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Synthesis, Characterization, and Photocatalytic Potential of *meso*-Porphyrins Derived from Cardanol and Vanillin in the Reduction of 4-Nitrophenol.

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Abstract

Heterogeneous photocatalysis is a critical industrial process with applications in toxic waste treatment, environmental impact mitigation, and resource efficiency, supporting sustainable chemistry. Recent research has sought efficient heterogeneous catalysts, with porphyrin-type macromolecules emerging as promising due to their chemical stability, visible light absorption, and electron-capturing properties. This study aimed to synthesize a new meso-porphyrin derived from cardanol and vanillin, along with its zinc (Zn) and copper (Cu) metalated analogs, evaluating their potential in the heterogeneous photocatalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in aqueous solutions. The meso-porphyrins-cardanol-vanillin (PCV) and its metalated analogs (Cu-PCV and Zn-PCV) were synthesized using cardanol, the main component of cashew nut shell liquid (CNSL), and vanillin, derived from lignin, both sourced from regional biomass, and characterized by ^1H NMR, FT-IR, and UV-Vis spectroscopy. The photocatalytic reduction of 4-NP was studied with each catalyst using an aqueous solution of 4-NP and excess NaBH4 as the reducing agent, with UV-vis measurements taken every 30 minutes. The synthesis was successful, yielding pure PCV and its Zn and Cu analogs with good efficiencies (precursors: 65%, meso-porphyrin: 59%, Cu-PCV: 89%, Zn-PCV: 73%). During reduction, a decrease in absorbance at 400 nm (p-nitrophenolate ion) was observed, with a simultaneous rise at 300 nm, indicating 4-AP formation. Cu-PCV completed the reduction in 90 minutes, while Zn-PCV required 150 minutes, demonstrating the catalytic efficiency of these metal-porphyrins in electron transfer and charge separation. These results highlight the effectiveness of metallated porphyrins in electron transfer, essential for the separation of photogenerated charges, which enhances photocatalytic performance. The presence of metals in the porphyrin structure boosts this charge separation, making the new Zn- and Cu-PCV promising, sustainable catalysts with significant potential for effluent remediation and the treatment of contaminated wastewater.

Keywords: meso-porphyrins, cardanol, vanillin, heterogeneous photocatalysis.

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