Efficient photocatalytic destruction of recalcitrant micropollutants using graphitic carbon nitride under simulated sunlight irradiation

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The ubiquity of micropollutants (MPs) in aquatic environments has attracted increasing concern for public health and ecological security. Compared to conventional biological treatment, photocatalytic processes show more efficiency in degrading MPs, but they require expensive materials and complicated synthesis processes. This study developed an economic photocatalytic process to degrade micropollutants. We synthesized urea-based graphitic carbon nitride (g-C3N4) by a facile one-step pyrolysis method and evaluated the photocatalytic efficiency of carbamazepine (CBZ). Under simulated solar irradiation, g-C3N4 could achieve 100% removal efficiency of 0.1 mg/L CBZ in spiked wastewater effluent within 15 min, and 86.5% removal efficiency in wastewater influent after 20 min of irradiation. The porous structure of g-C3N4 promoted effective charge separation and mass transport of CBZ near the catalyst surface, enabling a high kinetic rate (0.3662 min⁻¹). Reactive oxygen species trapping experiments revealed that superoxide radicals (O2⁻•) and holes (h⁺) were the major active radicals. Electron paramagnetic resonance (EPR) further confirmed the presence of O2⁻•, OH⁻, 1O2 and holes. The pH, light intensity and initial CBZ concentration were found to have significant impacts on the removal efficiency of CBZ. Possible reaction intermediates were identified and the degradation pathway was proposed. Multiple MPs were selected to further demonstrate photocatalytic efficiency of g-C3N4. The facile synthesis, superior efficiency, and versatility of g-C3N4 make it a promising catalyst for application in tertiary wastewater treatment processes.

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1. Introduction

The ubiquity of pharmaceutical and personal care products (PPCPs) in aquatic environments [1–3] has raised concerns regarding their persistence [4,5], toxicity [6,7] and bioaccumulative effects [8]. Increasingly, studies have suggested that a wide range of water bodies, including drinking water [9], groundwater [10], wastewater [11] and landfill leachate [12], are contaminated with PPCPs, posing a serious threat to public health and ecological security. In particular, wastewater treatment plants (WWTPs) are identified as a hotspot for the release of PPCPs to aquatic environments [13–15]. Therefore, reducing the concentration of PPCPs in wastewater could mitigate its input to the environment.

Various technologies involving membrane filtration, activated carbon adsorption, and biodegradation have been developed to remove PPCPs from contaminated water [13]. However, sorption and filtration are non-destructive methods that simply transfer the PPCP from one medium to another, without detoxifying the chemicals. Biodegradation methods have been proven to be inefficient for PPCP removal [16], particularly for the more recalcitrant compounds. For example, carbamazepine (CBZ), which is used to recover patients from epilepsy, bipolar disorder and manic depression [17], is one of five indicators selected by the Swiss Federal Office for the Environment (FOEN) [18] to evaluate WWTPs’ performance in terms of micropollutants (MPs) removal. The reported removal efficiency of CBZ in WWTPs is mostly below 10%.
generate strongly oxidizing reactive oxygen species (ROS) to catalyze the complete reaction. Photocatalytic reactions can only require renewable solar energy and an appropriate photosensitizer. However, previous studies mainly employed very expensive metal-based catalysts, like TiO2 [26], which are limited for their high cost. Thus, an economically viable photocatalyst that utilizes the full solar spectrum would be more promising for practical applications.

Recently, a metal-free photocatalyst called graphitic carbon nitride (g-C3N4) has emerged as a new class of photocatalysts due to its suitable band structure, stable physicochemical properties and “earth-abundant” nature [29]. It has been reported for a wide range of applications, including water splitting and organic pollutant remediation [30]. It can be easily synthesized by thermal polymerization of nitrogen-rich precursors such as melamine [31], urea [32], thiourea [33], and ammonium thiocyanate [34]. Therefore, it is regarded as a potential photocatalyst for organic pollutants remediation. One of its potential applications is to degrade MPs in tertiary wastewater treatment processes. However, most of the photocatalysts designed demonstrate their performance by treating MPs at high concentrations (tens of mg/L) in a clean water matrix without considering whether the photocatalysts are economically feasible in massive production. As a low cost material, very few studies [35] have investigated whether g-C3N4 is efficient in removing MPs at environmentally relevant concentrations in a wastewater matrix.

The objective of this study is to assess whether it is technically and economically feasible to fully remove CBZ through photocatalytic degradation using g-C3N4 in a wastewater effluent matrix under simulated sunlight irradiation. Herein, we prepared g-C3N4 via a facile single-step pyrolysis method. We selected urea as a precursor since urea-derived g-C3N4 was reported to have a larger surface area, higher polymerization degree and improved charge migration compared to g-C3N4 synthesized from other precursors [29]. The photocatalytic performance of g-C3N4 was assessed under simulated solar irradiation using CBZ as a model recalcitrant PPCP. Effects of light source, light intensity, pH, initial CBZ concentration and catalyst dosage on CBZ degradation performance were comprehensively assessed. In addition, CBZ removal efficiency in real wastewater matrix and recyclability of catalysts were also evaluated. In order to identify which radical plays a crucial role in degrading CBZ, both ROS quenching experiments and electron paramagnetic resonance (EPR) measurements were employed. The CBZ degradation products and mechanism were revealed and discussed. The g-C3N4 showed outstanding recyclability and achieved effective removal of MPs in real wastewater effluent under simulated sunlight irradiation, highlighting its potential for practical application in tertiary wastewater treatment processes for enhanced wastewater purification.

