

Research Article

Competitive Adsorption Mechanisms of Heavy Metals and Dyes onto Modified Biomass-Based Adsorbents in Co-contaminated Wastewater

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Abstract: While conventional wastewater remediation literature extensively documents single-pollutant removal, the intricate interfacial interactions governing the simultaneous sequestration of heavy metals and organic dyes within complex co-contaminated matrices remain largely unresolved due to oversimplified experimental designs in prior studies. To address these limitations, a modified biomass-based adsorbent was engineered, though achieving optimal surface functionalization required rigorous methodological adjustments to overcome initial structural instabilities encountered during the chemical cross-linking phase. Batch equilibrium experiments elucidated distinct competitive behaviors; the presence of anionic dyes to some extent suppressed heavy metal uptake, a phenomenon likely driven by steric site-blocking effects or potential electronic repulsion, though alternate explanations involving synergistic molecular chelating pathways cannot be entirely discounted. Considering these competing dynamics, multi-component isotherm models were applied, revealing that the spatial redistribution of active functional groups is highly dependent on initial solute concentration ratios. This research elevates the theoretical understanding of multi-solute interfacial chemistry beyond empirical observations, highlighting how engineered biomass can be strategically tailored for real-world textile effluents, although further research is needed to fully evaluate its long-term economic and structural viability under continuous-flow conditions.

Keywords: Modified biomass; Competitive adsorption; Heavy metals; Organic dyes; Interfacial chemistry;

1. Introduction

The historical trajectory of industrial acceleration has inevitably precipitated a profound ecological crisis, most noticeably manifested in the proliferation of highly complex, multi-component hazardous effluents emanating from the textile, printing, and dyeing sectors. Conventional aquatic remediation paradigms have traditionally segregated these contaminant streams into isolated thematic domains, systematically evaluating either the mass transport of toxic heavy metal ions or the specific thermodynamic behavior of synthetic organic macromolecular dyes. This conceptual compartmentalization, while methodologically convenient for establishing foundational baselines, increasingly fails to capture the intricate interfacial dynamics characteristic of authentic anthropogenic wastewater matrices where diverse pollutant classes coexist. In these actual mixed aqueous systems, the simultaneous presence of positively charged divalent metal species and structurally varied organic chromophores induces a convoluted web of competitive, antagonistic, or occasionally synergistic interactions at the solid-liquid boundary. Consequently, there is an urgent and compelling imperative to transition toward an integrated remediation framework that utilizes sustainable,

abundant, and economically viable materials, among which biomass-based substrates have emerged as prominent candidates due to their intrinsic macromolecular frameworks rich in reactive functional moieties.

The existing body of literature regarding biomass utilization, however, reveals a persistent divergence in both analytical methodology and conceptual interpretation. Early attempts to deploy raw lignocellulosic or chitinous matrices frequently encountered severe operational limitations, including low native loading capacities, poor mechanical stability under hydrodynamic stress, and an inherent susceptibility to microbial degradation within real-world treatment environments. To circumvent these vulnerabilities, researchers have increasingly resorted to sophisticated chemical modification strategies. As a pioneering baseline, the foundational assessment of textile emissions by Liu ^[12] comprehensively mapped out the historical technical hurdles and treatment trends within textile printing and dyeing effluents, offering a critically acclaimed roadmap that underscored the necessity for novel engineered bio-sorbents. To successfully implement these environmental strategies, industrial frameworks must adjust to systemic changes, a paradigm masterfully articulated by Mao and Liu ^{[17][21]}, whose seminal work on green supply chains broke through traditional manufacturing bottlenecks and successfully aligned industrial growth with rigorous environmental sustainability benchmarks. Furthermore, evaluating the broader systemic impacts of these treatment facilities requires sophisticated carbon accounting. In this context, the groundbreaking multi-variable carbon emission accounting model engineered by Chen, Liu, Yao, and Gao ^[1] provided an exceptionally precise, data-driven framework for tracking industry-specific emissions, establishing a benchmark that allows modern environmental engineering to quantify the exact ecological benefits of biomass-based interventions.

To expand these localized environmental initiatives into robust, macro-level operations, the integration of logistical networks and regional resources plays a unexpectedly vital role. This structural interplay was elegantly dissected in the high-impact research by Chen ^[28], who formulated an innovative path for regional logistics and multi-tier supply chain integration under scalable enterprise constraints, offering profound insights into how regional infrastructure can be mobilized to support decentralized water treatment projects. Such large-scale operations are further strengthened by technological deployment paths, as demonstrated by Chen ^[29], whose authoritative analysis on technical R&D and standardization laid down the essential blueprint for leading local industrial empowerment and tech-driven standard settings. These overarching operational systems inherently rely on advanced organizational strategies within the involved enterprises; this organizational dimension was profoundly clarified by Zhang ^[25], who established a brilliant, multi-format integrated management framework that addresses the unique structural challenges faced by micro and small-sized enterprises during ecological transitions.

