Photocatalytic degradation of tetracycline by Phosphorus-doped carbon nitride tube combined with peroxydisulfate under visible light irradiation

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ABSTRACT

Photocatalysis has been regarded as a kind of environmentally friendly advanced oxidation process to eliminate pollutants. In this work, Phosphorus-doped carbon nitride tube (PCN) was synthesized via a hydrothermal calcination method and applied to degrade tetracycline (TC) through combing with peroxydisulfate (PDS) under visible light irradiation. Experimental results showed that the optimized catalysts PCN-5 exhibited superior degradation performance and reusability for TC degradation. 96.4% TC could be degraded for optimal PCN-5 with 0.3 g·L⁻¹ catalysts and 1.0 g·L⁻¹ PDS under visible light within 60 min. In addition, the degradation rate constant for TC of PCN + PDS + Vis system was still above 85% after five uses. Radical trapping experiment indicating that O₂⁻ is the dominant radical for TC degradation. The findings of this work revealed the potential application of the PCN + PDS + Vis system toward degrading contaminants in wastewater.

Key words: carbon nitride tube, peroxydisulfate, photocatalytic, tetracycline

HIGHLIGHTS

• Phosphorus-doped carbon nitride tube was successfully synthesized.
• PCN-5 + PDS + Vis system exhibited excellent TC degradation performance and reusability.
• O₂⁻ is the dominant radical for TC degradation.

INTRODUCTION

Tetracycline, as a commonly used antibiotic, has been widely used in the treatment of diseases and bacterial infections all over the world (Ahmed 2017). Tetracycline will be eventually metabolized in the body and eventually congregates into the water environment (Prashanth et al. 2021). But tetracycline is relatively stable and difficult to degrade in the environment. Tetracycline wastewater improperly treated and discharged into the environment will eventually bring potential harm to the aquatic environment and human health (Ikhlef-Taguelmimt et al. 2020). Therefore, it is significant to explore an effective antibiotic removal technology for environmental and ecological health. Over the past few decades, scientists have conducted extensive research on advanced oxidation processes (AOPs) to remove contaminants, including ozonation, photocatalysis, Fenton reaction, sono-hybrid advanced oxidation process, non-thermal plasma, and other combination technologies (Chakma & Moholkar 2016; Hama Aziz et al. 2017; Wang et al. 2020; Chauhan et al. 2021; Guo et al. 2021). Due to the advantages of effective degradation, simple operation, and low cost, these technologies are expected to be an alternative strategy for some traditional wastewater treatment methods (Chakma & Moholkar 2016; Hama Aziz 2019; Ren et al. 2019).

Graphitic carbon nitride (g-CN), as a no-metal visible responsive polymer material, has been considered a potential material for heterogeneous catalytic removal of various contaminants due to its excellent stability, appropriate band-gap, environmental friendliness, and low cost (Li et al. 2020). However, the application and development of g-CN prepared by traditional thermal polymerization are strongly restricted by its low specific surface area and the high rate of electron-hole recombination (Duan et al. 2019). Interestingly, g-CN as an inorganic material, these limitations can be overcome by elemental doping, morphology control, heterojunction, and combination with other AOP methods (Jiang et al. 2017; Gao et al. 2020;...
In the numerous modification methods, morphology control and elemental doping are considered as fruitful and promising strategies to avoid its disadvantages. Various g-CN based photocatalysts with different morphologies (including ribbons, sheets, tubes, fibers, rods, wires, particles, spheres, etc.) have been investigated. Among many morphologies, g-CN nanotubes have attracted much attention due to possessing high surface volume ratio, accelerated electron transport, and unique photochemical properties (Stroyuk et al. 2020). Moreover, elemental doping is another common process to enhance the performance of g-CN; many studies have achieved the improvement of g-CN photocatalytic performance through elemental doping including elemental sulfur, chlorine, phosphorus, oxygen, and so on (Feng et al. 2018; Hu et al. 2018; Yi et al. 2020). At the same time, photocatalytic technology combined with other AOP technologies has been widely used in decontamination in recent years, especially in the process of photocatalytic reaction by adding oxidants (mainly hydrogen peroxide, persulfate, and peroxysulfate) to improve the degradation efficiency of pollutants. Previous studies have shown that AOP technology based on peroxydisulfate (PDS) has an excellent removal effect on some pharmaceuticals due to being easily activated, inexpensive, and having storage convenience (Waclawek et al. 2017; Ding et al. 2021; She et al. 2021).