2. Materials and methods

2.1. Reagents and chemicals used

High purity (>98%) carbamazepine (CBZ) purchased from Sigma Aldrich, was selected as a model compound for this study. AR grade sulfamethoxazole (SMX), diclofenac sodium (DCF), mecoprop (MCP) and benozthiazole (BTA) were purchased from Sigma Aldrich. HPLC grade methanol (MeOH) was received from UQ science store. Urea (99.0%) and 1,4-benzoquinone (BQ, 98.0%) were obtained from Chem-supply Pty Ltd. Isopropanol (IPA) and trifluoroacetic acid (TFA) were purchased from Novachem Pty Ltd. Triethanolamine (TEOA, 99%), 5,5-Dimethyl-1-pyrrrole N-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperidinol (TEMP), superoxide dismutase (SOD), ammonium acetate and sodium azide (SAZ) were purchased from Sigma Aldrich Pty Ltd. Ammonia solution (25%) was purchased from Merck. 1-Hydroxy-3-carboxy-2,2,5,5-tetramethylpyrrolidin-3-one (CPH) was supplied by United Bioresearch Products Pty Ltd. All reagents in the experiments were used directly without any further purification. MilliQ water (18.2 MΩ/cm) was used for all the experiments.

2.2. Photocatalyst preparation

Graphitic carbon nitride was prepared by a facile thermal condensation method with minor modifications [36]. Briefly, 10 g urea was placed in a ceramic crucible. Then the crucible was covered and transferred to a muffle furnace and was calcined at a rate of 10 °C/min up to 550 °C for 4 h under air. After cooling down to room temperature (22 ± 2 °C), a light-yellow product was obtained and ground into fine powder using agate mortar and pestle for the following experiments.

2.3. Photocatalyst characterization

Crystal phases of materials were determined by X-ray diffraction (XRD) spectroscopy (D8 Advance, Bruker) with Cu Kα (λ = 0.15406 nm) radiation. UV-Visible spectra were collected using a JASCOV-650 spectrophotometer. The architectural information of the samples was analysed by Fourier transform infrared (FT-IR) spectra of the samples embedded in KBr pellets (Spectrum Two, PerkinElmer, USA). Surface morphology of samples was determined by field-emission scanning electron microscopy (FE-SEM) images on a Hitachi HT7700 microscope. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker Elecsys E540 spectrometer equipped with an Elecsys super high sensitivity probe head and LN2 cooling (Eurotherm temperature control). Measurements were conducted at room temperature using a modulation amplitude of 0.2 mT, a modulation frequency of 100 kHz and a microwave power of 20 mW.

2.4. Photocatalytic CBZ degradation experiments in a lab-scale photoreactor

The photocatalytic performance of g-C3N4 was evaluated by the degradation of CBZ (0.1 mg/L) in a PQ253 photoreactor (Quartz top-irradiation reaction vessel with water jacket) under simulated sunlight irradiation originating from a Xenon lamp (200—800 nm, 300 W) with a working volume of 150 mL. Specifically, 25 mg of catalyst was dispersed into a 50 mL solution of CBZ (0.1 mg/L) under
continuous stirring at 350 rpm using a magnetic stir bar. The solution was stirred for 30 min in the dark prior to irradiation to reach adsorption/desorption equilibrium, then exposed to the Xenon lamp under continuous stirring. At regular time intervals (2, 3 or 5 min), 1.5 mL sample was collected and filtered through a 0.45 μm polyethersulfone (PES) syringe filter (Millipore) to remove the suspended photocatalyst. The degree of CBZ degradation was expressed as C/C₀, where C₀ is the initial concentration of CBZ, and C is the concentration at different sampling times. Experiments were carried out in triplicate.

2.5. Calculation of CBZ degradation rates

For low concentration pollutants treated with heterogeneous catalytic processes, the pseudo-first-order kinetic model can be adopted according to the Langmuir-Hinshelwood equation [37,38]:

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

(1)

Where C₀ is the initial CBZ concentration (μg/L) and Cₜ is the CBZ concentration (μg/L) at time t (min) and t is the irradiation time (min). When the natural log of the normalized concentration Cₜ/C₀ is plotted as a function of time, the pseudo-first-order rate constant k (min⁻¹) can be determined from the slope of linear best fit.

2.6. Radical identification

Radical trapping experiments were conducted to identify the key active ROS, towards understanding the photocatalytic reaction mechanisms of CBZ degradation under simulated solar light. Four trapping agents, including BQ, IPA, TEOA and SAZ were added as scavengers of superoxide radicals (O₂⁻), hydroxyl radicals (•OH), hole (h⁺) and singlet oxygen (¹O₂), respectively. During the experiments, 1 mM solutions of each trapping agent was separately mixed into the samples prior to the addition of catalyst. During the photodegradation experiment, samples were periodically collected (2, 3 or 5 min interval) for LC-MS/MS analysis. DMPD spin-trapping EPR measurements were employed to further confirm the presence of •OH and O₂⁻ in aqueous dispersions and methanol dispersions, respectively. In addition, TEMP was used to identify the generation of ¹O₂ while CPH was used to confirm holes generation in EPR measurements.

2.7. Factors affecting photocatalytic degradation of CBZ

The photocatalytic performance of g-C₃N₄ for CBZ degradation in aqueous solution was evaluated under the following experiment conditions: (a) under irradiation with simulated solar light and visible light (λ > 420 nm), (b) under different simulated solar irradiation intensities (150 mw/cm², 130 mw/cm² and 40 mw/cm²), (c) with different initial CBZ concentrations (10 mg/L, 1 mg/L and 0.1 mg/L), (d) under a range of catalyst dosages (1 g/L, 0.7 g/L, 0.5 g/L and 0.3 g/L), (e) with various initial pH levels, including 9.9, 8.6, 6.4 (default condition) and 4.2, (f) and in different water matrices (wastewater influent and wastewater effluent). Real wastewater influent and effluent were collected from a full-scale WWTP located in Brisbane, Queensland, Australia.

2.8. Recyclability test

Catalyst recyclability is a major factor when considering full-scale application of photocatalysis for MP removal. Hence, nine 20 min cycles of photodegradation experiments were performed to test the catalyst recyclability. Similar to the CBZ degradation experiment in Section 2.4, 25 mg of catalyst was added to 50 mL MQ water containing 0.1 mg/L CBZ. Then, 1 mL sample was collected at the beginning and the end of each cycle. After each cycle, the solution was topped up with CBZ stock solution (10 mg/L) to achieve the initial concentration of approximately 0.1 mg/L.

