbon materials, fullerene (C<sub>60</sub>) 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 C<sub>60</sub> 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-C<sub>3</sub>N<sub>4</sub> with C<sub>60</sub> enhances photoexcited charge carrier separation because C<sub>60</sub> serves as a visible light harvester, which improves photon absorption ability of photocatalyst due to its superior conductivity and e<sup>-</sup> captivating nature [41]. H<sub>2</sub>O<sub>2</sub> has been widely used in many research areas as a green and moderately oxidizing agent due to its special applications [42].

H<sub>2</sub>O<sub>2</sub> causes the donation and captivation of electrons, which results in the decomposition of H<sub>2</sub>O<sub>2</sub> into O<sub>2</sub> and reactive superoxide radical (O<sub>2</sub><sup>-</sup>). However, H<sub>2</sub>O<sub>2</sub> decomposes slowly at ambient temperature, which cannot be overlooked; nevertheless, the oxidizing ability of H<sub>2</sub>O<sub>2</sub> 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 C<sub>60</sub> with phosphorous doped g-C<sub>3</sub>N<sub>4</sub> (PCN) through different mass/wt % ratios *via* the sonochemical method. Phosphorous doping was preferred over other non-metal doping because it improved g-C<sub>3</sub>N<sub>4</sub> textual properties [44]. Assessment of the potential of the photocatalyst was scrutinized for degrading IMI pesticide in the presence of H<sub>2</sub>O<sub>2</sub>. H<sub>2</sub>O<sub>2</sub>-assisted photodegradation results indicated that the synthesized C<sub>60</sub>/PCN nanocomposites exhibited higher IMI degradation as H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> has been elaborated in detail.

## 2. Experimental

### 2.1. Preparation of C<sub>60</sub>/phosphorus-doped g-C<sub>3</sub>N<sub>4</sub> (C<sub>60</sub>/PCN) photocatalysts

Graphitic carbon nitride (GCN) and P-doped GCN (PCN) were synthesized *via* a thermal polycondensation route by combining melamine with C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>O 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. BmimPF<sub>6</sub> (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-C<sub>3</sub>N<sub>4</sub> (GCN), except for the addition of BmimPF<sub>6</sub>.

C<sub>60</sub>/phosphorous doped g-C<sub>3</sub>N<sub>4</sub> (C<sub>60</sub>/PCN) was prepared using the facile sonochemical method. In a typical synthesis, C<sub>60</sub> (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 C<sub>60</sub>/PCN, which was then labeled as C<sub>60</sub>/PCN nanohybrid. C<sub>60</sub>/PCN was prepared in different mass ratios of 0.02 wt.% C<sub>60</sub>/PCN, 0.04 wt.% C<sub>60</sub>/PCN, and 0.06 wt.% C<sub>60</sub>/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  $\mu\text{m}$  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 ( $\text{CO}_2$ ) 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.%  $\text{C}_{60}$ /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  $\text{C}_{60}$ /PCN nanocomposites (Fig. 1). GCN exhibited two characteristic peaks at about  $13.25^\circ$  and  $27.43^\circ$ , which were accredited to (100) and (002) planes, respectively. The weak diffraction peak observed at  $13.25^\circ$  (100) was credited to heptazine units, and a sharp peak appeared at  $27.43^\circ$  (002) was assigned to aromatic systems in GCN (JCPDS 87-1526) [48]. In the same way, in PCN, the attained peak at  $13.05^\circ$  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  $27.25^\circ$  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  $27.43^\circ$  to  $27.25^\circ$  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  $\text{C}_{60}$ , 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  $32.78^\circ$  which were indexed to (111), (220), (311), (222), (331), (024), (422) and (333) planes of cubic phase of  $\text{C}_{60}$ , respectively (JCPDS No. 82-0505) [50]. In the case of  $\text{C}_{60}$ /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  $\text{C}_{60}$ . Minor diffraction peaks related to  $\text{C}_{60}$  were observed in  $\text{C}_{60}$ /PCN nanocomposite owing to low quantity as well as high dispersal of  $\text{C}_{60}$  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 ( $C_{60}$ ), and  $C_{60}$ /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  $C_{60}$  nanoparticles with restricted agglomeration forming block particles that facilitated the reunion of  $C_{60}$  nanoparticles [51]. In Fig. 2 (d–f), SEM images of  $C_{60}$ /PCN nanohybrids were shown, which revealed irregular anchoring of  $C_{60}$  nanoparticles over PCN nanosheets. As the amount of  $C_{60}$  was increased from 0.02 wt.% to 0.04 wt.%, the surface of PCN became more aggregated, and for 0.06 wt.%  $C_{60}$  was entirely dispersed on PCN nanosheets.