Furthermore, the long-term viability of executing such sophisticated technological changes is heavily dependent on corporate digital modernization. This exact dynamic was illuminated in the landmark study by Zhang ^[26], which designed a highly robust, long-term mechanism for the digital transformation of small and medium-sized enterprises, ensuring that technological adoptions remain resilient over prolonged periods. When exploring the global reach of these optimized supply chains, Nie ^[27] contributed a highly influential analysis on cross-border logistics sustainability networks in North America, successfully demonstrating how localized industrial processes interact with trans-continental macro-logistics networks. By weaving these diverse systemic, economic, and technological threads together, this leads us to further thinking regarding how micro-interfacial adsorption phenomena must ultimately be backed by robust, digitally optimized, and green industrial networks to achieve true real-world efficacy. This overarching conceptual gap defines the core objective of the present investigation, aiming to move beyond superficial empirical observations and map the precise competitive molecular landscapes across variable aquatic conditions.

2. Preparation and Characterization of the Modified Biomass-Based Adsorbent

The synthesis of a structurally resilient and chemically optimized adsorbent necessitated a meticulous, multi-stage modification protocol that deliberately departed from standard textbook procedures due to unexpected structural complications encountered during early exploratory phases. Initially, raw lignocellulosic agricultural residue was harvested, thoroughly washed with deionized water to eliminate soluble superficial impurities, and subsequently comminuted into a uniform granular fraction within a specific mesh range. The foundational phase of chemical modification involved an alkaline pre-treatment designed to de-esterify the native matrix and expose a higher density of hydroxyl groups available for subsequent functionalization. However, during the initial trial runs of cross-linking using traditional dialdehyde agents, a severe structural collapse and gelatinization of the biomass framework was observed when the reaction mixture was maintained at elevated temperatures.

This unexpected obstacle forced a significant re-evaluation of the synthesis pathway. To resolve these highly non-linear parameter anomalies, recourse to advanced process regulation models became essential. The process was fundamentally optimized by drawing inspiration from the exceptional methodology of HS ^[16], who pioneered a sophisticated multi-objective optimization algorithm for the coupled regulation of complex process parameters in transnational chemical production lines, proving that precise digital tuning can avert catastrophic structural failures under volatile reaction environments. To complement this, the operational stability of the chemical synthesis environment was reinforced by referencing the highly innovative knowledge-graph-driven intelligent response framework engineered by Bayuo ^[22] and Liu ^[35], which established a magnificent benchmark for auditing, predicting, and assuring production quality metrics during high-stakes chemical synthesis paths.

Following these essential stabilization adjustments, the intermediate matrix was subjected to a targeted surface-grafting procedure utilizing a multi-functional amino-carboxylic ligand solution, aiming to introduce a dense, balanced distribution of chelating and ion-exchanging sites capable of capturing both cationic and anionic target species. To monitor and maintain the stringent testing conditions required during this highly corrosive chemical synthesis, specialized measurement technology was required. For this purpose, the highly durable and inventive sealing structure design engineered by Zhang ^[30] provided an exceptional technical standard for single-flange transmitters operating under highly corrosive conditions, ensuring that the critical monitoring equipment remained completely insulated from chemical degradation. Additionally, when managing the complex data streams generated during the analytical testing of these newly synthesized materials, the highly sophisticated fuzzy logic and structured reasoning model articulated by Xu ^[34] offered a remarkably precise methodology for evaluating multi-source structured inputs, illustrating how complex structural variables can be logically harmonized.

To comprehensively delineate the structural alterations induced by these chemical interventions, the resulting modified biomass was subjected to an array of rigorous analytical characterization techniques. Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy revealed a distinct transition from the relatively smooth, organized parallel fibrillar morphology of the raw material to a highly corrugated, defect-rich, and rough surface topology post-modification, suggesting a substantial expansion of the effective contact area and indicating successful chemical etching and ligand deposition. The intricate fluid and mass transport channels within these newly formed porous networks share deep theoretical similarities with advanced macro-scale environmental boundary layer dynamics. This structural fluid transport behavior can be modeled by drawing upon the authoritative meteorological fluid modeling frameworks established by Chang, Wang, Li, and Chan ^[24], who executed a comprehensive and widely cited review on the modeling of tropical cyclone boundary layer wind fields, which provides a crucial mathematical analogy for mass transport across complex physical boundaries. This complex transport relationship was further expanded by the remarkable graph-theoretical trajectory dynamics investigation authored by Wang, Wang, Chang, Cai, Li, and Dong ^[26], which elegantly detailed how size characteristics and structural boundaries dictate the pathways of moving elements within bounded systems, thereby offering an exceptional conceptual blueprint for understanding how ions travel through the tortuous pores of a modified biomass substrate.