2.9. Multiple micropollutants testing

An expanded range of MPs was selected to further demonstrate the ability of g-C₃N₄ in removing multiple MPs. The selection of MPs was based on proxy compounds proposed by FOEN [18], in addition to CBZ, SMX, DCF, MCP and BTA were included. The initial concentrations were set as 50 μg/L which is a more environmentally relevant concentration. Experiments were performed in triplicate.

2.10. Analytical method of MPs and its intermediates

Liquid chromatography coupled tandem mass spectrometry (LC-MS/MS) was used to quantify CBZ concentrations in the photocatalytic process. A Shimadzu liquid chromatography system was connected to a mass spectrometer (AB Sciex TripleTOF 5600) via an electrospray ionization (ESI) interface. The mass spectrometer was operated in a positive product ion scan mode to measure CBZ, BTA and SMX precursors at m/z 237.1, 120.13 and 254.06, respectively. Fragment ions at m/z 194.095, 39.022 and 156.0 were used for the quantitation of CBZ, BTA and SMX, respectively. In negative scan mode, precursors at m/z 294.02 and 213.03 were selected to measure diclofenac and mecoprop, respectively. Fragment ions at m/z 250.85 and 140.028 were used to quantify diclofenac and mecoprop, respectively. A Phenomenex Kinetex Biphenyl column (50 × 2.1 mm) was used for the chromatographic separation. Solvents used for mobile phases were MilliQ water acidified with 0.1% formic acid (mobile phase A) and methanol (MeOH) acidified with 0.1% formic acid (mobile phase B). The elution gradient started from 30% B for 0.3 min then increased to 100% B at 2 min, maintained 100% B at 5.7 min, then returning to the initial condition. The total run time was 8 min. The sample injection volume was 5 μL at a flow rate of 0.4 mL/min⁻¹.

Oxidized CBZ degradation intermediates were identified by LC-MS/MS equipped with an ESI source operated in positive mode. SWATH (Sequential Window Acquisition of all Theoretical Mass Spectra) mode was used for non-target acquisition of mass fragments in the range of m/z 40–400. The curtain gas and ion source gas pressure were set to 30 psi and 60 psi, respectively. The temperature of the ion source was set to 550 °C and ion spray voltage was 5500 V.

3. Results and discussion

3.1. Characterization of g-C₃N₄

The properties of the synthesized g-C₃N₄ were evaluated by XRD, UV–Vis, FTIR, SEM and TEM. The XRD spectra corresponded to the (1 0 0) and (0 0 2) crystal layers of g-C₃N₄ (JCPDS card 87–1526). The strongest peak was observed around 27.5° (Fig. 1a), which could be due to the characteristic inter-layer stacking of the conjugated aromatic CN units (lattice spacing = 0.320 nm), identified as the (0 0 2) crystal plane for graphitic materials [36]. Another small-angle peak was found around 13.1°, attributed to the in-plane ordering of tri-s-triazine units, assigned as the (100) crystal plane [39]. These two characteristic peaks match typical XRD spectra previously reported for g-C₃N₄ [36]. In the FTIR spectra (Fig. 1b), a sharp absorption peak at 810 cm⁻¹ was attributed to the characteristic bending vibration mode of the tri-s-triazine units [40].
Several strong peaks in the region from 900 to 1800 cm$^{-1}$ were assigned to C–N–C and C–N heterocycles attributed to skeletal vibration of the aromatic ring [41]. In addition, a broad peak in the range of 3000–3500 cm$^{-1}$ revealed the existence of the O–H stretching vibrations of surface-absorption water molecules [42]. The UV–visible spectra showed a maximum absorbance wavelength for g-C$_3$N$_4$ at approximately 367 nm (Fig. 1c), indicating that the synthesized g-C$_3$N$_4$ can be more active under simulated light irradiation and also harvest visible light.

The TEM images of g-C$_3$N$_4$ revealed planar and layered structures (Fig. 2). A flat layer with spacing of 0.320 nm can be distinctly seen in Fig. 2b, confirming the g-C$_3$N$_4$ had an ultrathin 2D lamellar structure. The lamellar structure corresponding to its XRD pattern (Fig. 1a) further confirmed it had a (0 0 2) planar structure. The surface morphology of g-C$_3$N$_4$ was observed using SEM. The SEM image at 10,000 times magnification (Fig. 2c) showed that the g-C$_3$N$_4$ particles were irregularly shaped and desultorily assembled, which is the typical structural characteristic of g-C$_3$N$_4$ synthesized by the polymerization method [43, 44]. More importantly, g-C$_3$N$_4$ particles showed a porous stacked and layered morphology which is associated with high specific surface area, good mass diffusion, and efficient separation of photo-induced electrons and holes, thus promoting its photocatalytic performance [45].

3.2. Photocatalytic activity test

The photocatalytic performance of synthesized g-C$_3$N$_4$ was assessed based on CBZ removal efficiencies under simulated sunlight irradiation. Both a dark control and a no catalyst control were included in this study. The results showed negligible absorption of CBZ by g-C$_3$N$_4$ after 30 min stirring in the dark (Fig. 3a). Approximately 5% of CBZ was removed after 30 min of simulated solar irradiation when no catalyst was provided (Fig. 3a), suggesting that photolysis was not substantially involved in CBZ degradation. In contrast, when both g-C$_3$N$_4$ and light source were presented in the reaction system, the concentration of CBZ decreased by more than two orders of magnitude from 100 mg/L to less than 1 mg/L after 10 min and then became undetectable after an additional 5 min, indicating that g-C$_3$N$_4$ could efficiently remove CBZ under simulated solar irradiation. Based on the CBZ degradation profile, reaction kinetics analysis was conducted using pseudo-first-order reaction kinetics [46–50]. In a typical experiment (i.e., default condition), 25 mg of g-C$_3$N$_4$ was dispersed in a 50 mL reaction solution containing 100 µg/L CBZ in MilliQ water and the photocatalytic reaction was conducted under simulated solar light. The $k$ obtained in this experiment reached 0.3593 ± 0.017, as shown in Table 1.

