



Study on Removal of Tetracycline from Water by Ag_3PO_4 and $\text{Ag}_3\text{PO}_4/\text{PU}$ Composite Membranes

Kuo Zhang¹, Hu Zhou*, Yusheng Zhang*

¹Hunan University of Science and Technology, Yuhu District, Xiangtan 411201, China

*corresponding author: Hunan University of Science and Technology, Yuhu District, Xiangtan 411201, China
zhouhu@hnust.edu.cn, yushengzhang@hnust.edu.cn

Abstract. Ag_3PO_4 is a photocatalytic material with visible light response, which has a broad application prospect in environmental treatment. However, due to its susceptibility to photocorrosion, high cost and secondary pollution in water, it is limited to some extent. Therefore, we combined Ag_3PO_4 photocatalyst with PU membrane in the way of polymer membrane loading, and obtained $\text{Ag}_3\text{PO}_4/\text{PU}$ composite photocatalyst for tetracycline removal in water. This method can not only improve the stability of the material, but also reduce the cost of use and reduce secondary pollution.

Keywords: photocatalysis, Ag_3PO_4 , $\text{Ag}_3\text{PO}_4/\text{PU}$.

1. Introduction

In recent years, with the development of society, the demand for antibiotic drugs in the public healthcare sector has been steadily increasing. At the same time, a large amount of antibiotics is being discharged into the environment, causing not only serious pollution to water bodies but also posing a potential threat to human health through bioaccumulation in organisms [1,2]. Tetracycline, as an efficient broad-spectrum prescription antibiotic, is widely used in both medical treatments and livestock farming [3,4,5]. However, due to its incomplete absorption in the body, tetracycline is primarily excreted into the environment through urine and feces [6,7]. Furthermore, tetracycline's chemical stability makes it resistant to degradation, resulting in its persistence in the environment, where it is difficult to eliminate [8,9,10]. Therefore, addressing the critical issue of removing antibiotics from water has become an urgent task.

Currently, methods for treating antibiotic-contaminated wastewater include both physicochemical and biological approaches. Among them, the most commonly used physicochemical methods are membrane separation, adsorption, photocatalysis, electrochemical oxidation, physical coagulation and precipitation, and Fenton oxidation[11]. Photocatalytic technology, as a green and efficient method, has garnered significant attention in wastewater treatment. However, conventional photocatalysts are usually in powder form, which can lead to secondary environmental pollution. In this context, photocatalytic membrane materials have emerged as an ideal solution for environmental remediation.

Polyurethane (PU) is a versatile polymer that can take various shapes and serves as an ideal substrate for the deposition of nanoparticles. Its porous structure, rich in ester groups, provides a large surface area and numerous binding sites, which facilitate the growth and attachment of nanoparticles[12,13]. The coupling of polyurethane with photocatalysts has been widely studied, and compared to powder-based materials, PU offers significant potential in terms of application and recyclability[14,15,16]. For example, Zhao et al. reported a PU/SF/GO/AgI photocatalytic membrane that, due to its improved hydrophilicity and enhanced charge separation rate, effectively removed tetracycline under visible light[17]. This highlights the feasibility of loading photocatalysts onto PU membranes for various environmental applications.

Ag_3PO_4 was a visible-light-responsive photocatalytic semiconductor material with a quantum efficiency of up to 90%. As a novel visible-light photocatalyst, it exhibited strong photocatalytic oxidation ability and potential for pollutant degradation[18,19]. However, its high cost, poor stability, and difficulty in recovery limited its practical applications in photocatalysis. Therefore, the combination of Ag_3PO_4 with PU membranes was explored to develop a more stable photocatalytic membrane material.

In this study, Ag_3PO_4 /PU photocatalytic composite membrane materials were prepared using the wet-phase transformation method and the impregnation-precipitation method. The optical properties of the Ag_3PO_4 loaded PU membranes were investigated through scanning electron microscopy (SEM), BET analysis, UV-visible diffuse reflectance spectroscopy, photocatalytic degradation experiments, and free radical capture experiments. This work provides a new perspective for the research on membrane catalytic materials for antibiotic removal.