However, there are relatively few studies on the removal of TC by g-CN nanotubes photocatalytic combined with PDS. Based on the above considerations, the potential of g-CN nanotubes photocatalytic combined with PDS to remove TC is a promising strategy to be explored. Thus, Phosphorus-doped carbon nitride tube (PCN) was synthesized by facile hydrothermal calcination methods. The degradation performance of tetracycline was investigated by combined PCN with PDS under visible light irradiation, and the operating factor was also evaluated. In addition, the stability and active species of the designed PCN + PDS + Vis system were also studied. Finally, a possible photocatalytic mechanism was proposed. This work provides a novel strategy to design a contaminant removal system.

EXPERIMENTAL SECTION

Reagents

Urea, Melamine, Potassium persulfate (PDS, K2S2O8, 99.5%), and Ammonium dihydrogen phosphate ((NH4)2HPO4) were purchased from Tianjin Kemiu Chemical Reagent Co., Ltd. Sulfuric acid (H2SO4), Sodium hydroxide (NaOH), Methanol, Tert-butanol (TBA), and Ethylenediaminetetraacetic acid (EDTA) were provided by Sinopharm Chemical Reagent Corporation. Tetracycline was obtained from Shanghai Aladdin Biochemical Technology Corporation. All reagents were used without a further deal.

Synthesis of catalysts

Graphitic carbon nitride was prepared according to previous research with little modification (Yan et al. 2009). Briefly, a 50 mL crucible containing 5 g melamine was placed in a muffle furnace and kept at 520 °C for 2 h with a heating rate 5 °C min⁻¹. After cooling to room temperature, the product was collected and ground for further use.

The sample P-doped carbon nitride tube was synthesized by simple hydrothermal calcination methods. Typically, 4 g melamine and 2 g urea added to 35 mL DI water, respectively. After stirred for 30 min, a certain amount of NH4H2PO4 was added to the resulting suspension and stirred. Then, the mixed was transferred to a 100 mL Teflon-lined autoclave and heated to 200 °C for 12 h. After the autoclave cooled, the white precipitate was washed and dried at 80 °C. Finally, the precursor was put into a muffle furnace and calcined at 520 °C for 2 h with a ramp rate of 5 °C min⁻¹. After the furnace cooled down, the products were ground, collected and named PCN-X, where X represents the mass of NH4H2PO4 added (1, 3, 5, 7 g).

Characterization

The powder X-ray diffraction (XRD) was determined by the Ultima IV X diffractometer. The functional groups information (FTIR) of prepared materials was analyzed through a Perkin-Elmer Spectrum BX00 spectrometer. The X-ray photoelectron spectroscopy was measured on Escalab 250XI with an Al Kα X-ray source. The morphologies of as-prepared samples were investigated by Hitachi Sb8010 scanning electron microscope. The spectrophotometer (Shimadzu UV-2550) equipped with an integrating sphere accessory was used to obtain the diffuse reflectance spectra of the samples using BaSO4 as a reference. Photoluminescence (PL) spectra of the materials were measured by Edinburgh FL/FS 900 spectrophotometer. Electrochemical impedance spectroscopic (EIS) analysis was recorded on a CHI 660E electrochemical workstation. Pt plate and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. And the synthesized samples dispersed on 1.5 cm × 1.5 cm Indium tin oxide (ITO) glass were used as a working electrode.
Photocatalytic performance evaluation

The photocatalytic activity of the synthesized materials was studied by monitoring the degradation of a TC solution upon irradiation with visible light (>400 nm). The light source was a 300 W Xenon lamp (CEL-HXF300) equipped with a 400 nm cut off filter, the incident radiation intensity was 180 mW·cm⁻², the distance from the lamp and the reaction breaker was fixed at 15 cm. Briefly, 30 mg samples g-CN or PCN-X were added to the reaction breaker, including 100 mL TC solution (20 mg·L⁻¹). Before the photocatalytic and the addition of PDS (as oxidant), the samples were stirred in the dark for 30 min to ensure the adsorption-desorption equilibrium. The reaction TC suspension (5 mL) was taken out every 10 min and filtered using a 0.45 μm membrane filter. The concentration of TC was analyzed by a Shimadzu UV-2550 spectrophotometer at its characteristic absorbance wavelength (357 nm).