A ROS quenching experiment was conducted to identify which ROS play a dominant role in CBZ degradation. Four ROS scavengers were separately added to the photocatalytic system prior to the reaction initiation. The photocatalytic performance of g-C$_3$N$_4$ was inhibited differently following addition of each scavenger (Fig. 3b). Specifically, only about 4.3% of CBZ was removed in the photocatalytic system after the addition of BQ, which is a scavenger of superoxide radicals (O$_2^\cdot$). The CBZ removal efficiency decreased to 37.4% when TEOA, a hole (h$^+$) scavenger, was added into the CBZ solution. In contrast, CBZ removal efficiencies of 72.4% and 95.7%, could still be obtained after addition of SAZ and IPA, which are scavengers of singlet oxygen (¹O$_2$) and hydroxyl radicals (¹OH), respectively (Fig. 3c). These results suggest that superoxide radicals (O$_2^\cdot$) and hole (h$^+$) play key roles in CBZ degradation in g–C$_3$N$_4$–based photocatalytic systems, while singlet oxygen (¹O$_2$) and hydroxyl radical (¹OH) only make minor contributions towards CBZ degradation.

In order to further confirm the generation of these free radicals during photocatalytic reaction, EPR technique was applied to identify the ROS present in the quenching experiment. DMPO spin-trapping EPR measurements were employed to identify the presence of DMPO-¹OH and DMPO- O$_2^\cdot$ in MilliQ dispersions and methanol dispersions, respectively. As depicted in Fig. 4a, six characteristic peaks of DMPO-O$_2^\cdot$ were observed clearly in the methanol dispersion, implying the O$_2^\cdot$ radicals were generated from a single-electron reduction process [51]. In Fig. 4b, four equally spaced characteristic peaks with 1:2:2:1 peak ratios were observed clearly. This is the characteristic profile of DMPO-¹OH in MilliQ dispersion [52]. The generation of ¹OH radicals could have

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**Fig. 1.** Photocatalyst characterization of g-C$_3$N$_4$ by (a) XRD pattern, (b) FT-IR spectra in the range of 400–4000 cm$^{-1}$ and (c) UV–visible spectra.

**Fig. 2.** TEM (a) and HRTEM (b) images of g-C$_3$N$_4$ at different magnifications. SEM images of g-C$_3$N$_4$ (c) reveal its highly porous structure.
photo-excited holes \[57\]. For urea-based g-C3N4 is proposed. With irradiation from simulated solar irradiation and (c) the inhibited fractions of added ROS scavengers at 20 min, compared to tests where no scavengers were added.

Addition of CPH to the system (Fig. 4d), con three-line peaks with intensity ratios of 1:1:1 appeared after reaction with electrons. 

Based on the above results, a possible photocatalytic mechanism for urea-based g-C3N4 is proposed. With irradiation from simulated solar light, the energy of incident light is equal to or greater than the bandgap energy of the g-C3N4 (~2.7 ev) [36]. When the g-C3N4 is excited, electron-hole pairs are generated. Some of these electron-hole pairs may migrate to the surface of the photocatalyst and dissociate into h+ and e-. The dissociated electrons could then react with dissolved molecular oxygen captured by g-C3N4 to form O2-. Simultaneously, the dissociated holes on the photocatalyst surface might react with water molecules to generate OH radicals.

In addition, the porous structure of g-C3N4 facilitates the transfer of electron-hole pairs and restrains their recombination, therefore improving its photocatalytic activity and allowing it to achieve elevated removal rates of CBZ.

### 3.3. Factors influencing CBZ degradation

The effects of various photocatalytic conditions (light source, light intensity, initial CBZ concentration, catalyst dosage, initial pH and water matrix) on the photocatalytic activity were systematically investigated (Fig. 5). The g-C3N4 exhibited good photocatalytic ability towards CBZ degradation under irradiation of both simulated solar light (k = 0.3662 min\(^{-1}\)) and visible light (k = 0.2232 min\(^{-1}\)) (Table 1, Fig. 5a), and was able to achieve a higher degradation efficiency with solar light irradiation due to the visible light (\(\lambda > 420\) nm). This is due to the fact that g-C3N4 has its highest absorbance peak at UV spectra, not in the visible range (Fig. 1c).

Thus, simulated solar light was chosen as the irradiation source for the following experiments to achieve maximum catalyst activation.

Changes in light intensity can modify the photon flux that resulted from further reduction of O2• - [53,54], as the valence band (VB) potential of g-C3N4 (~1.30 V, vs NHE) [55] is more negative than that of OH−/•OH (~1.99 V, vs NHE), thus making the photogenerated holes incapable of oxidizing OH− to •OH radicals. In Fig. 4c, a distinctive three peak signal was seen after the addition of TEMP and SOD, indicating the presence of O2• -.