2. Experiment

2.1 Material and reagent

Table 1. experiment reagent.

Reagents	specification	manufacturer
4-OH-TEMPO	AR	Shanghai Aladdin Industry Co., LTD.
AgNO_3	AR	Guangdong Guanghua Technology Co., LTD.
$\text{CH}_3\text{CH}_2\text{OH}$	AR	Sinopsin Group Chemical Reagents Co., LTD.
Na_2HPO_4	AR	Sinopsin Group Chemical Reagents Co., LTD.
EDTA-2Na	AR	Tianjin Guangfu Technology Development Co., LTD.
DMF	AR	Guangdong Guanghua Technology Co., LTD.
IPA	AR	Tianjin Fuyu Fine Chemical Co., LTD.
Methyleneblue(MB)	AR	Tianjin Kemiou Chemical Reagents Co., LTD.
Rhodamine B(RhB)	AR	Tianjin Kemi Ou Chemical Reagent Co., LTD.
Tetracycline(TC)	AR	Shanghai Maclin Biochemical Technology Co., LTD
Polyurethane(PU)	AR	Shanghai Maclin Biochemical Technology Co., LTD

2.2 Synthesis of the samples

2.2.1 Synthesis of Ag_3PO_4

A certain amount of AgNO_3 powder was dispersed in 50 mL ethanol solution (ethanol: water = 2:3) by ultrasound for 1 h. Dissolve an appropriate amount of Na_2HPO_4 powder in 30 mL water, then add

it to the AgNO₃ solution drop by drop, and stir away from light for 4 h. Then the suspension is filtered or centrifuged and dried in a mixing tank at 60 °C for 12 h.

2.2.2 Synthesis of Ag₃PO₄/PU

Take 6 g of PU particles, 3 g of CaCO₃ powder, and 20 mL of DMF solution, mix and stir for 4 hours to completely dissolve the particles. Then, the solution was poured onto one side of three 10 cm*10 cm glass plates wrapped with two layers of adhesive tape, and pushed flat with a glass rod. Then, the glass plates were immersed in 200 mL of 0.5 mol/L, 1 mol/L, and 2 mol/L HCl solutions for 3 hours, respectively, and then removed and soaked in clean water for 2 hours. Then, the membrane was sequentially placed in a 0.075 mol/L (100 mL) AgNO₃ solution and a 0.025 mol/L Na₂HPO₄ solution for 10 h and 2 h, respectively. Finally, remove the membrane, clean it with deionized water, and place it in a freeze-drying box for 4 hours. Remove it for use.

2.2.3 Characterization techniques

The properties of the composites were characterized by various photocatalytic analysis techniques. The structure and phase composition of the composites were investigated by X-ray diffractometer (XRD, X'Pert PRO MPD) running at A scan rate of 5°/min in the 2θ range of 5°-90° using Cu-*ka* monochromatic radiation (1.5406 Å, 45 KV, 40 mA). The surface morphology and structure of the prepared samples were characterized by scanning electron microscopy (SEM) (Hitachi Regulus8100). The optical properties of the monomers and composites were studied by visible light diffuse reflection spectrophotometer (UV-vis DRS, PE lambda 750). The absorbance of methylene blue dye in different time periods was determined by UV-1800PC (Shanghai).

2.2.4 Photocatalytic degradation experiments

The photocatalytic performance was evaluated by degradation of TC pollutants in 300W xenon lamp (CEL-HXF300) under visible light irradiation ($\lambda > 420$ nm). For each experiment, before the light source was turned on the 20 mg Ag₃PO₄ photocatalyst was dispersed into 50 mL of TC pollutants (30 mg/L). The mixture was stirred in the dark for 30min to achieve the adsorption-desorption equilibrium. During illumination, approximately 4 mL of the solution was sampled every 20 minutes, and the catalyst powder was removed using a 0.45 μm filter. The absorbance of the TC solution was measured at 357 nm using a UV-visible spectrophotometer.

