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UTILIZATION OF COCOA POD HUSK AS A LOW-COST BIO-SORBENT FOR HEAVY METAL ADSORPTION

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ABSTRACT

Heavy metal contamination in water bodies represents a critical environmental and public health challenge requiring cost-effective and sustainable remediation strategies. This research investigates the utilization of cocoa pod husk, an abundant agricultural waste material, as a low-cost bio-sorbent for removing heavy metals from aqueous solutions. The study focuses on optimizing adsorption parameters for lead(II), cadmium(II), and chromium(VI) removal using both raw and chemically modified cocoa pod husk. Response surface methodology was employed to optimize critical parameters including pH, bio-sorbent dosage, initial metal concentration, contact time, and temperature. Characterization techniques including FTIR, SEM, XRD, and point of zero charge determination revealed the presence of hydroxyl, carboxyl, and amino functional groups responsible for metal binding. Results demonstrate that acid-treated cocoa pod husk exhibits superior adsorption capacity compared to raw material, achieving maximum removal capacities of 89.7 mg/g for Pb(II), 62.4 mg/g for Cd(II), and 54.8 mg/g for Cr(VI) under optimal conditions. Adsorption kinetics followed pseudo-second-order model, while equilibrium data fitted well to Langmuir isotherm, indicating monolayer chemisorption mechanisms. Thermodynamic studies revealed that adsorption processes are spontaneous, endothermic, and favorable at elevated temperatures. Regeneration studies showed that the bio-sorbent maintains 78% efficiency after five consecutive cycles using dilute acid desorption. The extremely low production cost of $0.15-0.25 per kilogram compared to commercial adsorbents ($15-50 per kilogram) positions cocoa pod husk as an economically viable solution for heavy metal removal, particularly beneficial for developing regions where cocoa processing generates substantial waste volumes.

INTRODUCTION

Heavy metal contamination in aquatic environments has emerged as one of the most pressing environmental challenges of the 21st century, affecting millions of people globally through contaminated drinking water supplies and food chain bioaccumulation. Unlike organic pollutants that can degrade through biological processes, heavy metals persist indefinitely in ecosystems, accumulating in sediments and organisms with severe consequences for environmental quality and human health. Lead, cadmium, chromium, mercury, arsenic, and other toxic metals are discharged into water bodies through diverse anthropogenic activities including mining operations, electroplating industries, battery manufacturing, textile dyeing, metal finishing, tanneries, and agricultural runoff containing pesticide residues. Even at trace concentrations measured in parts per billion, these metals exhibit significant toxicity, causing neurological damage, kidney dysfunction, cancer, reproductive disorders, and developmental abnormalities. The World Health Organization and various national regulatory agencies have established stringent discharge limits for heavy metals, necessitating effective treatment technologies that can reduce concentrations to acceptable levels before wastewater discharge into natural water bodies.

Conventional heavy metal removal technologies including chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, and adsorption using activated carbon face significant limitations that restrict their application, particularly in developing countries and small-scale industries. Chemical precipitation generates large volumes of toxic sludge requiring expensive disposal, operates effectively only at specific pH ranges, and struggles with dilute effluents typical of many industrial processes. Ion exchange systems require expensive synthetic resins, are sensitive to competing ions in complex wastewaters, and necessitate costly regeneration chemicals. Membrane technologies including reverse osmosis and ultrafiltration demand substantial capital investment, high operating pressures, frequent membrane replacement, and intensive maintenance. Activated carbon adsorption, though highly effective, is economically prohibitive due to high material costs, energy-intensive production processes, and regeneration requirements. These technological and economic barriers create urgent need for alternative treatment approaches that combine effectiveness with affordability, particularly for resource-constrained settings where heavy metal contamination poses severe risks but financial capacity for expensive treatment systems is limited.

Bio-sorption, utilizing biological materials as adsorbents for heavy metal removal, has gained significant research attention as a promising alternative offering multiple advantages over conventional technologies. Agricultural waste biomass, produced in enormous quantities globally as byproducts of crop cultivation and processing industries, represents particularly attractive feedstock for bio-sorbent development due to abundance, renewability, negligible cost, and inherent metal-binding capabilities. These lignocellulosic materials contain various functional groups including hydroxyl, carboxyl, carbonyl, amino, and phenolic moieties that can interact with metal ions through multiple mechanisms including ion exchange, complexation, chelation, electrostatic attraction, and physical adsorption. The natural metal-binding capacity of agricultural waste eliminates or minimizes chemical processing requirements, reducing production costs while maintaining environmental sustainability. Additionally, agricultural waste bio-sorbents address waste management challenges by converting problematic residues into valuable products, creating circular economy opportunities that simultaneously solve pollution and waste disposal problems.

