Adsorption and Photocatalytic Degradation of Tetracycline by Porous g-C₃N₄/TiO₂

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Research Article

Keywords: porous g-C₃N₄/TiO₂, adsorption, photocatalytic degradation, tetracycline

Posted Date: January 21st, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1172368/v1>

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Abstract

Porous g-C₃N₄/TiO₂ (MCNT) were successfully synthesized via hydrothermal-calcination method for removal of tetracycline from aqueous solutions. The as-prepared photocatalysts were characterized by XRD, XPS, SEM, TEM, and ESR. The adsorption and photocatalytic experiments show that the optimal g-C₃N₄ to TiO₂ mass ratio is 12:100 (MCNT-12). After adsorption equilibrium, 70 mg of MCNT-12 could remove 88.43% of tetracycline from 70 ml of aqueous solution (10 mg/L) under 90 min xenon lamp irradiation, and only 64.73% of tetracycline is removed by TiO₂ under the same conditions. The study shows that this is a synergistic effect of the construction of heterojunction and the adsorption of tetracycline by MCNT through multiple adsorption mechanisms. The quenching experiments and ESR characterization indicate that $\cdot\text{O}_2^-$ is the main active substance in the photocatalytic process. Four cycling photocatalytic tests and reactions in different pH solutions confirmed that the MCNT is a promising photocatalyst for environmental remediation.

Introduction

Hundreds of emerging contaminants (EC) have been discovered in water bodies in recent years (Sutherland and Ralph 2019). The majority of EC are synthetic organic chemicals, such as pharmaceuticals and personal care products, pesticides (Simon and Joshi 2021), and so on. Tetracycline (TC) are a class of broad-spectrum antibiotics that have caused resistance genes to be produced due to their widespread use in medicine, livestock, and aquaculture (Scaria et al 2021). Residues are constantly released into the environment, aiding in the spread of resistance genes among bacteria. This endangers both human health and the stability of the ecosystem (Cai et al 2021). As a result, there is an urgent need to develop suitable methods for degrading TC.

TC has a stable chemical structure and low biodegradability, making it difficult to remove completely using conventional wastewater treatment technologies (Park et al 2017). Adsorption is a cost-effective and efficient method of removing TC (Zhang et al 2021). However, the adsorbent has a limited adsorption capacity, and conventional regeneration methods can result in TC leaching. Photocatalytic regeneration can not only restore adsorption capacity but also degrade and mineralize TC. This synergistic effect contributes to the efficient removal of TC by performing adsorption and photocatalytic degradation of TC at the same time (Ajiboye et al 2021). As a result, it is critical to create new materials that have both adsorption and photocatalytic properties.

TiO₂ has been widely investigated as a photocatalyst for TC removal due to its excellent photocatalytic activity and superhydrophilicity (Wu et al 2020). The main disadvantages of TiO₂ are its agglomeration susceptibility and UV response (Pelaez et al 2012). To improve the material's adsorption/photocatalytic performance, researchers have attempted to use modification strategies such as elemental doping (Liu et al 2021; Li et al 2022), surface sensitization (Chang and Cho 2019, Goulart et al 2020), and heterojunction construction (Shi et al 2016; Li et al 2020)

Carbon-based materials have been identified as promising adsorbents and photocatalysts for removing TC from aqueous solutions (Minale et al 2020; Pandi et al 2021). As an emerging carbon material, g-C₃N₄ is made up of C,N atoms that have been hybridized with sp² to form a π -conjugated structure. It has good structural stability and a high absorption of visible light (Zhang et al 2021). Coupling g-C₃N₄ increases the electron-hole separation efficiency and significantly improves the visible light absorption properties of TiO₂. For example, Zhang et al. (2020) used quantitative analysis to demonstrate that TiO₂/g-C₃N₄ is able to achieve faster electron transfer in the presence of O-Ti-N bond. Fang et al. (2021) synthesized Co-TiO₂/g-C₃N₄ by doping Co atom as carrier transport bridge, and the oxidation rate of MgSO₃ is 3.56 times that of TiO₂/g-C₃N₄. Ma et al. (2018) constructed TiO₂@g-C₃N₄ with enhanced visible photocatalytic degradation of RhB performance attributed to the compact interfacial contact of the core-shell structure. Furthermore, the reactive sites of TC can be increased by modifying the morphology of g-C₃N₄ prior to forming the composite, which improves adsorption and photocatalytic processes (Li et al 2018).