The main schemes of active free radicals were determined by radical trapping experiments. According to the evaluation of reaction activity, under neutral conditions, 100 μL isopropyl alcohol (IPA), 1 mmol

EDTA-2Na and 1 mmol 4-OH-TEMPO were added to the reaction system as trapping agents for $\cdot\text{OH}$, h^+ and $\cdot\text{O}_2^-$ radicals, respectively.

3. Results and discussion

The XRD pattern was used to characterize the composition and crystal structure of the catalyst. The crystal structure and phase purity of the sample were analyzed by powder X-ray diffraction detection, and the results were shown in Fig. 1a. The prepared Ag_3PO_4 samples showed excellent sharp diffraction peaks, good crystallinity and purity. The characteristic peaks of the prepared pure Ag_3PO_4 samples were matched with the standard cubic Ag_3PO_4 (PDF#84-0192). The characteristic diffraction peaks at 33.26° , 36.54° , 54.98° and 57.26° can be observed in the XRD pattern of Ag_3PO_4 samples, corresponding to (210), (211) (320) and (321) crystal faces, respectively, which are consistent with the standard cards of Ag_3PO_4 . This indicates that the crystal morphology of the prepared Ag_3PO_4 is consistent with that of the standard cube Ag_3PO_4 .

The microstructure and structure of the prepared Ag_3PO_4 were characterized and analyzed using scanning electron microscopy, with the results shown in Fig. 1(b,c). As shown in the figure, the as-prepared Ag_3PO_4 photocatalyst was stacked in granular form, with a particle diameter of approximately 200-300 nm and a pore diameter of approximately 10-15 nm. The specific surface area, pore volume and pore size of Ag_3PO_4 were further determined by physical adsorption instrument, as shown in Table 2.

Fig. 1d showed the degradation spectra of TC solution (30 mg/L) removed by Ag_3PO_4 powder, and the TC degradation rate can reach about 80% under simulated sunlight for 1h. Fig. 1e was the first-order kinetic linear simulation curves, from which it can be seen that Ag_3PO_4 has a faster photodegradation rate. The primary active species of Ag_3PO_4 in the photocatalytic process was identified through radical trapping experiments (Fig. 1f), by using EDTA-2Na, IPA, and 4-OH-TEMPO

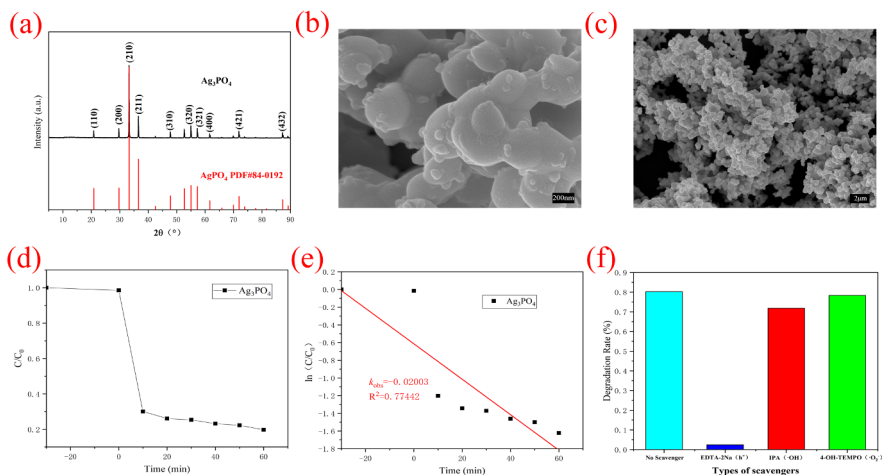


Fig. 1. (a) XRD patterns and SEM images of (b,c) Ag₃PO₄; (d) Photodegradation of TC (50 mL, 30 mg/L) by Ag₃PO₄ photocatalysts under visible-light irradiation ($\lambda > 420$ nm); (e) kinetic linear simulation curves; (f) Free radical trapping experiments of Ag₃PO₄ under different scavengers;