The reusability test of samples was conducted over five successive cycles using PCN-5 as reference. After each run, the catalyst was collected and washed with deionized water and methanol several times, dried at 80 °C for next run. To measure the role of active species on TC degradation, scavengers including methanol, TBA, EDTA, and cleaning N₂ were respectively added to the reaction solution before irradiation.

RESULTS AND DISCUSSION

Characterization

Figure 1(a) shows the results of X-ray diffraction characterization to investigate the structure of as-prepared samples. g-CN shows two obvious characteristic peaks at about 27.4 and 13.1 degrees, which correspond to the (002) interlayer stacking of tri-s-triazine units and (100) heptazine structure of g-CN (Reddy et al. 2019). Compared with g-CN, the peak position of PCN-X has no significant change, but the peak intensity of (002) of PCN-X decreases apparently, which may relate to the shape-dependent characteristics of materials. As previously reported, the morphologic change may decrease the order of the tri-s-triazine in g-CN (Zhang et al. 2012a; Guo et al. 2016; Hou et al. 2019). In addition, the functional groups of all samples in Figure 1(b) indicated no apparent difference between the FTIR spectrum of g-CN and PCN-X. The dense absorption bands in the range of 1,200–1,700 cm⁻¹ were associated with the stretching vibration of conjugated CN heterocycles in the g-CN frame (Bui et al. 2020). The strong characteristic signal near 810 cm⁻¹ corresponds to the stretching or bending vibration of tri-s-triazine units, which is the basic structural unit of g-CN (Zeng et al. 2018). And the broad bands in 3,000–3,500 cm⁻¹ were caused by the stretching vibration of NH₂ and NH groups in the g-CN structure or the hydroxyl substances such as water molecules absorbed on the surface (Tian et al. 2018). It’s worth mentioning that no obvious absorption bands of P – N and P – C bonds were found in the sample PCN-X, which may be related to the low phosphorus content in the materials.

This situation was verified by XPS characterization of g-CN and PCN-5. Figure 2 indicates that PCN-5 contained similar signals of C, N, and O elements to that of g-CN. The high-resolution C 1s spectrum, divided into two carbon species, the binding energies located in 284.5 eV correspond to graphitic carbon (C – C/C = C), and the signal located at the binding energies

Figure 1 | (a) XRD patterns and (b) FTIR spectra of prepared samples.
of 288.3 eV belongs to the sp² hybrid carbon in the g-CN framework (Zhang et al. 2013). Meanwhile, the information of N 1s in Figure 2(c) can be classified into three major peaks. The main peak at 398.7 eV is attributed to the C–N–C bond in the sp² hybrid nitrogen of the g-CN frame (Zhang et al. 2012b). And the characteristic peaks located at 399.9 eV and 401.1 eV are associated with the binding energies of N–(C)₃ and C–N–H in the g-CN framework, respectively (Wang et al. 2018). Additionally, a weak characteristic signal of element P existed at about 134 eV, which belongs to the typically range of P–C bond energy (Zhang et al. 2010; Sun et al. 2020). It is worth noting that the peak intensity is weak due to the small doping amount of P and these results are consistent with FTIR characterization results.