In this work, porous g-C₃N₄ was used as a substrate for TiO₂ growth to obtain porous g-C₃N₄/TiO₂ (MCNT) catalyst. The adsorption and photocatalytic performance of MCNT was tested by investigating the removal of TC from water and the best catalyst (MCNT-12) was screened. At the same time, a possible adsorption and photocatalytic degradation mechanism was proposed.

Experimental Part

Preparation of porous g-C₃N₄

5 g of urea and 5 g of melamine were mixed and ground into a powder. After calcination at 550°C for 4 h, The lump product formed was ground to obtain a light yellow powder. It was denoted as MCN. (Wang et al 2018).

Preparation of TiO₂ and porous g-C₃N₄/TiO₂

Mix 10 ml of tetrabutyl titanate and 10 ml of anhydrous ethanol, and drop 30 ml of Mixture solution (V anhydrous ethanol: V ultrapure water = 2:1) into it under vigorous stirring. After the drop, continue to stir for 2h to obtain the TiO₂ precursor. Transfer it into 100ml Teflon-lined stainless-steel autoclave, heated at 120°C for 4h, followed by wash, dry, grind and calcine at 500°C for 2h to obtain TiO₂.

Add g-C₃N₄ powder to the TiO₂ precursor, sonicate and stir to form a mixture solution, then transferred it to a 100 ml autoclave. The subsequent steps were the same as the preparation of TiO₂. The products with different MCN: TiO₂ mass ratios of 8:100, 12:100, 16:100, 20:100 and 24:100 were denoted as MCNT-8, MCNT-12, MCNT-16, MCNT-20, MCNT-24, respectively. The synthesis process of MCNT was illustrated in Fig. 1.

Characterization

Table 1
Characterization Methods

method	Equipment Type	Role
XRD	PANalytical X'Pert PRO	Analysis of the physical phase and structure of the sample
SEM	Hitachi,S-4800	Observe the surface morphology of the sample
TEM	FEI Talos F200X	Observation of the internal lattice structure of the sample
XPS	ThermoFisher ESCAI AB 250Xi	Confirmation of the elemental composition and chemical bonding of the sample surface
ESR	BRUKER A300	Detection of free radicals generated during the reaction

Adsorption and photocatalytic degradation experiments

A quartz glass tube containing 70 mL of tetracycline solution (10 mg/L) was added with 70 mg of the sample and then placed in a reactor for adsorption and photocatalytic degradation experiments.

Adsorption experiment: 6 mL of sample solution was taken every 10 min, centrifuged twice at 8000 r/min for 5 min each time, and the absorbance of tetracycline in the supernatant was measured at 357 nm by UV-Vis spectrophotometer (A580).

Photocatalytic degradation experiments: The light source was a xenon lamp ($50 \text{ uW/cm}^2_{365\text{nm}}$). Each sample was stirred in the dark for 30 min to reach adsorption-desorption equilibrium. Under illumination conditions, 6 mL of sample solution was removed at the given time interval, centrifuged at high speed and the absorbance of tetracycline in the supernatant was measured using a UV-Vis spectrophotometer.

Results And Discussion

Characterization

XRD patterns of the three catalysts are shown in Fig. 2a. The characteristic peaks of the prepared MCN are located at $2\theta=12.90^\circ$, 27.61° . can be indexed to the $\text{g-C}_3\text{N}_4$ (100) and (002) plane, respectively. the strong XRD peak at 27.61° indicates an interlayer stacking distance of 0.32 nm for MCN, while the weaker XRD peak at 13.1° is attributed to the in-plane repetition of 3-s-triazine units (Wang et al 2009). The diffraction peaks of MCNT and TiO_2 are consistent with the appearances of (101),(004),(200),ect crystal planes in PDF#21-1272, indicating that the synthesized two samples are anatase. No diffraction peak of MCN was observed in MCNT-12. This can be attributed to the low content and low crystallinity of MCN (Ma et al 2018). The peak of MCNT is sharper than that of TiO_2 , reflecting better crystallinity.

