

Photocatalytic degradation of Nylon 6 microplastics using TiO₂@(Cu/Fe) HKUST-1 composite under UV-Visible radiation

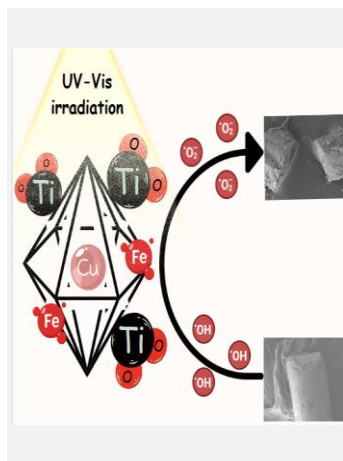
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The heterogeneous photocatalysis (HP) using TiO₂@(Cu/Fe)HKUST-1 15 wt% composite was evaluated in the Nylon-6 microplastics (N6MPs) removal at pH 7 under UV/Vis radiation. The TCFH85:15 was synthesized via a solvothermal route and characterized by the XRD, SEM-EDS, N₂ physisorption, and UV-Vis/DRS. The photocatalytic activity of TCFH85:15 in the degradation of N6 was monitored by measuring the TOC concentration in the solution and the turbidity of the suspension. Incorporating (Cu/Fe)HKUST-1 into TiO₂ increased the surface area and the crystallite size and decreased the E_g value (from 3.16 to 2.83 eV), favoring the material's activity in the visible region. The TCFH85:15 photocatalyst exhibited enhanced performance on the N6MPs degradation than TiO₂, allowing the reduction in the turbidity ratio (0.24) and the increase in TOC (11.38 mg/L) related to water-soluble compounds generated during degradation. In contrast, the N6MPs were slowly degraded by TiO₂-based photocatalysis (turbidity ratio = 0.58, TOC content = 8.85 mg/L).

Introduction

Approximately 0.85 million tons of polyamides were generated in 2020 [1]. Nylon-6 (N6), a semicrystalline polyamide, is widely used in pharmaceutical and textile industries owing to its good mechanical properties [2]. In 2019, SEM analysis evidenced the presence of N6MPs (MPs < 5 mm) in two water treatment plants located in Valle de Bravo, Mexico [3]. In this sense, HP has been described as a useful treatment technology for removing MPs from water due to its high efficiency, low cost, and operation facility. The HP has been used to eliminate different polymer types of MPs, including N6, using TiO₂ photocatalyst [3]. The coupling of TiO₂ with metal-organic frameworks (MOFs) such as HKUST-1(Cu) is a strategy to enhance the surface area, increase absorption in the visible region, and decrease the recombination rate of electron-hole pair, improving the TiO₂ photocatalytic performance. The incorporation of Fe on HKUST-1(Cu) enhances its water and thermal stability, maintaining its photocatalytic response in the visible region of the spectrum. Therefore, the TiO₂ with a bimetallic (Cu/Fe)HKUST-1 composite was synthesized for the N6MPs photocatalytic removal under UV/Vis radiation.

Material and Methods

(Cu/Fe)HKUST-1 was synthesized by a solvothermal method where Cu(NO₃)₂•3H₂O, FeCl₃•6H₂O using Cu:Fe 95:5 molar ratio and 1,3,5-benzenetricarboxylic acid were dissolved in ethanol/DMF (1:1) and heated at 110°C for 12 h. The

composite with 15 wt% of (Cu/Fe)HKUST-1 (coded as TCFH85:15) was prepared by solvothermal route by adding titanium (IV) butoxide and the MOF in ethanol/2% acetic acid. This suspension was heated at 180°C for 18 h. The same procedure without incorporating (Cu/Fe)HKUST-1 was used for the TiO₂ synthesis. The as-prepared materials were washed with ethanol and dried at 70°C for 12 h; the MOF was activated at 110°C for 12 h; the composite and TiO₂ were calcined at 350°C for 2 h. The catalysts were supported on borosilicate glass slides by coating the glass slide with a slurry prepared in 2% (v/v) isopropanol/acetic acid (1:1) and then annealing at 350°C for 2 h.

The materials were characterized by XRD, N₂ physisorption, UV/DRS, and SEM.

For photocatalytic experiments, a suspension of 0.2 g/L of N6MPs adjusted to pH 7 using 0.1% NH₄OH was collocated in a reactor with the catalyst supported on the glass slide (1 g/L of catalyst) and then irradiated under UV-Vis light (Philips lamp, 300-700 nm) for 5 h. Samples taken during the reaction were analyzed for turbidity (Lovibond TB 250 WL portable nephelometer). The total organic carbon (TOC) content was determined using a TOC analyzer (TOC-VCSH, Shimadzu).

