Synthesis of high-molecular-weight poly (itaconic-co-methacrylic acid) copolymers for fabrication of nanocomposite hydrogels for cationic dyes removal

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This study reports the synthesis and characterization of copolymers of itaconic acid (IA) and methacrylic acid (MAA) as precursors for fabricating physically and ionically crosslinked nanocomposite hydrogels (NCHs) for cationic dye removal. Copolymers were synthesized via free-radical polymerization in a deep eutectic solvent using VA-044 as initiator, yielding high-molecular-weight polymers characterized by NMR, IR, and TGA. Thermal analysis revealed four degradation stages, with increased MAA content enhancing thermal stability at early decomposition stages, while poly(itaconic acid) showed the highest thermal resistance and char yield.

Hydrogels were formed with Laponite RD, resulting in stable, elastic 3D networks (G′ > G″). Higher IA content correlated with increased stiffness, while high MAA content reduced mechanical integrity. WAXS/SAXS and TEM confirmed complete clay exfoliation and polymer intercalation, with further basal spacing expansion upon dye adsorption, indicating dye intercalation between platelets.

Swelling behavior varied with ionic conditions: hydrogels expanded significantly in deionized water but shrank in saline solutions, particularly in $CaCl_2$, where swelling was reduced by 60%. Batch adsorption tests using basic fuchsin (BF) showed 99.5% removal under optimized conditions with only 0.2 g L^{-1} of adsorbent. Kinetic modeling indicated that adsorption followed a pseudo-first-order model (physisorption). Thermodynamic analysis confirmed the process was spontaneous and exothermic ($\Delta H° = -39.19$ kJ mol^{-1}), with decreased entropy—hallmarks of physical adsorption. IR and NMR analyses supported the physisorption mechanism.

Calcium ion co-crosslinking significantly enhanced hydrogel mechanical strength and reduced swelling, enabling efficient reuse. Reusability tests demonstrated BF removal (99.2 ± 0.2%) over five adsorption–desorption cycles. Overall, IA/MAA-based NCHs offer a green, robust, and reusable platform for efficient removal of cationic dyes from wastewater, highlighting their potential for sustainable water treatment applications.

Keywords: Itaconic acid, deep eutectic solvents, adsorption, cationic dyes, organic-inorganic composite, Freundlich isotherm.

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