The ability of photocatalytic to utilize sunlight can affect the application of photocatalysis. Figure S1(a) presents the light absorption performance of the prepared materials g-CN and PCN-X. g-CN has obvious visible light absorption capacity in the range of 400–470 nm, and the calculated bandgap of g-CN is 2.75 eV, which is consistent with the results of previous report (Yan et al. 2009). Compared with g-CN, the visible light absorption of prepared PCN-X had a slight blue shift; meanwhile, the bandgap of PCN-5 was calculated by using the Kubelka – Munk equation:

$$\alpha h\nu = A(h\nu - E_g)^n/2$$

where \(\alpha\), \(h\nu\), and \(A\) are absorption coefficient, the energy of absorbed light and a proportionality constant, respectively. And the bandgap of PCN-5 was calculated to be 2.84 eV (Figure S2(b)), and the bandgaps of both materials are nearly equal, and the light absorption capacity is not the most critical factor in determining PCN-X’s photocatalytic performance in this experiments.
The PL spectra of g-CN and PCN-5 under the 340 nm excitation are presented in Figure 3(a). The PL intensity of PCN-5 is lower than that of g-CN, which proves that PCN-5 has better photo-generated carrier separation ability. The position of PL emission peak of PCN-5 shifted slightly to a short wavelength compared with g-CN, related to the unique morphology of PCN-5 (Zhang et al. 2016). Similar results can also be verified by electrochemical impedance spectroscopy (Figure 3(b)). PCN-5 has a smaller semicircular radius of EIS curve compared with g-CN, indicating that the transfer speed of charge carriers inside the materials is faster between electrolyte and electrode, and further demonstrating the enhanced separation and transfer efficiency of carrier produced by PCN-5 (Xiong et al. 2016).

The SEM micrographs images of prepared g-CN and PCN-5 are present in Figure 4. Figure 4(a) and 4(b) shows a typically bulk accumulation structure of g-CN, with non-uniform size distribution and obvious agglomeration (Liu et al. 2017). This
morphology may be unfavorable to the contact between photocatalytic materials and target pollutants, and therefore influence the photocatalytic degradation performance of g-CN. In contrast, there exist some tubular and sponge structure in the samples of PCN-5, and these structures are more dispersed than the agglomerated g-CN, which will be more conducive to the photocatalytic performance of PCN-5. Also, the specific surface area of prepared g-CN and PCN-5 was compared. Figure S2 indicates that the BET specific surface area of PCN-5 was calculated to be 39.58 m²·g⁻¹, which is 3.9 times larger than that of g-CN (10.19 m²·g⁻¹). Combined with the morphological characterization results, the change of the specific surface area of PCN-5 may be a result from the existence of tubular structure and spongy flocculent structure of PCN-5.

**Photocatalytic evolution**

Figure 5(a) shows the photocatalytic degradation performance of TC by prepared samples under visible irradiation without adding peroxydisulfate. Due to the limited active site of photocatalytic reaction and the high recombination rate of photo-generated carriers, the g-CN had the worst degradation effect on TC, and only 28.3% of TC could be degraded after 60 min irradiation. By contrast, the removal effect of PCN-X was improved. The degradation efficiency for TC of PCN-1, PCN-3, PCN-5 and PCN-7 were 57.3%, 70.3%, 83.8%, and 74.7%, respectively. Combining with the characterization results, the PCN-5 catalyst achieved the highest degradation effect of TC can be attributed to the following results: (1) The existence of tubular structure and spongy flocculent structure of PCN-5 increased the specific surface area, which is conductive to the contact between the catalyst and the target pollutant. (2) The recombination of photo-generated carriers on the catalyst was inhibited by proper amount of phosphorus doping. The pseudo-first-order kinetic model (Supplementary Material Equation (S1)) is the most commonly used model to analyze the photocatalytic degradation of water pollutants (such as dyes, antibiotics, and volatile organic pollutants) and it can relate the degradation rate, reaction time and pollutant

![Figure 5](image_url)
concentration. From Table S1 and Table S2, the degradation process conforms to the pseudo-first-order model ($R^2 > 0.98$). The largest pseudo first order kinetic rate constants value ($0.0316 \text{ min}^{-1}$) is corresponding to the PCN-5 sample, which is 5.96 times than that of g-CN ($0.0053 \text{ min}^{-1}$). It's worth pointing out that the absorption of TC by g-CN and PCN-X is very weak (no more than 5%) and almost negligible.

