

Size-Controlled Ag@UiO-66-NH₂ Nanostructures for Tetracycline Removal via Adsorption and Photocatalysis under visible light irradiation.

Ayla Roberta Borges Serra,¹ Caio Iwashita,² Osvaldo Antonio Serra^{2*}.

¹Departamento de Engenharia Química, UFSCar, São Carlos, SP, Brasil. ²Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto (FFCLRP-USP), Ribeirão Preto, SP, Brasil.

Resumo/Abstract (Helvética, tam. 12)

RESUMO - A contaminação de corpos d'água por antibióticos, como a tetraciclina, representa um desafio emergente de saúde ambiental. Neste trabalho, investigou-se a síntese, caracterização e aplicação de nanomateriais baseados em UiO-66-NH₂ modificados com íons prata (Ag) para remoção de tetraciclina via adsorção e fotocatalise sob radiação no espectro visível. Os materiais foram obtidos a partir de oxoclusters de zircônio, utilizando metodologia com regulação cinética, que permitiu o controle do tamanho de partícula (5, 40 e 200 nm). A incorporação de Ag foi confirmada por FRX (até 35%) e associada ao aumento da atividade redox. Os resultados indicam que o desempenho dos catalisadores depende fortemente do tamanho e das propriedades ópticas dos materiais. Dentre os três tamanhos testados, a estrutura de 40 nm apresentou o melhor desempenho geral, combinando elevada capacidade adsorptiva com atividade fotocatalítica sob luz solar. Ensaios de TGA e FTIR demonstraram a estabilidade estrutural dos catalisadores após os testes. Esses resultados reforçam o potencial das nanoestruturas Ag@UiO-66-NH₂ como plataformas promissoras para aplicações em fotocatalise ambiental utilizando luz solar simulada

Palavras-chave: MOFs, UiO-66-NH₂, Fotocatalise. Degradação de tetraciclina.

ABSTRACT - The contamination of water bodies by antibiotics such as tetracycline poses a significant environmental threat. In this study, we report the synthesis, characterization, and application of Ag-modified UiO-66-NH₂ nanomaterials for the removal of tetracycline through adsorption and photocatalysis under simulated solar irradiation (visible light). The materials were synthesized from zirconium oxoclusters using a kinetically controlled method that enabled particle size tuning (5, 40, and 200 nm). EDX confirmed silver incorporation up to 35%, correlating with enhanced redox properties. Photocatalytic performance was found to depend strongly on particle size and band gap. Among the tested materials, the 40 nm sample exhibited the best overall performance, combining high adsorption capacity with visible-light-driven photocatalytic activity. TGA and FTIR analyses confirmed the structural stability of the catalysts after the reaction. These findings highlight the potential of Ag@UiO-66-NH₂ nanostructures as efficient materials for environmental remediation using sunlight.

Keywords: MOFs, UiO-66-NH₂, Photocatalysis, Tetracycline degradation.

Introduction

Pharmaceutical pollutants like tetracycline pose serious ecological risks due to their persistence and contribution to antimicrobial resistance. Up to 75% of administered tetracycline is excreted unmetabolized, accumulating in water systems where conventional treatments are ineffective.

Photocatalysis offers a promising route for degrading such compounds under mild, solar-driven conditions. Metal-organic frameworks (MOFs), especially UiO-66(Zr), are attractive photocatalysts due to their structural robustness and tunable functionality. The amino-functionalized UiO-66-NH₂ variant improves visible-light absorption and allows further modification. Nonetheless, limitations such as poor charge separation and fast recombination reduce its catalytic efficiency. To address this, Ag incorporation has been explored to enhance redox activity, while particle size

reduction can further improve light harvesting and interfacial reactivity.

In this work, we investigate Ag@UiO-66-NH₂ nanostructures with controlled sizes (5, 40, and 200 nm) for tetracycline degradation under simulated solar light. Emphasis is placed on understanding how structural and optical properties govern photocatalytic performance. Among the materials, the 40 nm sample demonstrated superior efficiency, combining effective light-induced degradation with structural stability — highlighting its potential for solar-driven environmental remediation.