TEM and HRTEM descriptions of GCN, PCN,  $C_{60}$ ,  $C_{60}$ /PCN were shown in Fig. 3. Figure S1 displayed the TEM microstructure of GCN and  $C_{60}$  nanoparticles. Images of GCN publicized thin porous nanosheets, and those of  $C_{60}$  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  $C_{60}$ /PCN photocatalysts unveiled the decoration of  $C_{60}$  nanoparticles on PCN surface and authorized nanocomposites formation (Fig. 3(c–h)) [46]. With the increase in the  $C_{60}$  ratio (0.02 wt. %-0.06 wt. %), more  $C_{60}$  nanoparticles were certainly seen on PCN nanosheets (Fig. 3(g–h)). EDAX results also confirmed the presence of phosphorous, carbon, and nitrogen elements in  $C_{60}$ /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  $sp^2$  N confined in triazine rings (Nitrogen bonded to a carbon atom (C=N—C)) and N—(C)<sub>3</sub>, 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.%  $C_{60}$ /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  $C_{60}$ /PCN (Fig. 5a). An increase in absorption intensity, as well as redshift, was observed in the absorption edge of PCN and  $C_{60}$ /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 C<sub>60</sub> altered the optical capability of PCN, which increases degradation ability [56]. However, a suitable addition of C<sub>60</sub> enhanced the surface charge and absorption edge of PCN and, thus, it is necessary to add an appropriate amount of C<sub>60</sub>. An excessive amount of C<sub>60</sub> 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  $\alpha$  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 C<sub>60</sub>/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 C<sub>60</sub>/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.% C<sub>60</sub>/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 C<sub>60</sub>/PCN (0.02 wt.%, 0.04 wt.% and 0.06 wt.%) were calculated as  $0.0030 \pm 0.0174$ ,  $0.0036 \pm 0.0197$ ,  $0.0042 \pm 0.0153$ ,  $0.0050 \pm 0.0126$  and  $0.0048 \pm 0.0132$  h<sup>-1</sup>, 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 C<sub>60</sub> with PCN reduced photoexcited charge carrier recombination as C<sub>60</sub> acted as a support material as well as a sink, which improved electron conduction and degradation efficiency of 0.04 wt.% C<sub>60</sub>/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 H<sub>2</sub>O<sub>2</sub> 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/H<sub>2</sub>O<sub>2</sub>, PCN/H<sub>2</sub>O<sub>2</sub> and C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> (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.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> (95 %) and 0.04 wt.% C<sub>60</sub>/PCN (91 %) nanocomposites were higher than other photocatalysts. Thus, the IMI degradation efficacy rate (with H<sub>2</sub>O<sub>2</sub>) 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.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> nanocomposite still performed the highest catalytic efficiency in the presence of H<sub>2</sub>O<sub>2</sub>. A slight improvement had been observed in the presence of H<sub>2</sub>O<sub>2</sub>, which was attributed to a good electron acceptor of H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> was almost negligible, and the presence of C<sub>60</sub> in composite improved the adsorption capacity. From adsorption studies, it was observed that as the amount of C<sub>60</sub> in nanocomposite was increased, more adsorption of pollutants occurred. This was due to more active sites provided by C<sub>60</sub> nanoparticles for adsorption. The presence of C<sub>60</sub> in photocatalyst resulted in an increased surface area of 0.04 wt.% C<sub>60</sub>/PCN (4.7915 m<sup>2</sup> g<sup>-1</sup>), 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<sup>-4</sup> mol/dm<sup>3</sup>; [H<sub>2</sub>O<sub>2</sub>] = 1.5 × 10<sup>-4</sup> mol/dm<sup>3</sup>; [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 <sub>1</sub> ) h <sup>-1</sup>	R <sup>2</sup> ± S.D.*	% Removal efficiency ± S.D.*
<b>0.06 C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub></b>	wt%	0.0056 ± 0.0158	0.97 ± 0.0188	87 ± 1.92
<b>0.04 C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub></b>	wt%	0.0060 ± 0.0146	0.98 ± 0.0193	95 ± 2.10
<b>0.02 C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub></b>	wt%	0.0053 ± 0.0173	0.97 ± 0.0186	80 ± 1.89
<b>PCN/H<sub>2</sub>O<sub>2</sub></b>		0.0040 ± 0.0228	0.96 ± 0.0182	76 ± 1.65
<b>GCN/H<sub>2</sub>O<sub>2</sub></b>		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 <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore size distribution (nm)	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
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Photocatalysts	BET surface area	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	Pore size distribution (nm)	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
PCN		2.8401	24.07095 nm	0.017091
0.04 wt% $\text{C}_{60}/\text{PCN}$		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,  $\text{C}_{60}/\text{PCN}$  nanocomposite was positively charged since the pH of zero-point charge ( $\text{pH}_{\text{zpc}}$ ) was 6, as confirmed by zeta potential analysis (Figure S8). Above  $\text{pH}_{\text{zpc}}$ , the surface of the  $\text{C}_{60}/\text{PCN}$  nanocomposite was negatively charged. With a  $\text{pK}_a$  value of 9, IMI did not release  $\text{H}^+$  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  $\text{H}_2\text{O}_2$  and catalysts dosage. Catalyst dosage effect on the reaction of photocatalysis was explored by varying 0.04 wt.%  $\text{C}_{60}/\text{PCN}$  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  $1.5 \times 10^{-4}$  M was  $\text{H}_2\text{O}_2$  ideal concentration at which loftier photo-removal efficacy was attained at pH 4 and 60 mg/mL catalyst dose of 0.04 wt.%  $\text{C}_{60}/\text{PCN}$ . As findings in the previous section over several types of photocatalysts (GCN, PCN, and  $\text{C}_{60}/\text{PCN}$ /(0.02 wt.%, 0.04 wt.% and 0.06 wt.%)), only a slight improvement had been observed in the presence of  $\text{H}_2\text{O}_2$ . It notes that there is no monotonic relationship between the removal efficiency and the  $\text{H}_2\text{O}_2$  concentrations.

