



Hierarchical NiFe-LDH@ZIF-67 with optimized pore chemistry for multi-pollutant adsorption: Integrating DFT and machine learning for industrial water remediation

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ABSTRACT

This study develops a NiFe-LDH@ZIF-67 composite for efficient co-adsorption of methyl green (MG, 239.05 mg/g) and oxytetracycline (OTC, 147.39 mg/g) in various water matrices. Comprehensive characterization (FTIR, SEM-EDS, XRD, XPS, TGA) confirmed the material's structural integrity. Adsorption followed pseudo-second-order kinetics ($R^2 > 0.98$) and Langmuir isotherms, with MG showing higher affinity due to stronger electrostatic and π - π interactions. Real-water tests demonstrated superior performance in tap water (231.34 mg/g) versus lake water (209.61 mg/g), with faster kinetics ($\alpha = 899.501$ vs 485.279). The composite exhibited excellent reusability (>95 % efficiency after 5 cycles) and stability post-regeneration. Computational studies revealed binding energies of -1.54 eV (MG) and -1.21 eV (OTC), with hydrogen bonding (N/OH...O) driving preferential adsorption of MG. An optimized ANN model predicted optimal conditions (pH 6, 40 °C) with < 5 % error, facilitating industrial scale-up. The work combines experimental validation with multiscale simulations (DFT/Monte Carlo) to establish structure–property relationships, while machine learning enables process optimization. This integrated approach advances the design of hybrid adsorbents for practical water treatment applications, addressing key challenges of selectivity and stability in complex wastewater systems. The study provides both fundamental insights into adsorption mechanisms and a practical framework for developing efficient, reusable materials for multi-pollutant removal.

Introduction

Water pollution by industrial effluent, particularly cationic dyes (e.g., methyl green, MG) and antibiotics (e.g., oxytetracycline, OTC), threatens ecosystem and human health [1,2]. MG, a cationic dye used in textiles, paper, cosmetics, and biological applications [3], can cause severe health effects, including cancer, genetic mutations, and neurological disorders, while also disrupting natural nutrient cycles in ecosystems. Similarly, OTC, a broad-spectrum antibiotic extensively used in human medicine, veterinary practices, and aquaculture to treat bacterial infections [4]. However, its widespread use and improper disposal have led to significant environmental and health hazards [5,6]. OTC persists in the environment, due to its non-degradable nature, promoting the

proliferation of antibiotic-resistant bacteria and antibiotic-resistance genes [7]. Furthermore, it has a high level of residual toxicity. Both pollutants are highly persistent, toxic, and resistant to conventional degradation methods, making their removal from wastewater a critical challenge [8].

Conventional wastewater treatment methods, including chemical coagulation [9], ion exchange [10], photocatalysis [11–13], and catalytic oxidation [14], often fail to completely remove these persistent pollutants due to their complex structures and low efficiency. Among available technologies, Adsorption has gained significant interest due to its simplicity, excellent efficiency, and affordability. However, traditional adsorbents like activated carbon [15,16], clay minerals [17,18] and zeolite [19] suffer from limitations such as low selectivity, poor

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