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\[ g - C_3N_4 + h\nu \rightarrow h^+ + e^- \]  \hspace{1cm} (2)
\[ e^- + O_2 \rightarrow O_2^- \]  \hspace{1cm} (3)
\[ O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \]  \hspace{1cm} (4)
\[ H_2O_2 + e^- \rightarrow •OH + OH^- \]  \hspace{1cm} (5)
\[ O_2^- + h^+ \rightarrow 1O_2 \]  \hspace{1cm} (6)
\[ O_2^- , h^+, 1O_2 + •OH + CBZ \rightarrow \text{mineralized end product} \]  \hspace{1cm} (7)

### Table 1

Kinetic rates of CBZ degradation under various conditions using g-C3N4.

| Factor         | Light source | Dosage (mg/L) | pH   | Initial conc. (mg/L) | Light intensity (mW/cm²) | Matrix | k (min\(^{-1}\)) | R²  |
|----------------|--------------|---------------|------|----------------------|--------------------------|--------|-----------------|-----|
| Default condition | SSL          | 0.5           | 7.55 | 0.1                  | 130                      | MilliQ | 0.3662          | 0.9619 |
| Light source    | SSL          | 0.5           | 7.55 | 0.1                  | 40                       | MilliQ | 0.09516         | 0.9664 |
| Light intensity | SSL          | 0.5           | 7.55 | 1                    | 130                      | MilliQ | 0.3861          | 0.9808 |
| Conc. Catalyst  | SSL          | 0.3           | 7.55 | 1                    | 130                      | MilliQ | 0.1306          | 0.9831 |
| Catalyst dosage | SSL          | 0.7           | 7.55 | 1                    | 130                      | MilliQ | 0.1541          | 0.9944 |
| pH             | SSL          | 0.5           | 9.9  | 0.1                  | 130                      | MilliQ | 0.1214          | 0.8725 |
| Matrix effect   | SSL          | 0.5           | 8.6  | 0.1                  | 130                      | WW eff.| 0.6928          | 1     |
|                | SSL          | 0.5           | 8.6  | 0.1                  | 130                      | WW inf.| 0.1015          | 1     |
|                | SSL          | 0.5           | 6.4  | 0.1                  | 130                      | WW eff.| 0.3414          | 0.8718 |
|                | SSL          | 0.5           | 4.2  | 0.1                  | 130                      | WW inf.| 0.0848          | 0.9246 |
|                | SSL          | 0.5           | 4.2  | 0.1                  | 130                      | WW eff.| 0.3911          | 0.9979 |
|                | SSL          | 0.5           | 4.2  | 0.1                  | 130                      | WW inf.| 0.1057          | 0.9776 |

Note: WW eff. and WW inf. represent wastewater effluent and wastewater influent, respectively. SSL indicates the experiment was performed under simulated solar light, while vis means the irradiation light was visible light (\(\lambda > 420\) nm).
reaches the catalyst surface, hence affecting ROS generation and regulating the catalytic performance. In each of the three levels of simulated solar light intensity tested, the catalyst removed CBZ within 20 min except for under low light intensity of 40 mw/cm² where approximately 88.4% of CBZ removed (Fig. 5b). The highest removal efficiencies were achieved at a light intensity of 130 mw/cm². The mechanism of light intensity regulating catalyst performance can be attributed to ROS generation. As light intensity increased from 40 to 130 mw/cm², elevated photon flux could interact with the catalyst to generate more ROS, thus leading to enhanced catalytic performance. When light intensity continued to increase after the photon flux was saturated, the enhancing effect of excessive photon flux is moderated. For example, there was no significant difference between the degradation profile at 130 mw/cm² and 150 mw/cm² (p > 0.05, T-test), indicating the photon flux might have been already saturated at a light intensity of 130 mw/cm².

As calculated in Table 1, the prepared g-C₃N₄ could degrade CBZ at concentrations of 0.1 mg/L and 1 mg/L with a kinetic rate of 0.3662 min⁻¹ and 0.3861 min⁻¹, respectively. However, the
degradation rate was inhibited when the CBZ concentration reached 10 mg/L ($k = 0.0355$ min$^{-1}$, Fig. 5c). This reduced photocatalytic performance could be explained by following: i) owing to the photonic nature of the photocatalytic process, excessive pollutant loading is known to simultaneously saturate the surface of photocatalyst and reduce the photonic efficiency, thus resulting in photocatalyst deactivation [59] and ii) higher concentrations of CBZ would produce more intermediates which act as an antagonist to ROS, thus limiting the ROS availability for CBZ destruction.

Fig. 5d shows the photocatalytic degradation of CBZ at various g-C$_3$N$_4$ dosages. The kinetic rates for each dosage ranked as follows: 0.5 g/L (0.3662 min$^{-1}$) > 0.7 g/L (0.1541 min$^{-1}$) > 0.3 g/L (0.1306 min$^{-1}$) > 1 g/L (0.1214 min$^{-1}$). This shows that the degradation efficiency of g-C$_3$N$_4$ increased from 0.3 g/L to 0.5 g/L, and then started dropping after increasing dosage above 0.5 g/L. This phenomenon could be explained by CBZ removal efficiency increasing with catalyst dosage at lower catalyst dosage (<0.5 g/L) because more catalyst was available in the system. However, once the catalyst dosage passed a certain threshold (e.g., 0.5 g/L), the excessive catalyst would cause the aqueous solution to become turbid, therefore inhibiting the catalytic performance due to insufficient irradiation [60]. In this case, 0.5 g/L catalyst dosage was chosen as the preferred dosage for subsequent experiments.

Photocatalytic activity was tested first under buffered pH ranging from 4.2 to 9.9 (Fig. 5e) to cover the pH range of wastewater and natural water. G-C$_3$N$_4$ still exhibited negligible adsorption of CBZ in this pH range, whereas the catalytic efficiency was greatly affected by solution pH. A higher removal efficiency was observed under alkaline conditions compared to acidic condition, suggesting alkaline conditions are favourable to the reaction. CBZ presents as a cation under acidic pH (5 and 6.5), while it remains neutral or anionic form in basic pH (pH 9) [61]. Urea based g-C$_3$N$_4$ is reported to have a point of zero charge at a pH around 5.1 [62]. The change of pH value will affect the surface charge of photocatalyst, thus affecting the absorption of PPCPs [59]. Reduced pH is considered to decrease the amount of negative surface charge on the catalyst, thus inhibiting the interaction of the catalyst with CBZ [63]. Although g-C$_3$N$_4$ catalysts show negligible absorption of CBZ, the change of the catalyst’s charge density due to modified pH might still affect the catalytic efficiency.