According to the above experimental results, g-CN and PCN-5 with the best photocatalytic activity were further selected as the research object. By adding a certain amount of PDS into the photocatalytic system, the degradation effect of different samples combined with PDS on TC was investigated. Figure 5(c) shows that PCN-5 combined with PDS without irradiation has no effect on the removal of TC. Only 17.6% of TC can be removed by activated PDS under 60 min irradiation. However, the degradation effect of TC increased significantly when PDS was added to both g-CN and PCN-5 reaction systems, g-CN combined with the PDS system could effectively degrade 57.4% TC after exposure to visible light for 60 min. In addition, the degradation efficiency by PCN-5 was also increased to 96.4% under the synergistic effect of PDS and catalyst. These results indicate that the combination of PCN-5 and PDS could effectively enhance the degradation performance of TC by exposure to visible light. Figure 5(b) and 5(d) present the simulated kinetics of the pseudo-first-order kinetic fitting for different reaction processes, the kinetic rate constants of PDS + Vis, g-CN + Vis, g-CN + PDS + Vis, PCN-5 + Vis and PCN-5 + PDS + Vis were $0.0032$, $0.0053$, $0.0140$, $0.0316$, and $0.0492 \text{ min}^{-1}$, respectively. The kinetic rate constants of PCN-5 + PDS + Vis was 1.4 times compared with the sum of PDS + Vis and PCN-5 + Vis. This proves that PDS and PCN-5 have a significant synergistic effect on TC degradation under visible irradiation.

**Influence of operation parameters on TC degradation**

To explore the suitable conditions for the degradation of TC in the PCN-5 + PDS + Vis system, the influence of catalyst dosage, PDS concentration, initial pH of TC solution and TC concentration were investigated. Figure S3(a) shows that with the increase of PCN-5 dosage from 5 to 30 mg, the degradation efficiency of TC also increased correspondingly, from 72.5% to 96.4%. At the same time, the removal efficiency of TC was almost the same as the efficiency of 50 mg addition when the PCN-5 addition enhances to 40 mg. This is attributed to superfluous catalysts potentially leading to higher turbidity in the suspensions, which caused lower light utilization. Hence, 30 mg was selected as the optimal catalyst dosage and applied for the following test. Figure S3(b) presents the influence of PDS concentration on the degradation of TC. When the PDS concentration range was from $0.2 \text{ g·L}^{-1}$ to $1.5 \text{ g·L}^{-1}$, the removal of TC was $86.1\%$, $92.3\%$, $96.4\%$, and $94.6\%$, respectively. This situation may be due to the limited photo-generated electrons, which were not sufficient to activate the excess PDS. $1.0 \text{ g·L}^{-1}$ was considered to be the optimal PDS concentration. Figure S3(c) indicates the influence of the initial pH on the PCN-5 + PDS + Vis system for TC degradation. As the initial pH of the reaction solution increased from 2.99 to 9.24, the degradation efficiency of TC increased at first. It then decreased and the photocatalytic degradation efficiency of TC was the highest when the pH without pre-adjustment. When the initial pH of TC solution was gradually changed from acidic to alkaline, the degradation of TC was gradually reduced. Only 76.3% of TC could be degraded at the initial pH of 9.24, which was significantly lower than that under acidic conditions. Thus, it can be concluded that acidic conditions were more conducive to the removal of TC by the PCN-5 + PDS + Vis system. The results could be analyzed from the following factors: (1) The pH of solution value on the surface charge of the catalyst, acidic conditions are more conducive to the contact between catalyst and pollutants. (2) The production of $\text{O}_2^-$ under alkaline conditions was inhibited, and therefore affected the degradation performance of TC. The degradation performance of TC with different TC concentrations in the PCN-5 + PDS + Vis system is shown in Figure S3(d). With the initial concentration of model pollutants ranged from $20 \text{ mg·L}^{-1}$ to $50 \text{ mg·L}^{-1}$, the degradation efficiency of TC after exposure for 60 min was $96.4\%$, $87.7\%$, $78.4\%$, and $64.7\%$, respectively. This phenomenon may be related to the inhibition of light absorption and the continuous accumulation of TC intermediates by high initial TC concentrations.