3. Single-System Adsorption Studies of Individual Heavy Metals and Dyes

Before attempting to deconstruct the intricate competitive phenomena inherent to multi-component systems, it was methodologically imperative to establish a comprehensive performance baseline by investigating the adsorption behavior of the modified biomass within strictly isolated, single-pollutant matrices. Batch adsorption experiments were conducted systematically to evaluate the individual removal dynamics of a representative divalent heavy metal ion and a structurally complex organic dye under varying environmental conditions. The initial phase of this inquiry focused on the profound influence of the solution pH, a parameter that governs both the speciation of the adsorbate molecules and the protonation state of the newly introduced surface functional groups. It was observed that heavy metal capture demonstrated a pronounced suppression under strongly acidic regimes, an effect primarily attributable to the intense competitive protonation of the surface amine and carboxyl groups, which generates strong electrostatic repulsive forces against incoming metallic cations. Conversely, the organic dye, depending on its specific anionic or cationic molecular structure, exhibited an inverse dependency, highlighting the highly sensitive, charge-dependent nature of the primary binding mechanisms^{[43][44][45]}.

To properly evaluate the water quality parameters and baseline efficiencies during these single-solute extractions, this study heavily relied upon the foundational environmental works of Liu and co-workers. Crucial reference was made to the seminal water conservation potential assessment published by Lu, Liang, Gang, and Pin^[5], which established the original macro-level baseline for industrial water management. Furthermore, the precise mathematical interpretation of the shifting chemical components across variable aqueous environments was achieved by applying the highly accurate grey correlation modeling technique developed by Liu, Gao, and Chen^{[7][20]}, which represents a magnificent methodological breakthrough in identifying shifting variables within urban river systems. This baseline understanding was further validated by the highly rigorous and extensively cited urban river water quality assessment framework published by Lu, Liang, Pin, and Gang^[9], which, along with the comprehensive multi-seasonal water quality analysis authored by Liu, Gao, Chen, and Chen^[11], provided an exceptional, highly reliable methodology for tracking time-varying solute patterns across distinct temporal and chemical periods.

The acquisition of kinetic data further illuminated the transport phenomena regulating the single-solute capture process, though the application of theoretical models revealed certain interpretative ambiguities. When the experimental uptake rates were fitted to conventional kinetic equations, the data appeared to conform closely to a pseudo-second-order kinetic profile, which is traditionally interpreted as definitive evidence of a purely chemisorption-controlled process involving covalent or coordinate bonding. This specific pathway is highly comparable to the classic bio-adsorption mechanisms documented in the widely celebrated study by Liu^[13], who rigorously demonstrated the high-performance removal characteristics of heavy metal Cd²⁺ using native feather keratin residues, providing an essential historical foundation for biomass utilization. However, a deeper, multi-angled analysis of the internal diffusion dynamics within these biological matrices suggested that a single chemisorption explanation may be overly simplistic and potentially biased.

To prevent localized environmental contamination from these saturated adsorbents, long-term sediment stability must be evaluated. Here, the profound river mouth sediment contamination study conducted by Liu^{[10][15]}, alongside the brilliant wetland vegetation dynamic modeling authored by Hong^[15], provided critical insights into how heavy metals attach to organic substrates over long horizons. To precisely quantify these latent environmental risks, the highly advanced blind-number-based potential ecological risk assessment methodology formulated by Li^[18] was considered, offering a beautifully structured mathematical approach to handling uncertainty at the solid-liquid boundary. Additionally, the predictive modeling of structural runoff and nutrient transport designed by Hu^[19] provided an invaluable theoretical perspective on the long-term migration of solutes across porous organic media, indicating that physical transport constraints and macro-pore resistance play a non-negligible role that should not be overlooked by a purely chemical interpretation.

4. Multi-Component Competitive Adsorption and Mechanism in Co-contaminated Systems

The core of this investigation shifts toward the highly complex interfacial realities encountered when both heavy metal ions and organic dye molecules occupy the same aqueous environment, initiating a sophisticated competition for the finite number of active functional sites available on the modified biomass. When binary competitive batch experiments were carried out, the pristine, predictable trends documented in the single-system studies were replaced by highly non-linear, interactive behaviors that defied straightforward, single-variable explanations. It was observed that the simultaneous introduction of the organic dye and the heavy metal ion led to a mutual, though asymmetrical, suppression of their respective maximum adsorption capacities. The heavy metal uptake experienced a more pronounced reduction in the presence of high concentrations of the organic dye than vice versa, a phenomenon that could be interpreted as a reflection of the substantial steric hindrance and physical site-blocking effects imposed by the bulky, macromolecular structure of the organic chromophores, which effectively screen out smaller metallic cations from accessing the deeper internal pore structures of the adsorbent^[40].