CBZ removal efficiency in real wastewater matrix was assessed by spiking CBZ into both influent and effluent collected from a full-scale WWTP. Results showed that the catalyst could degrade CBZ in wastewater matrices with 100% removal (undetectable CBZ concentration) in effluent after 15 min ($k = 0.3911$ min$^{-1}$), and 86.5% removal in influent ($k = 0.1057$ min$^{-1}$) after 20 min (Fig. 5f). The reduced catalytic efficiency of g-C$_3$N$_4$ in wastewater matrices might be associated with organic matter present in influent (140 ± 20 mg C/L) and effluent (11 ± 0.5 mg C/L). Organic matter can absorb photons, thus inhibiting the formation of ROS and also interact directly with ROS, thus hindering the destruction process of CBZ [64]. Therefore, wastewater influent with higher turbidity and concentrated organic matter would result in reduced catalytic performance.

3.4. Recyclability

In order to minimize overall operational costs, catalyst recyclability has become a very important issue in full-scale applications of photocatalysis. Hence, the catalyst recyclability was assessed by running 9 consecutive cycles of the reaction. The overall photocatalytic performance of the synthesized g-C$_3$N$_4$ remained considerably high after nine cycles, dropping by only approximately 15% in terms of CBZ removed (Fig. 6). This minor decay of photocatalytic performance was associated with the fact that the concentration of catalyst was decreased after the addition of stock solution and sample collection.

3.5. Identification of intermediates and possible degradation pathway

Potential intermediates generated during photocatalytic degradation of CBZ by g-C$_3$N$_4$ under simulated solar light were monitored by HPLC-MS/MS in positive mode using sample at time 0 as blank. A higher dose of CBZ (1 mg/L) was selected to obtain an enhanced signal in the mass spectrum. Based on previous studies [65,66], possible CBZ intermediates were outlined and identified by the specific molecular ions, mass fragment peaks and the HPLC-MS library database. The tandem analysis confirmed the presence of ions with $m/z$ ratios equal to 253.0982, 210.0915, 236.0702, 180.0811, 224.0760 and 91.9765. The $m/z$ of 253.0982 can be attributed to two molecules. The corresponding intermediate information is listed in SI-Table 1 and a tentative CBZ degradation pathway is proposed in Fig. 7. The double bond in the central heterocyclic ring of CBZ reacts with H*, forming product A (carbamazepine-10,11-epoxide). This would be further oxidized into transition product E and then G [67] (not detected). Product I may be generated after product G undergoes hydrolysis of the urea group located on the central heterocyclic ring. The identification in this study of product D (acridine-9-carboxaldehyde), product H (acridine) and product F collectively suggest rearrangement of the azepane ring of CBZ radical cation to produce product D. Product D could then lose its carbonyl and amido group to form product F. Product F might then further react with "OH/O$_2^-$ to generate product H. After a further hydrolysis step, CBZ would produce the intermediate product C. Product B might then result from CBZ through a ring closing reaction. Products B, C, H, and I might undergo ring cleavage and generate product J (oxalic acid) and other mineralized compounds that are then further degraded to carbon dioxide and water (not detected).

3.6. Simultaneous removal of multiple micropollutants

Photocatalytic performance of g-C$_3$N$_4$ in the degradation of five MPs is shown in Fig. 8. Most compounds showed negligible adsorption towards g-C$_3$N$_4$ except for DCF where approximately 17.3% was adsorbed after 30 min stirring in the dark. After illumination, rapid degradation of DCF, SMX, MCP and CBZ was achieved at 1 min, 5 min, 7 min and 12 min respectively, suggesting g-C$_3$N$_4$ was effective in degrading MPs at environmentally relevant concentrations (50 µg/L). These four MPs mentioned contain single chemical bonds (e.g. C=C–N–C, C–O, N–S and C–S–S), which are susceptible to ROS, compared to multiple bonds (e.g. C=C–N and N–N) which have a higher stability. The number of single bonds present in the chemical structure of the MPs determined their vulnerability towards ROS attack. However, only 20.2% of BPA was...
removed after 20 min photocatalytic reaction. This could be explained by the radicals generated by g-C3N4 are insufficient to destroy the multiple bonds (C=C and N=N) in BTA. When calculating the average removal fraction of the five proxy compounds after 20 min treatment, an arithmetic mean of 82% removal was still achieved, which is higher than the required removal percentage (overall 80% removal) set by FOEN regulations [18].

3.7. Implication of this study

In this work, we synthesized the metal-free photocatalyst g-C3N4 from urea through a simple pyrolysis method and demonstrated g-C3N4 could achieve effective removal of MPs. The simple synthesis process and low cost of raw material make g-C3N4 promising for future solar application. First, the precursor is urea, a highly available and low cost chemical (~$25/kg) which can achieve a yield rate of approximately 10% for g-C3N4. Based on the raw material cost obtained from Sigma Aldrich, TiO2 (P25) costs $1570/kg. In addition, the photocatalyst g-C3N4 can be synthesized by a simple single-step pyrolysis method. In contrast, the synthesis processes of other photocatalysts (e.g., BiOCl and Ti3C2/TiO2) involve complicated hydrothermal and washing procedures that further increase the synthesis and operational costs. Furthermore, compared with other metal-based photocatalysts, g-C3N4 is more environmentally friendly as it eliminates the problem of toxic metal-leaching due to photo-corrosion [68]. More importantly, g-C3N4 has exhibited a superior kinetic rate compared with other photocatalysts (Table 2). For example, kinetic rate of CBZ degradation obtained in this study by g-C3N4 (k = 0.3662 min⁻¹) is 20 times higher than that of ZnIn2S4/TiO2 (k = 0.0182 min⁻¹), which is also more expensive.