The XPS survey spectra as shown in Fig.2b indicates the presence of C , O, Ti and N elements in the MCNT catalyst. Fig. 2c shows the fine spectrum of C 1s ,the three peaks at 284.3ev , 285.6ev and 288.0ev can be derived from C-C, C-(N)₃, N-C=N, respectively, and these results confirm the presence of MCN. The

Ti 2p XPS spectrum as shown in Fig. 2d exhibits two characteristic peaks, with binding energies of 458.1 eV and 463.8 eV, these correspond to $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$ of TiO_2 , respectively. The fine spectrum of O 1s as shown in Fig. 2e, The two peaks at 529.4 eV and 531.2 eV belong to Ti-O and H-O bonds. The OH groups on the surface of MCNT tends to form hydrogen bonds with hydrophilic TC molecules. the N 1s spectra of MCNT is shown in Fig.2f the two peaks at 397.9 eV and 401.3 eV can be assigned to Ti-N and C-NH bonds, respectively. the formation of Ti-N bond makes MCNT more resistant to photocorrosion (Cheng and Wen 2004). In addition, the peak at 399.3 eV can be attributed to O-Ti-N. Thus, despite the low N content, these results confirm that the MCN complexation with TiO_2 is successful. N can enter the TiO_2 lattice to form O-Ti-N bond, which serve as a bridge for efficient transfer of photogenerated electrons, and the presence of O-Ti-N bond further enhances the photocatalytic performance of the material (Zhang et al 2020).

Fig.3a shows the morphology of MCN and TiO_2 and their composite product MCNT, where the TiO_2 is clearly seen as sphere-like particles. MCN was synthesized as shown in equations (1)(2), where the gas generated from the thermal decomposition of urea makes MCN appear as fragmented lamellae. TiO_2 particles are uniformly distributed on the lamellae to form MCNT. MCN lamellae in MCNT are more fragmented, which is attributed to the thermal exfoliation effect from calcination (Yan et al 2020). Thus, the modified $\text{g-C}_3\text{N}_4$ has a larger specific surface area, exposing more binding sites with TiO_2 and reducing TiO_2 agglomeration. The pore structure facilitates the TC to reach the surface and interior of MCNT through the pore filling way and the deep absorption of light, which improves the adsorption and photocatalytic efficiency.

(2)

From Fig. 3b-c, it can be seen that MCNT exposes distinct lattice stripes with lattice spacing of about 0.35, 0.24 and 0.19 nm, corresponding to the (101), (004) and (200) plane of anatase TiO_2 , respectively. The results are consistent with the XRD analysis. The IFFT spectrum in Fig. 3d shows a cluster of flat and clear stripes with a lattice spacing of about 0.35 nm, which corresponds to highly crystalline TiO_2 . Fig. 3f shows the measurement of the lattice spacing for the red boxed part in Fig. 3e. The IFFT spectrum shows a cluster of fuzzy stripes and a cluster of clear stripes arranged next to each other with a lattice spacing of about 0.35 and 0.32 nm, which correspond to the (101) plane of TiO_2 and (002) plane of $\text{g-C}_3\text{N}_4$ respectively. It indicates that a tight interface is formed between MCN and TiO_2 . In other words, a heterojunction is successfully constructed (Fang et al 2020). Moreover, the low crystallinity of MCN is confirmed.

Adsorption and photocatalytic degradation performance

The adsorption and photocatalytic performance of the synthesized samples on TC are shown in Fig. 4a-b. In the absence of photocatalyst, the concentration of TC did not change significantly, indicating that the photolytic effect of TC can be negligible.

The dark adsorption rates of the composites were all larger than that of TiO_2 , and the overall variation was within 10%, which could be attributed to the π - π interaction between MCNT and the aromatic backbone of TC (Azari et al 2021). The adsorption of TC by the catalyst increased sharply in the first 10 min, and then, the adsorption gradually decreased as the remaining sites became less attractive to TC molecules, reaching saturation at 30 min. The G^0 of MCNT-12 calculated by equations (3)(4)(Sharma et al 2013) was -1.34 kJ/mol, which was in the range of -20~0 kJ/mol, confirming the presence of physical adsorption during the adsorption process.

$$K_c = \frac{q_e}{C_e} \quad (3)$$

$$\Delta G^0 = -RT \ln K_c \quad (4)$$

Where K_c represents the distribution coefficient, q_e is the adsorbed amount at equilibrium (mg/g), C_e is the TC concentration at equilibrium (mg/L), ΔG^0 indicates the change in free energy (kJ/mol), T is the temperature (K) and R is the gas constant (8.31 J/mol).