Experimental

Ag@UiO-66-NH₂ nanostructures were synthesized via a kinetically controlled route using pre-formed zirconium oxoclusters, enabling precise size control (5, 40, and 200 nm) through solvent ratio adjustments. The framework

was built using 2-aminoterephthalic acid, and the solids were recovered by centrifugation, washed, and vacuum-dried. Post-synthetic Ag incorporation was carried out by impregnation with AgNO₃ solution (1 mol·L⁻¹), followed by washing. EDX confirmed silver content up to 35.5 wt%. Photocatalytic tests were performed under simulated solar light using a ULTRA-VITALUX lamp and tetracycline solutions (30 mg·L⁻¹). Catalyst suspensions were stirred, and aliquots were analyzed by UV-Vis spectrophotometry ($\lambda = 363$ nm). Additional tests at lower catalyst doses were conducted to distinguish adsorption from photodegradation. The materials were characterized by UV-Vis (DRS), FTIR, TGA, and EDX, before and after catalysis, to evaluate optical properties and structural stability.

Results and Discussion

The photocatalytic activity of Ag@UiO-66-NH₂ nanostructures was evaluated under simulated solar light, focusing on the effects of particle size and structural features. In tests using 12.5 mg of catalyst (Figure 1a), the 40 nm material completely removed tetracycline during the dark adsorption phase, precluding assessment of its photocatalytic behavior. Conversely, the 200 and 5 nm samples showed partial adsorption, enabling their light-induced degradation capacity to be evaluated.

To isolate the photocatalytic effect of the 40 nm sample, a second experiment was conducted using only 5.0 mg of catalyst (Figure 1b). Under these conditions, residual tetracycline remained in solution after adsorption, and a significant decrease in concentration was observed upon illumination, confirming the material's photocatalytic efficiency beyond its high adsorption capacity.

Catalytic performance varied significantly with particle size, band gap, and crystallinity. The 5 nm MOF, despite its high surface area (940 m²·g⁻¹), exhibited poor activity due to its broad band gap (>3.6 eV) and reduced long-range order. The 200 nm sample, with a lower band gap (~2.80 eV) and sharper PXRD peaks, showed better light absorption and structural integrity, but limited surface area (496 m²·g⁻¹) hindered its adsorption performance. The 40 nm catalyst achieved the best balance: moderate surface area (660 m²·g⁻¹), adequate crystallinity, and an intermediate band gap suitable for visible-light activation. PXRD analysis confirmed a loss of crystallinity in smaller particles. The 5 nm sample exhibited only broad features, while the 40 and 200 nm materials retained well-defined diffraction peaks, essential for efficient charge transport and photocatalytic function. EDX analysis indicated Ag incorporation near 35.5 wt%, consistent across samples. Silver plays a key role in enhancing photocatalytic activity by facilitating electron-hole separation and promoting reactive oxygen species (ROS) generation under light.

Post-reaction FTIR and TGA analyses supported the structural stability of the catalysts. FTIR spectra showed

new bands near 1600 cm⁻¹ in the 40 and 200 nm samples, suggesting surface-bound intermediates. TGA curves remained unchanged, indicating thermal robustness and reusability.

These results demonstrate that MOF photocatalytic performance depends not on surface area or band gap alone, but on the interplay of crystallinity, light absorption, and interfacial reactivity. The 40 nm Ag@UiO-66-NH₂ sample achieved the best balance of these factors, showing high efficiency and structural stability under visible light, confirming its potential for solar-driven water treatment applications.

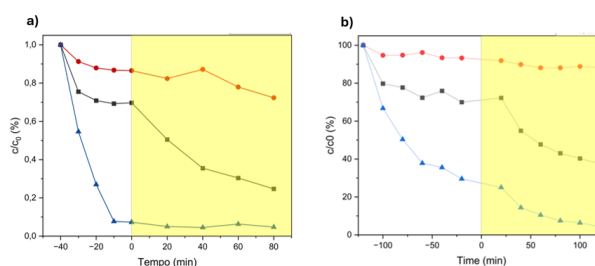


Figure 1. Tetracycline degradation under simulated solar light using Ag@UiO-66-NH₂. (a) 12.5 mg: full adsorption. (b) 5.0 mg: photocatalytic activity observable after partial adsorption.

Conclusion

The 40 nm Ag@UiO-66-NH₂ nanostructure showed the best photocatalytic performance for tetracycline degradation under simulated solar light, balancing surface area, crystallinity, and visible-light absorption. A two-step testing strategy confirmed its photocatalytic contribution beyond adsorption. Despite higher surface area, the 5 nm material underperformed due to poor crystallinity and wide band gap. Structural stability was confirmed post-reaction by FTIR and TGA. These results emphasize the importance of tuning size and electronic structure to optimize MOF-based photocatalysts for environmental remediation using solar-driven heterogeneous catalysis.

Acknowledgments

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