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Fabrication of a Porous Nanoplatform for Controlled Delivery of Agrochemicals to Plants

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ABSTRACT

Modern agriculture faces challenges due to the inefficiency of traditional agrochemical application methods. These methods suffer from low selectivity and high loss of active ingredients into the environment. Such inefficiencies limit agricultural productivity and accelerate farmland degradation. In this context, the development of smart delivery systems has become a critical priority, playing a decisive role in ensuring future food security. Metal-organic frameworks (MOFs) represent a promising class of materials for agrochemical delivery systems due to their high porosity, tunable functionality, and diverse chemical compositions. In this study, we selected a stable zirconium-based MOF UiO-66-NH_2 with 2-aminobenzene-1,4-dicarboxylate (BDC-NH_2) ligands as a platform. Its high sorption capacity enables efficient drug loading and controlled release, while surface modification offers opportunities to develop biocompatible coatings that enhance rhizosphere accumulation and interaction with agrochemicals. UiO-66-NH_2 was synthesized by dissolving $ZrCl_4$ in dimethylformamide (DMF), followed by the addition of water and BDC-NH_2 at a molar ratio of $ZrCl_4$: BDC-NH_2 : H_2O : DMF of 1 : 1 : 3 : 300. The reaction mixture was maintained at 120°C for 24 h. The precipitate was isolated, washed, and dried. For surface modification, UiO-66-NH_2 was treated with an aqueous polyvinylpyrrolidone (PVP) solution (1 mg/mL) at room temperature for 24 h. Methylene blue (MB) dye uptake was monitored via optical spectroscopy. PVP coating did not induce structural changes or impurity phases in UiO-66-NH_2. FTIR spectra revealed intense bands at 2850 and 2920 cm^{-1}, attributed to CH_2 groups in PVP. In neutral media, PVP exhibits a negative ζ-potential due to electron density delocalization from nitrogen atoms, while UiO-66-NH_2 has a ζ-potential of +42 mV in aqueous suspension. This electrostatic attraction ensures successful PVP coating. UV-Vis spectroscopy showed that UiO-PVP effectively adsorbed MB in alkaline conditions (pH > 7) but exhibited negligible uptake in acidic media (pH < 6). MB release occurred at pH < 6 and pH > 9. The mechanism is governed by the following processes. In alkaline conditions (pH > 7) neutral MB molecules are absorbed via MOF pores and hydrogen bonding with PVP. When pH is less than 6, positively charged MB is repelled by the cationic UiO-66-NH_2 surface. XRD confirmed UiO-66-NH_2 stability in acidic media but degradation in strong alkali, explaining MB release at high pH due to framework collapse. Thus, we developed a nanoplatform for controlled agrochemical delivery, demonstrating its sorption kinetics and pH-responsive release using MB as a model compound.

Keywords: metal-organic frameworks, synthesis, porosity, agrochemical delivery systems

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