In the photocatalytic process, the photocatalytic reactions of the samples followed the pseudo-first-order kinetic, and it was observed that the photocatalytic activity of all MCNT samples was higher than that of TiO_2 , and the photocatalytic activity of MCNT was related to the MCN content. the kinetic constants of MCNT-12 were greater than those of any other samples and showed the best TC removal rate (88.43%). It may be that the MCN content is too low for the formation of tight and homogeneous heterojunction. On the contrary, the excess MCN obstructs visible light absorption.

The spectral scan Fig. 4c reflects the change of TC content, the original TC solution shows two characteristic peaks, corresponding to the wavelengths of 275 nm and 357 nm. the intensity of the two peaks gradually decreased during the adsorption and photocatalytic processes, proving the removal and degradation of TC. After 10 min of light exposure, the peak at 275 nm broadened, probably due to the generation of intermediate products. To ensure the accuracy of the measurement, the absorbance value of TC was chosen to be read at 357 nm.

Effect of calcination temperature on adsorption and photocatalytic performance

Fig. 4d-e shows the effect of calcination temperature on TC removal. In these experiments, MTCN(500) showed the best photodegradation efficiency (81.7%), indicating that high- activity anatase of MTCN is more easily formed at 500°C. the lower total removal rate of MTCN(>500) can be attributed to its lower adsorption removal rate. For MTCN (<500), the degradation rate apparently slows down after 10 min

illumination, probably due to the difficulty of degradation at low TC concentration. Therefore, the adsorption and photocatalytic degradation performance of the catalyst on TC were studied at 500 °C.

Effect of pH on adsorption and photocatalytic performance

The effect of different pH on TC removal efficiency is shown in Fig.4f-g. It is clearly that pH of the solution has a significant impact on the sample's adsorption performance on TC. When the pH is 7, it had the strongest adsorption capacity for TC (38.11%) and 91.34% removal rate of TC. This result suggests that a neutral environment favors the removal of TC by MTCN, which may be the combined effect of electrostatic attraction and repulsion. When the pH value is between 3~8, TC existed mainly in the form of TC^0 molecules, the adsorption resistance between MTCN and TC was reduced leading to a stronger adsorption capacity. When $\text{pH} > 7$, TC exists mainly in the form of negatively charged molecules. The surface of MTCN is negatively charged, and the reduced adsorption capacity is attributed to powerful electrostatic repulsion (Zhang et al 2021).

Cycle experiment

As shown in Fig.4h, after four cycles of experiments, the adsorption removal rate of TC decreased by nearly 50% compared with that of fresh MCNT, probably because of the residue of adsorbed TC or intermediate products on the catalyst surface. However, the removal rate of TC could maintain 84.34%, indicating that MCNT has good stability and reusability in the adsorption and photocatalytic degradation of TC. This is crucial for the use of MCNT for practical water treatment.

Mechanism of adsorption and photocatalytic degradation

1 mmol/L EDTA-2Na, L-ascorbic acid and terephthalic acid were added to the TC solution as quenchers of h^+ , $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ to explore the active substances that play a major role in the reaction process, respectively. The experimental results are shown in Fig.5a.

As shown in Fig. 5b, the contribution rate (Fan et al 2021) of h^+ , $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ in the photocatalytic process were 32.49%, 84.31% and 12.04%, respectively. Therefore, the order of TC degradation contribution is $\cdot\text{O}_2^- > \text{h}^+ > \cdot\text{OH}$. Therefore, it can be tentatively confirmed that the main active species in the photocatalytic process is $\cdot\text{O}_2^-$, followed by h^+ and $\cdot\text{OH}$.