Results and Discussion

The X-ray diffraction pattern for the (Cu/Fe)HKUST-1 sample exhibited the characteristic peaks of the MOF [4], confirming the successful synthesis (Figure 1). When the MOF was thermally treated, it produced the CuO in the monoclinic structure

(JCPDS No. 48-1548). The TiO₂ and TCFH 85:15 composite presented a diffraction pattern corresponding to the anatase crystalline phase (JCPDS no. 73-1764) [5]. No additional peaks of copper or iron were found, implying that the metal species are highly dispersed in the TiO₂ or the Cu and Fe are below the XRD detection limit.

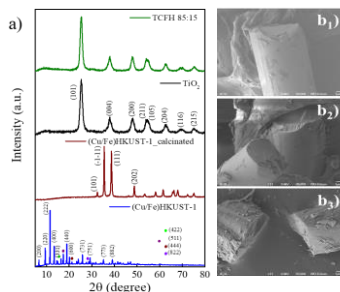


Figure 1. a) Diffractograms of (Cu/Fe)HKUST-1, (Cu/Fe)HKUST-1 calcined, TiO₂ and TCFH85:15 composite. b) SEM images of N6MPs (b1) before (b1) and after (b2) photocatalysis and (b3) photocatalytic treatment with TCFH 85:15.

The average crystallite size determined using the Scherrer equation (Table 1) evidenced that (Cu/Fe)HKUST-1 incorporation in TiO₂ increased the crystallite size, possibly due to an exchange of titanium, copper, and iron atoms inside the crystal structure, which have different ionic radius of 0.68, 0.73, and 0.64 Å, respectively.

The pore size distribution values (Table 1) showed that mesopores were predominant for the as-prepared materials. Incorporating (Cu/Fe)HKUST-1 into the TiO₂ slightly increased the surface area of the catalyst since the MOF was converted into CuO

during thermal treatment. The band gap energy calculated using the Kubelka-Munk function and Tauc plots (Table 1) showed that coupling (Cu/Fe)HKUST-1 into TiO₂ reduced the band gap energy from 3.16 to 2.83 eV, showing activity under visible light.

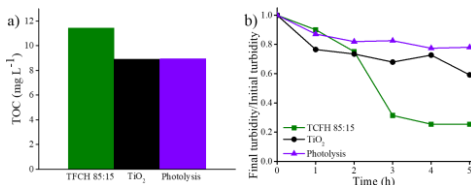


Figure 2. a) TOC content and b) turbidity at the end of the treatment using TCFH85:15, TiO₂, and photolysis control.

The effectiveness of the HP (TFCH85:15/UV-Vis) in N6MPs oxidation was assessed using a turbidity TOC analyzer and SEM. The TOC content (Figure 2a) increased during TFCH85:15/UV-Vis HP (11.42 mg/L) related to the water-soluble compounds generated during MPs oxidation. In contrast, direct photolysis and TiO₂-mediated photocatalysis slowly degraded MPs, 8.91 and 8.94 mg/L, respectively. Additionally, the turbidity ratio related to N6 fragmentation was high using TFCH85:15 photocatalyst (0.24) compared to the direct photolysis and TiO₂-mediated photocatalysis (0.78 and 0.59, respectively) (Figure 2b).

The SEM images of the N6MPs before and after the photolysis process showed that the N6 fibers were cavity-free. On the other hand, the N6MPs showed the presence of small cavities in the surface during the TCFH85:15 photocatalytic process, which resulted from the radicals' attack, generating volatile products that evolved from the polymer.

Table 1. Physico-chemical properties of the synthesized catalysts.^a

Material	Crystallite size (nm)	Specific surface area (m ² /g)	Pore size (nm)	Eg (eV)
(Cu/Fe)HKUST-1	493.8	871.46	5.75	2.86
TiO ₂	51.1	152.09	9.13	3.16
TCFH85:15	58.5	161.95	9.21	2.83

Conclusions

The incorporation of (Cu/Fe)HKUST-1 in TiO₂ increased the crystallite size and surface area and improved the activity of TiO₂ in the visible region of the spectrum, being the material with the highest photocatalytic activity in the degradation of N6 the TiO₂@(Cu/Fe)HKUST-1 at pH=7. HP was shown to be an efficient and viable alternative for removing N6MPs in water effluents, making it a promising option for the disposal of plastics in the environment.

Acknowledgments

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References

- [1] Plastics Europe and EPRO, Plastics - the Facts 2021 (2021).
- [2] L. Ye, X. Liu, K.B. Beckett, J.O. Rothbaum, C. Lincoln, L.J. Broadbelt, Y. Kratish, T.J. Marks, *Chem.*, 10 (2024) 172.
- [3] W. Hamd, E.A. Daher, T.S. Tofa, J. Dutta, *Front. Mar. Sci.*, 9 (2022) 885614.
- [4] M. Xiaobo, L. Xinyu, Z. Jie, H. Xiaoxian, Y. Weichun, *Environmental Technology*, 42(26) (2021) 4134.
- [5] P. Goyal, A. Paruthi, D. Menon, R. Behara, A. Jaiswal, V. Keerthy, A. Kumar, V. Krishnan, S.K. Misra, *Chem Eng J.*, 430 (2022) 133088.