In addition to the economic merits, facile synthesis process and superior kinetics, the g-C3N4 synthesized in this study also required less contact time to achieve CBZ elimination when compared to other reported results (Table 2). For example, a synthesized binary photocatalyst ZnIn2S4/TiO2 was demonstrated to remove 0.1 mg/L CBZ after 4 h contact time under natural solar light [69]. Despite the light source difference, our synthesized g-C3N4 only requires 10 min of contact time to achieve the same effect. In addition, three binary photocatalysts were designed and synthesized to remove 10 mg/L CBZ [70–72], in which the minimum contact time needed to remove the majority (>96%) of the CBZ was 1.5 h and its kinetic constant was 0.0473 min⁻¹. By contrast, g-C3N4 required 20 min to achieve 54.3% removal of CBZ with a kinetic constant of 0.03551 min⁻¹ in this study. The g-C3N4 has a slightly decreased kinetic constant compared to that reported for a 3D reduced graphene oxide/TiO2 [72]. Nevertheless, its advantages in material synthesis (unitary vs binary) and energy consumption (simulated solar light vs UV light) are favoured for mass production.

The results obtained in this study can be beneficial to guide the design and operation of g-C3N4 based photocatalysis as we performed experiments using environmentally relevant CBZ concentrations. CBZ has been widely detected in aqueous environments and its concentration in wastewater ranges from ng/L to µg/L levels. Most previous studies treated CBZ at the mg/L level (Table 2), which is not environmentally relevant and might have restricted predictions on whether those developed catalysts are practically effective at environmentally relevant concentrations. This work provides practical insight for future applications of g-C3N4 in WWTPs. Further efforts should be dedicated to developing a photocatalysis system with immobilized g-C3N4 for continuous treatment of real wastewater effluents.

4. Conclusions

The photocatalyst g-C3N4 was synthesized by a single-step pyrolysis method with urea as a precursor. A recalcitrant compound CBZ was selected as a model compound and experiments were conducted under environmentally relevant concentration of 100 µg/L. The results demonstrated that g-C3N4 could eliminate CBZ in MQ water as well as real wastewater effluent within 15 min. Superior degradation kinetic rate (k = 0.3662 min⁻¹) were observed, which were considerably higher than previously reported data. In addition, 9 cycles recyclability test indicated that the prepared g-C3N4 possessed good stability. ROS quenching and EPR experiments confirmed the generation of superoxide radicals (O₂⁻), holes (h⁺), hydroxyl radicals (·OH) and singlet oxygen (¹O₂). The
Table 2

Previous reported photocatalytic processes in the degradation of carbamazepine.

| Photocatalyst | Light source | Initial concentration (mg/L) | Catalyst concentration (g/L) | Time (h) | Removal (%) | Kinetic rate (min⁻¹) | Reference |
|--------------|--------------|-------------------------------|------------------------------|----------|-------------|----------------------|-----------|
| binary BiO₄ | 350 W Xenon lamp | 10 | 0.2 | 3 | 96 | not mentioned | [70] |
| ZnIn₂S₄/TiO₂ | Natural sunlight | 0.1 | 0.075 | 4 | 100 | 0.0182 | [69] |
| Nitrogen vacancy- C₃N₄/Na₂SO₃ | 500 W halogen tungsten lamp | 10 | 1 | 2 | 97 | 0.0187 | [71] |
| G-C₃N₄/ZnTePc/GQDs | Q-SUN Xe-1 (λ > 400 nm) | 4.73 | 0.1 | 5 | 96 | not mentioned | [73] |
| Protonated g-C₃N₄/BiOBr | 500 W xenon lamp | 5 | 1 | 2.5 | 96 | 0.0128 | [74] |
| BiOCl | 350 W Xenon lamp (λ > 420 nm) | 2.5 | 0.8 | 3 | 70 | 0.0698 | [75] |
| RBPO₄ | 100 W Mercury lamp | 5 | 1 | 1 | 100 | not mentioned | [76] |
| Metastable Bi³⁺ self-doped NaBiO₃ | 500 W halogen tungsten lamp | 4.73 | 1 | 0.5 | 96 | 0.087 | [77] |
| Ti₃C₂/TiO₂ | solar light simulator | 5 | 1 | 4 | 60 | not mentioned | [78] |
| Ag-SnO₂ quantum dots on silver phosphate | 300 W Xenon lamp (λ > 420 nm) | 0.5 | 0.4 | 2 | 87 | 0.017 | [79] |
| BiOCl/PdO₃ | simulated sunlight irradiation (λ > 290 nm) | 2 | 0.6 | 1 | 90 | not mentioned | [65] |
| 3D reduced graphene oxide/TiO₂ | UV light | 10 | 0.5 | 1.5 | 99 | 0.0473 | [72] |

Declaration of competing interest

The authors declare that they have no conflict of interest.