To further verify the presence of $\cdot\text{O}_2^-$, ESR tests were performed as shown in Fig. 5c-d. No peak signal was observed under dark conditions, indicating that no active material was produced during the dark reaction, but the adsorption removal rate of TC was reduced to different degrees, which might be related to the competitive adsorption between the quenchers and TC. During irradiation, strong $\cdot\text{O}_2^-$ and weaker $\cdot\text{OH}$ and h^+ signals were generated and the intensity of the respective signals gradually increased. It indicates that the degradation of TC is mainly due to the continuous production of $\cdot\text{O}_2^-$ under light irradiation.

Based on these results, the mechanism of MCNT adsorption and photocatalytic degradation of TC is proposed as shown in Fig. 5e Firstly, TC is adsorbed on the porous surface of the catalyst. Secondly, under xenon lamp irradiation, MCNT absorbs photons and excites, generating electrons in the conduction band (CB) and holes in the valence band (VB). e^- on MCN(CB) is transferred to TiO_2 (CB) and interacts with dissolved O_2 to form $\cdot O_2^-$. At the same time, $\cdot O_2^-$ may continue to react with the absorbed H_2O or H^+ to produce a small amount of $\cdot OH$ radicals (Zi et al 2021). The h^+ on TiO_2 (VB) is transferred to MCN(VB). Under the action of continuously generated $\cdot O_2^-$, h^+ , and $\cdot OH$, the TC is degraded on the MCNT surface and the vacated sites will absorb and degrade the new TC molecules. This uninterrupted adsorption-photocatalytic degradation process is the key to efficient TC removal.

Conclusion

In summary, the MCNT catalyst was successfully prepared by the hydrothermal-calcination method. MCNT-12 exhibited 88.43% TC removal under irradiation, while TiO_2 removed only 64.73% of TC. Through analyzing various data, it was found that this enhanced adsorption and photocatalytic performance was attributed to the formation of a tight heterojunction between MCN and TiO_2 and the adsorption of TC by MCNT in multiple ways, including pore filling, hydrogen bonding and π - π interactions, and electrostatic attraction. Active substance quenching experiments and ESR characterization indicate that $\cdot O_2^-$ plays a major role in degradation. Furthermore, the reusability of MCNT-12 and the removal of TC under different pH conditions indicated that it has a high potential for practical application.

Declarations

Funding

This work was supported by National Natural Science Foundation of China (51672196)

Competing Interests

There are no relevant financial or non-financial interests to disclose for the authors.

Contributions

Rui Chen and Prof. Xun Wang helped to conceptualize and design the study. Rui Chen was in charge of material preparation, data collection, and analysis. Rui Chen wrote the first draft of the manuscript. Pro. Xun Wang and Pro. Lei Zhu provided feedback on previous drafts of the manuscript. The final manuscript was read and approved by all authors.

Ethical Approval

There are no ethical issues in this article.

Consent to Participate

All authors agree to participate in this paper.

Consent to Publish

All authors agree to the publication of this paper

Availability of data and materials

Correspondence and requests for data and materials should be addressed to Prof. Xun Wang

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Figures

Figure 1

The synthesis process of MCNT catalyst

Figure 2

a XRD patterns of MCN, TiO₂ and MCNT-12. XPS spectra of MCNT-12: **b** survey .**c** C 1s. **d** Ti 2p. **e** O 1s. and **f** N 1s

Figure 3

a SEM/TEM images of MCN, TiO_2 and MCNT-12. TEM images of MCNT-12 at different scales: **b** 5nm. **c** 20nm. **e** 10nm. The process of measuring the lattice spacing of **d** TiO_2 and **f** MCNT-12

Figure 4

a Effect of different catalysts on the adsorption and photocatalytic degradation of TC. **b** Spectral scan of TC removal by MCNT-12. Adsorption and photocatalytic performance of MCNT-12 under different reaction conditions **d** The effects of pH. **f** calcination temperature. **c.e** and **g** Comparison of performance parameters. **h** cycle experiment with recycled MCNT-12.

Figure 5

a Active radical quenching experiments using MCNT-12. **b** corresponding k of photocatalysis (bar, left y-axis) and the contribution rate of active substances (curve, right y-axis). ESR spectra of MCNT-12: **c** $\cdot\text{O}_2^-$. **d** h^+ and $\cdot\text{OH}$.

e Adsorption and photocatalytic degradation mechanism