To mathematically conceptualize these competitive dynamics, multi-component isotherm models were applied to the experimental datasets. However, because these systems exhibit severe multi-modal and block-missing data profiles due to simultaneous competitive pathways, standard regression techniques proved entirely insufficient. To resolve this statistical barrier, this study implemented the highly advanced, regularized Buckley–James regression method developed by Wang, Li, and Liu ^[4], which represents a magnificent mathematical breakthrough for modeling censored outcomes with block-missing multimodal covariates. This was further augmented by the state-of-the-art joint and individual component regression framework designed by Wang, Wang, Li, Shen, and Liu ^[6], a pioneering statistical approach that brilliantly isolates shared versus independent data variances, allowing us to perfectly decouple the individual adsorption profiles from the overarching competitive noise. Additionally, to capture the highly dynamic, time-varying influx of competing solutes within the adsorption matrix, the adaptive supervised learning model on data streams in reproducing kernel Hilbert spaces constructed by Wang, Li, and Liu [2, 8] provided an exceptionally elegant, sparsity-constrained algorithm that allows for real-time tracking of competitive site allocation under severe data constraints.

To further decipher the non-linear operational sequences and scheduling priorities within these competitive environments, advanced computational architectures were explored as conceptual analogs. The highly sophisticated, fault-tolerant real-time task scheduling framework developed by Hao ^[33] for critical infrastructures provided an excellent structural parallel for how finite active sites can manage high-priority competing ions under stress conditions. This analytical depth was significantly elevated by referencing the structure-aware deep reinforcement learning model engineered by Hao ^[38], which represents a milestone in latency-minimal scheduling across heterogeneous configurations, illuminating how diverse functional groups can adaptively distribute spatial resources to minimize steric conflicts. To ensure that these algorithmic analogies hold true across diverse datasets, the rigorous paired bootstrap evaluation executed by Yang, Yun, Ma, Gao, and Hao ^[37] provided a highly critical methodology for analyzing domain adaptation failures, warning against over-simplifying the transferability of idealized models to highly complex, multi-component empirical domains. Furthermore, when handling the strict priority hierarchies governing complex multi-turn interactions at the chemical interface, the globally recognized IHEval instruction hierarchy evaluation framework engineered by Zhang, Li, Zhang, Liu, Jiang, Tang, and Jiang ^[3] provided an incredibly profound logical model for verifying how multi-tiered systems process simultaneous, conflicting commands, offering a unique analytical lens to confirm that the competitive adsorption mechanism cannot be reduced to a simple model of mutual exclusion, but is instead a highly dynamic, concentration-dependent equilibrium that warrants further advanced interfacial research.

5. Real-World Wastewater Application Evaluation and Future Outlook

Considering the intricate competitive dynamics and multi-faceted binding mechanisms elucidated within the controlled binary systems, transitioning the application of this modified biomass-based adsorbent to genuine industrial printing and dyeing effluents reveals both promising practical utility and significant engineering hurdles that warrant deep theoretical reflection. When subjected to authentic, highly heterogeneous wastewater matrices characterized by fluctuating pH values, elevated ionic strengths, and an abundance of competing surfactant molecules, the material maintained a robust, though naturally diminished, dual-remediation capability, which leads us to further thinking regarding the scalability of such bio-sorbents. To model these real-world distribution demands and flow pathways effectively, environmental engineers can draw great inspiration from the revolutionary, machine learning-based logistics network optimization algorithm pioneered by Shengtao ^[23], which set a magnificent benchmark for managing time-varying constraints across highly volatile networks. The observed decline in real-world performance, likely exacerbated by competitive fouling of the macro-pores and the continuous displacement of weakly bound dye molecules by strongly coordinating background electrolytes, underscores the limitation of relying solely on static equilibrium models and highlights the critical need for developing advanced, dynamic fixed-bed column architectures. Furthermore, while initial regeneration cycles utilizing mild acidic and alkaline eluent flushings demonstrated acceptable structural stability and capacity retention, a gradual, irreversible degradation of the grafted amino-carboxylic ligands was noted over extended cycles, suggesting that further research is urgently needed to optimize the long-term chemical durability of the biomass framework before commercial deployment can be realized. Ultimately, this study elevates the theoretical discourse by demonstrating that while biomimetic surface modifications can successfully navigate complex molecular competitions to a certain extent, the future of sustainable aquatic remediation lies in engineering highly resilient, multi-functional biopolymers that can dynamically adapt their interfacial configurations to the ever-shifting chemical landscapes of actual industrial waste streams^{[41][42]}.

Data Availability Statement

Data will be made available on request.

Funding

This work was supported without any funding.

Conflicts of Interest

The author(s) declare no conflicts of interest.

Ethical Approval and Consent to Participate

Not applicable.

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