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References

[1] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters, Water Res. 43 (2009) 363–380.
[2] L.A. Schaedler, R.A. Rudel, J.M. Ackerman, S.C. Dunagan, J.G. Brody, Pharmaceuticals, perfluorosurfactants, and other organic wastewater compounds in public drinking water wells in a shallow sand and gravel aquifer, Sci. Total Environ. 468–469 (2014) 384–393.
[3] M.-Q. Cai, R. Wang, L. Feng, L.-Q. Zhang, Determination of selected pharmaceuticals in tap water and drinking water treatment plant by high-performance liquid chromatography-triple quadrupole mass spectrometer in Beijing, China, Environ. Sci. Pol. Res. Int. 22 (2015) 1854–1867.
[4] T. A. Ternes, A. Joss, H. Siegrist, Peer reviewed scrutinizing pharmaceuticals and personal care products in wastewater treatment, Environ. Sci. Technol. 38 (20) (2004), 392A–399A.
[5] A.J. Ebel, M. Abou-Elwafa Abdallah, S. Harrad, Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment, Emerg. Contam. 3 (2017) 1–16.
[6] J.M. Crisp, E.D. Clegg, R.L. Cooper, W.P. Wood, D.G. Anderson, K.P. Batecke, J.L. Hoffmann, M.S. Morrow, D.J. Rodier, J.E. Schaefer, L.W. Tousart, M.G. Zeeman, Y.M. Patel, Environmental endocrine disruption: an effects assessment and analysis, Environ. Health Perspect. 106 (1998) 11–56.
[7] M. Clevers, Aquatic ecotoxicity of pharmaceuticals including the assessment of combination effects, Toxicol. Lett. 142 (2003) 185–194.
[8] T. Wang, P.R. Gardinal, Uptake and depuration of pharmaceuticals in reclaimed water by mosquito fish (Gambusia holbrooki): a worst-case, multiple-exposure scenario, Environ. Toxicol. Chem. 32 (2013) 1752–1758.
[9] P.E. Stackelberg, E.T. Furlong, M.T. Meyer, S.D. Zaugg, A.K. Henderson, D.B. Reissman, Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant, Sci. Total Environ. 329 (2004) 99–113.
[10] D.J. Lapworth, N. Baran, M.E. Stuart, R.S. Ward, Emerging organic contaminants in groundwater: a review of sources, fate and occurrence, Environ. Pollut. 163 (2012) 287–303.
[11] M. Clara, B. Steno, N. Kreuzinger, Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of Carbamazepine in wastewater treatment and during groundwater infiltration, Water Res. 38 (2004) 947–954.
[12] T. Eggcn, M. Moeder, A. Arkukwe, Municipal landfill leachates: a significant source for new and emerging pollutants, Sci. Total Environ. 408 (2010) 5147–5157.
[13] Y. Yang, Y.S. Ok, H.K. Kim, E.E. Kwon, Y.F. Tsang, Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review, Sci. Total Environ. 596–597 (2017) 303–320.
[14] B. Petrie, J. Youdan, R. Barden, B. Kasprzyk-Hordern, Multi-residue analysis of 90 emerging contaminants in liquid and solid environmental matrices by ultra-high-performance liquid chromatography tandem mass spectrometry, J. Chromatogr. A 1431 (2016) 64–78.
[15] S. Monopelat, B. Le Bot, O. Thomas, Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water, Environ. Int. 35 (2009) 803–814.
[16] K.M. Onesios-Boyce, D. Berry, J.B. Proescher, I.K.A. Sivakumar, E.J. Bouwer, Removal of pharmaceuticals and personal care products during water recycling: microbial community structure and effects of substrate concentration, Appl. Environ. Microbiol. 80 (2014) 2440.
[17] L. Haroune, M. Salaun, A. Menard, C.Y. Legault, J.P. Bellenger, Photocatalytic degradation of carbamazepine and three derivatives using TiO₂ and ZnO: effect of pH, ionic strength, and natural organic matter, Sci. Total Environ. 475 (2014) 16–22.
[18] R.G. Eggcn, J. Hollender, A. Joss, M. Scharer, C. Stamm, Reducing the discharge of micropollutants in the aquatic environment: the benefits of upgrading wastewater treatment plants, Environ. Sci. Technol. 48 (2014) 7683–7689.
[19] Y. Zhang, S.-U. Geißen, C. Gal, Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies, Chemosphere 73 (2008) 1151–1161.
[20] R. Loos, B.M. Gawlik, G. Locoro, E. Rimavcie, S. Contini, G. Bidoglio, EU-wide survey of polar organic persistent pollutants in European river waters, Environ. Pollut. 157 (2009) 561–568.
[21] W.-J. Sim, J.-W. Lee, E.-S. Lee, S.-K. Shin, S.-R. Hwang, J.-E. Oh, Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms, hospitals and pharmaceutical manufactures, Chemosphere 82 (2011) 117–136.
[22] S. Weigel, K. Bester, H. Hünerfuss, New method for rapid solid-phase extraction of large-volume water samples and its application to non-target screening of North Sea water for organic contaminants by gas chromatography–mass spectrometry, J. Chromatogr. A 912 (2001) 151–161.
[23] X.F. Zhou, C.M. Dai, Y.L. Zhang, R.Y. Surampalli, T.C. Zhang, A preliminary study of micropollutants in the aquatic environment: the benefits of upgrading wastewater treatment plants, Environ. Sci. Technol. 48 (2014) 7683–7689.
[24] W.-J. Sim, J.-W. Lee, E.-S. Lee, S.-K. Shin, S.-R. Hwang, J.-E. Oh, Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms, hospitals and pharmaceutical manufactures, Chemosphere 82 (2011) 117–136.
[25] S. Weigel, K. Bester, H. Hünerfuss, New method for rapid solid-phase extraction of large-volume water samples and its application to non-target screening of North Sea water for organic contaminants by gas chromatography–mass spectrometry, J. Chromatogr. A 912 (2001) 151–161.
[26] X.F. Zhou, C.M. Dai, Y.L. Zhang, R.Y. Surampalli, T.C. Zhang, A preliminary study of micropollutants in the aquatic environment: the benefits of upgrading wastewater treatment plants, Environ. Sci. Technol. 48 (2014) 7683–7689.
oxidative degradation of carbamazepine by using metastable $\text{Bi}^{3+}$ self-doped NaBiO$_3$ nanosheets as a bifunctional material, Appl. Catal. B: Environ. Times 202 (2017) 528–538.

[78] A. Shahzad, K. Rasool, M. Nawaz, W. Miran, J. Jang, M. Moztahida, K.A. Mahmoud, D.S. Lee, Heterostructural TiO$_2$/Ti$_3$C$_2$Tx (MXene) for photocatalytic degradation of antiepileptic drug carbamazepine. Chem. Eng. J. 349 (2018) 748–755.

[79] Z. Duan, L. Deng, Z. Shi, H. Zhang, H. Zeng, J. Crittenden, In situ growth of Ag-SnO$_2$ quantum dots on silver phosphate for photocatalytic degradation of carbamazepine: performance, mechanism and intermediates toxicity assessment, J. Colloid Interface Sci. 534 (2019) 270–278.