as scavengers for h^+ , $\cdot OH$, and $\cdot O_2^-$, respectively. After the addition of EDTA-2Na, the degradation rate of the TC solution by Ag₃PO₄ decreased by about 78% compared to no scavengers was added, indicating that h^+ was the main active species in the photocatalytic degradation process of Ag₃PO₄.

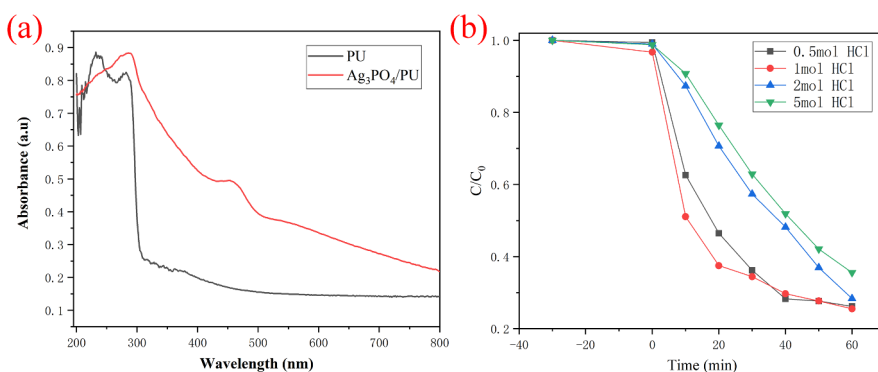


Fig. 2. (a) UV-vis DRS spectra; (b) Degradation diagram of Ag₃PO₄ loaded PU soaked with different HCl content.

The UV-vis DRS analysis was conducted to investigate the light absorption properties of the prepared Ag₃PO₄ photocatalyst and PU-Ag₃PO₄ composite photocatalyst, and the results are shown in

Fig. 2a. The absorption edge of PU is approximately at 300 nm, while the absorption edge of $\text{Ag}_3\text{PO}_4/\text{PU}$ is around 450-500 nm. As shown in the figure, the band gap of PU underwent a significant redshift upon the addition of Ag_3PO_4 . The loading of Ag_3PO_4 onto the PU membrane not only enhanced the light absorption of the photocatalytic material in the visible light range, but also prevented the secondary pollution of Ag_3PO_4 powder in water. Fig. 2b showed the degradation performance of PU-supported Ag_3PO_4 after soaking in HCl solutions of different concentrations. It was evident that during the first 20 minutes of the photocatalytic degradation stage, the $\text{Ag}_3\text{PO}_4/\text{PU}$ sample soaked in 1 mol/L HCl exhibited the best degradation rate (62.49%).

In order to highlight the photocatalytic performance and advantages of the $\text{Ag}_3\text{PO}_4/\text{PU}$ composite photocatalytic material prepared by us, relevant reports on the degradation of TC by Ag_3PO_4 based photocatalyst in recent years were summarized (Table 3).

Table 2. BET parameters of Ag_3PO_4

Materials	Specific Surface Area (m^2/g)	Pore Volume (mL/L)	Pore Diameter (nm)
Ag_3PO_4	0.5161	0.0017	13.1757

Table 3. Recent reports on Ag_3PO_4 based photocatalysts

Photocatalysts	the degradation rate of TC (30 mg/L) by $\text{Ag}_3\text{PO}_4/\text{degradation time}$	References
$\text{Ag}_3\text{PO}_4/\text{Bi-MOF}$	50% / 50 min	[20]
$\text{ZnO}/\text{GO}/\text{Ag}_3\text{PO}_4$	48% / 75 min	[21]
$\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2/\text{Ag}_3\text{PO}_4$	62% / 120 min	[22]
Ag_3PO_4	90% / 120 min	[23]
$\text{LaFeO}_3 / \text{Ag}_3\text{PO}_4$	36% / 60 min	[24]
$\text{Ag}_3\text{PO}_4 / \text{PU}$	75% / 60 min	This work