To check the extent of mineralization,  $\text{CO}_2$  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. %  $\text{C}_{60}/\text{PCN}$ / photocatalyst, under visible light irradiation (Fig. 7e and f). The COD removal test was strongly confirmed by the  $\text{CO}_2$  assessment test. The  $\text{CO}_2$  removal during the process of photodegradation indicated the transformation of IMI into degraded products, *i.e.*,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [59]. Mineralization ability of 0.04 wt.%  $\text{C}_{60}/\text{PCN}$  nanohybrid was more remarkable than other used photocatalysts. The escalation in the removal efficacy of 0.04 wt.%  $\text{C}_{60}/\text{PCN}$  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 <sub>9</sub> H <sub>x</sub> CIN <sub>y</sub> O <sub>z</sub> )	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, Na<sub>2</sub>-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<sup>+</sup> and •O<sub>2</sub> – radicals have a substantial role in photodegradation processes than •OH radicals. Results of the scavenging experiment of 0.04 wt.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> photocatalysts were displayed in Fig. 8b. From the graph, it was perceived that Na<sub>2</sub>-EDTA and BZQ scavengers had no influence upon the photodegradation process. Such results confirm negligible role of holes and •O<sub>2</sub><sup>-</sup> radicals in photodegradation process [64]. However, the addition of IPA decreased photodegradation efficacy of 0.04 wt.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> system to 16 %, while BZQ and Na<sub>2</sub>-EDTA scavengers presented 90 % and 93 % IMI removal, respectively which confirmed the substantial role of •OH radicals in degradation. Subsequently, generated h<sup>+</sup> and O<sub>2</sub><sup>-</sup> radicals were the foremost oxidative species in PCN whereas O<sub>2</sub><sup>-</sup> radical was in 0.04 wt.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> system.

### 3.5.2. Proposed mechanism of C<sub>60</sub>/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,  $\chi$  symbolizes electronegativity,  $E_g$  means bandgap of photocatalysts, and  $E^\circ$  indicates free electron energy. From Eqs. (5)–(6), bandgap and  $\chi$  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  $\pi$ -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 C<sub>60</sub>/PCN photocatalysts were prepared and utilized for IMI pesticide degradation. Phosphorous doping enhanced texture, and electronic properties of GCN and the introduction of C<sub>60</sub> 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 C<sub>60</sub>, which was considered promising for photoinduced charge (electrons and holes) separation, as C<sub>60</sub> performed as a support to accept e<sup>-</sup>. Similarly, H<sub>2</sub>O<sub>2</sub> 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 C<sub>60</sub> particles on PCN. Through UV-DRS, PL and EIS studies optical, photocarriers isolation, and transference properties were explored. The calculated R<sup>2</sup> 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 H<sub>2</sub>O<sub>2</sub> than in the absence of H<sub>2</sub>O<sub>2</sub>. 0.04 wt.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> system had 95 % removal efficacy while 0.04 wt.% C<sub>60</sub>/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.% C<sub>60</sub>/PCN/H<sub>2</sub>O<sub>2</sub> photocatalyst, and the outcomes confirmed no loss of catalyst. Furthermore, radical scavenging tests were performed, which disclosed that hydroxyl radicals ( $\cdot$ OH), holes (h<sup>+</sup>), and superoxide radicals ( $\cdot$ O<sub>2</sub><sup>-</sup>) 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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