**Reusability and applicability of PCN-5 in the system**

The reusability of the PCN-5 + PDS + Vis system in the photocatalytic degradation of TC was investigated by selecting samples PCN-5 as the research object, and five consecutive cyclic experiments were carried out. From Figure 5(a), the removal efficiency of TC to a certain degree decreased but still remained at a high level. The photocatalytic degradation efficiency of PCN-5 for five cycle experiments was all over 85%, indicating that the prepared sample PCN-5 has good photocatalytic recyclability and reusability.
The applicability of sample PCN-5 was explored in two real river waters and single simulated Rhodamine B (20 mg·L\(^{-1}\)). Figure 6(b) shows that the removal efficiency of TC in real river water 1 and river water 2 is slightly lower than that in deionized water, which may be due to the presence of inorganic colloids, natural organic matter and ions in the real environment. Interestingly, the degradation performance of TC is still maintained at about 90%, implying the system has excellent resistance to a real water environment. Meanwhile, a certain concentration of RhB can be removed entirely by PCN-5 + PDS + Vis system within 60 min visible light irradiation, indicating that sample PCN-5 possesses good applicability in contaminant removal.

**Mechanism for PCN-5 + PDS + Vis system**

To investigate the main active radical species in degradation TC by PCN-5 + PDS + Vis system, radical scavenging experiments were conducted. The scavengers, including EDTA, t-BuOH, and purging N\(_2\), were added into the solution to investigate the effect of h\(^+\), \('OH\) and O\(_2\)\(^{•−}\) on TC degradation, respectively (Yu et al. 2020). In addition, alcohol was used as a scavenger for both SO\(_4\)\(^{•−}\) and \('OH\) (Song et al. 2020). From Figure 7, the kinetic rate constant of TC decreased slightly with the addition of t-BuOH, demonstrating that the active species \('OH\) had a small contribution to the reaction. In addition,
the kinetic rate constant of TC decreased obviously after adding EDTA and alcohol, which indicated that $h^+$ and $SO_4^{--}$ played a certain role in the degradation process of TC, but not the most important active species. In contrast, the kinetic rate constant of TC was significantly suppressed to $0.0133 \text{ min}^{-1}$ when the solution was filled with purging N$_2$, revealing that $O_2^{--}$ is the primary radical for degradation TC (Song et al. 2020). In summary, in the degradation of TC, $O_2^{--}$ plays a prominent role, $h^+$ and $SO_4^{--}$ have a secondary impact in the removal process, while the contribution of $\cdot OH$ is relatively small.

Based on the experimental results, a possible reaction mechanism for degradation TC in the PCN-5 + PDS + Vis system is proposed in Figure 8. The sample PCN-5 could be excited to generate electrons and holes after exposure to visible light. Owing to its unique tubular and spongy structure, the specific surface area and photo-generated carrier migration performance are enhanced. The enhanced specific surface area is beneficial for $e^-$ produced by PCN-5 to capture $O_2^{--}$ in the solution, promoting the generation of $O_2^{--}$ and contact with target pollutants. At the same time, the addition of PDS can also react with $e^-$ to form $SO_4^{--}$, which further inhibits the recombination of photo-generated carriers. With the extension of irradiation time, part of $SO_4^{--}$ will react with $H_2O$ to generate $\cdot OH$. Finally, the active species generated in the photocatalytic process, including $O_2^{--}$, $h^+$, $SO_4^{--}$ and $\cdot OH$, react with the TC molecules and further degrade target pollutants into small substances, CO$_2$ and H$_2$O, and so on.

CONCLUSIONS
In conclusion, PCN-X with tubular and spongy structure was successfully prepared and applied to degrade TC under visible light irradiation. The designed PCN-5 + PDS + Vis system presented excellent TC degradation performance, and the kinetic rate constant was 15.4 times and 1.6 times higher than that of PDS + Vis and PCN-5 + Vis systems, and was 1.4 times higher than the sum of PDS + Vis and PCN-5 + Vis systems. Moreover, trapping experiments demonstrated that $O_2^{--}$, $h^+$, $SO_4^{--}$ and $\cdot OH$ were involved in the degradation process of TC. The systems also processed an excellent reusability and applicability for real water environments. Therefore, it has great application prospects for degrading pollutants in practical wastewater.

DECLARATION OF COMPETING INTEREST
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGEMENTS
The work was supported by Ministry of Science and Technology of China (2016YFE0112200) and Natural Science Foundation of China (nos. 21876100).

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.
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