4. Conclusion

Ag_3PO_4 photocatalysts were successfully prepared by a deposition method. This material demonstrates high photocatalytic activity for tetracycline (TC) degradation, but it suffers from the

drawback of poor recoverability. By doping CaCO₃ into the PU membrane and soaking it in HCl, Ag₃PO₄/PU composite membranes with varying loading amounts of Ag₃PO₄ were obtained, with the Ag₃PO₄/PU sample soaked in 1 mol/L HCl exhibiting the best catalytic activity. Additionally, we confirmed that the main active species in the Ag₃PO₄ photocatalytic process is h⁺. The loading method not only preserves the high photocatalytic activity of Ag₃PO₄, but also overcomes its poor recoverability in aqueous environments. This provides a new approach for using membrane materials to support catalysts for the removal of pollutants from water.

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Disclosure of Interests. Specifically state that the authors have no competing interests.

References

1. Mason, C. F.: Water pollution biology. Pollution: causes, effects and control, 82-112(1996).
2. Patnaik, P.: Handbook of environmental analysis: chemical pollutants in air, water, soil, and solid wastes. Crc Press(2017).
3. Dagher, R., Drogui, P.: Tetracycline antibiotics in the environment: a review[J].Environmental Chemistry Letters, 11(3), 209-227(2013).
4. A ,W,D., A,L,J., A,J,W., A,Y,P., B,Y,Z., A,Y,W., A,B,X.: Efficient and stable photocatalytic degradation of tetracycline wastewater by 3D Polyaniline/Perylene diimide organic heterojunction under visible light irradiation[J]. Chemical Engineering Journal, 397(2020).
5. Bartolomeo,D., Antonio.: Graphene Schottky diodes: an experimental review of the rectifying graphene/semiconductor heterojunction[J].Physics Reports, 606, 1-58(2016).
6. A,H,F., A,H,Z., A,W,L., B,S,G,A., B,G,Z.: Facile fabrication of 2d/2d step-scheme In₂S₃/Bi₂O₃CO₃ heterojunction towards enhanced photocatalytic activity. Applied Surface Science, 504, 144351(2019).
7. Feng, X., Yu, Z., Sun, Y., Shan, M., Li, X.: 3D mxene/Ag₂S material as schottky junction catalyst with stable and enhanced photocatalytic activity and photocorrosion resistance. Separation and Purification Technology, 266(37), 118606(2021).
8. Fu, J., Xu, Q., Low, J., Jiang, C., Yu, J.: Ultrathin 2D/2D WO₃/g-C₃N₄ step-scheme H₂-production photocatalyst. Elsevier, (2019).
9. Guo, Feng, Shi, Weilong, Wang, & HuiBo, et al.: Study on highly enhanced photocatalytic tetracycline degradation of type II AgI/CuBi₂O₄ and z-scheme AgBr/CuBi₂O₄ heterojunction photocatalysts. JOURNAL OF HAZARDOUS MATERIALS, 349, 111-118(2018).
10. A, F,G., B, W, S., C, M, L., C, Y, S., & A, H, W.: 2D/2D z-scheme heterojunction of CuInS₂/g-C₃N₄ for enhanced visible-light-driven photocatalytic activity towards the degradation of tetracycline - sciencedirect. Separation and Purification Technology, 210, 608-615(2019).
11. Xie, X.: Physiological and potential genetic toxicity of chlortetracycline as an emerging pollutant in wheat

- (triticum aestivum L.). *Environmental Toxicology & Chemistry*, 29(4), 922-928(2010).
12. Wang, W., Cao, L., Li, Q., Du, C., & Chen, S.: Copper sulfide anchored MXene improving photo-responsive self-healing polyurethane with enhanced mechanical and antibacterial properties. *Journal of Colloid and Interface Science*, 630, 511-522 (2023).
 13. Manjunatha, C., Patil, R. S., Sudeep, M., Srinivasa, N., Kumar, R. C., Aan, M. S., & Ashoka, S.: Rational design and synthesis of hetero-nanostructured electrospun PU@PANI@ FeS₂: A surface tailored hybrid catalyst for H₂ production via electrochemical splitting of water. *Surfaces and Interfaces*, 18, 100445(2020).
 14. Sundaran, S. P., Reshmi, C. R., Sagitha, P., & Sujith, A.: Polyurethane nanofibrous membranes decorated with reduced graphene oxide-TiO₂ for photocatalytic templates in water purification. *Journal of Materials Science*, 55, 5892-5907(2020).
 15. Yang, X., Pu, Y., Zhang, Y., Liu, X., Li, J., Yuan, D., & Ning, X.: Multifunctional composite membrane based on BaTiO₃@PU/PSA nanofibers for high-efficiency PM2.5 removal. *Journal of Hazardous Materials*, 391, 122254(2020).
 16. Zou, M., Tan, C., Zhang, Y., Hu, J., Ma, Z.: Exploring the potential of flexible CdS/ZnO/Polyurethane nanocomposite membrane for wastewater remediation. *Journal of Environmental Chemical Engineering*, 11(3), 110135(2023).
 17. Zhao, X., Liu, X.: Silk fibroin protein and graphene synergistically boosting the reactive oxygen species generation of PU/AgI photocatalytic membrane for tetracycline sustained removal. *Surfaces and Interfaces*, 53, 105090(2024).
 18. Yi, Z., Ye, J., Kikugawa, N.: An orthophosphate semiconductor with photooxidation properties under visible-light irradiation. *Nature materials*, 9(7), 559-564 (2010).
 19. Bi, Y., Ouyang, S., Umezawa, N.: Facet effect of single-crystalline Ag₃PO₄ sub-microcrystals on photocatalytic properties. *Journal of the American Chemical Society*, 133(17), 6490-6492 (2011).
 20. Ji, Y., Zou, C., Wang, Y., Zhou, Z., Liu, M., Xu, Y.: Preparation of a novel Ag₃PO₄/Bi-MOF heterojunction photocatalyst for the degradation of organic pollutants under visible light irradiation. *Journal of inorganic and organometallic polymers and materials*, 34, 5791-5804(2024).
 21. Zhu, P., Duan, M., Wang, R., Xu, J., Jia, H.: Facile synthesis of ZnO/GO/Ag₃PO₄ heterojunction photocatalyst with excellent photodegradation activity for tetracycline hydrochloride under visible light. *Colloids and Surfaces A Physicochemical and Engineering Aspects*, 602, 125118(2020).
 22. Wang, P., Han, X., Zheng, X., Wang, Z., Li, C., Zhao, Z.: Removal of tetracycline hydrochloride by photocatalysis using electrospun nanofibrous membranes coated with g-C₃N₄/Ti₃C₂/Ag₃PO₄. *Molecules*, 28(6), 2647(2023).
 23. Yan, Q. S., Xu, M. M., Liu, C. P., Hu, J. F., Liu, Y. G., Zhang, R. Q.: Efficient photocatalytic degradation of tetracycline hydrochloride by Ag₃PO₄ under visible-light irradiation. *Environmental Science and Pollution Research*, 23, 14422-14430(2016).
 24. He, N., Yu, Z., Yang, G., Tan, Q., Xiang, Q. X., Liu, Y.: Selective adsorption and photocatalytic degradation of antibiotics by LaFeO₃ modified Ag₃PO₄@sepiolite composite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 672, 131712(2023).

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