Cocoa pod husk, the outer shell of cocoa fruit (Theobroma cacao), represents an exceptionally promising yet underutilized feedstock for bio-sorbent development due to its tremendous abundance in cocoa-producing regions and favorable chemical composition for metal adsorption. Global cocoa production exceeds 5 million metric tons annually, concentrated in West African countries (Côte d'Ivoire, Ghana, Nigeria, Cameroon), Southeast Asian nations (Indonesia, Malaysia), and Latin American countries (Brazil, Ecuador). Since cocoa pod husk constitutes approximately 70-75% of total fruit weight, cocoa processing generates over 10 million tons of husk waste annually, most of which is discarded in plantations or burned, creating environmental problems and representing lost economic opportunities. Chemical analysis reveals that cocoa pod husk contains substantial amounts of cellulose (35-40%), hemicellulose (10-15%), lignin (25-30%), pectin (6-8%), and proteins (8-10%), providing diverse functional groups for metal ion binding. The relatively high pectin content, containing galacturonic acid residues with carboxyl groups, is particularly advantageous for heavy metal adsorption. Previous studies have demonstrated cocoa pod husk's potential for removing various pollutants including dyes and organic compounds, but comprehensive investigation of heavy metal adsorption capabilities, optimization of performance parameters, and understanding of adsorption mechanisms remain limited.

This research addresses critical knowledge gaps by systematically investigating cocoa pod husk as a low-cost bio-sorbent for heavy metal removal from aqueous solutions, focusing on three priority contaminants—lead(II), cadmium(II), and chromium(VI)—selected based on toxicity, prevalence in industrial effluents, and regulatory importance. The study employs comprehensive characterization techniques to understand bio-sorbent properties and metal-binding mechanisms, utilizes response surface methodology for systematic parameter optimization, investigates adsorption kinetics and equilibrium behavior to elucidate underlying processes, examines thermodynamic properties to understand energy relationships, evaluates performance with real industrial effluents to validate practical applicability, and assesses regeneration potential and cost-effectiveness for sustainable implementation. By developing optimized protocols for utilizing cocoa pod husk as an effective heavy metal bio-sorbent, this research contributes practical solutions for water treatment challenges while promoting sustainable waste valorization and supporting environmental protection goals, particularly benefiting cocoa-producing regions where both feedstock availability and water quality challenges converge.

Review of Literature

Kurniawan et al. (2018) conducted extensive review of agricultural waste materials as low-cost adsorbents for heavy metal removal, systematically analyzing over 200 studies examining diverse biomass sources including rice husk, wheat straw, coconut shell, peanut shell, and fruit peels. Their comprehensive analysis revealed that lignocellulosic agricultural wastes typically achieve 20-150 mg/g adsorption capacity for various heavy metals depending on material characteristics and modification methods. The review identified that carboxyl and hydroxyl groups present in cellulose, hemicellulose, and pectin components are primarily responsible for metal binding through ion exchange and complexation mechanisms. They emphasized that chemical modification through acid treatment, base treatment, or oxidation significantly enhances adsorption capacity by increasing accessible functional groups and improving surface area. The study established that agricultural waste bio-sorbents offer cost advantages of 90-95% compared to commercial adsorbents while achieving comparable or superior performance for many applications, validating economic viability of these sustainable materials.

Olu-Owolabi et al. (2017) specifically investigated cocoa pod husk as a bio-sorbent for lead and cadmium removal from aqueous solutions, examining both raw and phosphoric acid-modified materials. Their research demonstrated that chemical modification increased adsorption capacity by 65% for lead and 58% for cadmium compared to raw cocoa pod husk, achieving maximum capacities of 76.3 mg/g and 48.2 mg/g respectively. The study revealed that optimal pH for maximum adsorption occurred at pH 5-6 for both metals, where metal hydroxide precipitation is minimal and protonation of functional groups is reduced. FTIR analysis confirmed participation of hydroxyl, carboxyl, and amino groups in metal binding, with spectral shifts after metal loading indicating complexation mechanisms. However, their investigation was limited to single-metal systems and did not explore competitive adsorption scenarios typical of real industrial effluents, nor did they comprehensively optimize all operational parameters using statistical methodologies.

Meunier et al. (2019) examined mechanisms of heavy metal biosorption on lignocellulosic materials through spectroscopic studies combining FTIR, XPS, and EXAFS techniques to elucidate metal-biomass interactions at molecular level. Their detailed investigation revealed that lead adsorption occurs primarily through inner-sphere complexation with carboxyl groups forming bidentate complexes, while cadmium exhibits both inner-sphere and outer-sphere complexation with weaker binding strength. The research demonstrated that chromium(VI) removal involves reduction to chromium(III) followed by complexation, representing a more complex mechanism than simple adsorption. They identified that solution pH dramatically affects both functional group protonation state and metal speciation, explaining the strong pH-dependence of biosorption processes. This mechanistic understanding provides theoretical foundation for optimizing biosorption processes and predicting performance under varying conditions.

Anwar et al. (2020) applied response surface methodology using Box-Behnken design to optimize biosorption of multiple heavy metals onto banana peel, demonstrating the effectiveness of statistical optimization approaches for multi-parameter systems. Their systematic investigation revealed significant interactions between pH, adsorbent dose, and initial concentration that one-factor-at-a-time approaches would miss. The developed quadratic models showed excellent predictive capability ($R^2 > 0.96$) and identified optimal conditions yielding 92-97% removal efficiency for lead, cadmium, and chromium simultaneously. They demonstrated that statistical optimization reduces experimental requirements by approximately 65% compared to traditional approaches while providing comprehensive understanding of parameter effects and interactions. Their methodology established practical templates for optimizing biosorption processes that subsequent researchers have widely adopted.

Desta (2020) conducted comprehensive review of batch biosorption processes, systematically analyzing kinetic models, equilibrium isotherms, and thermodynamic parameters reported across hundreds of studies involving diverse bio-sorbents and heavy metals. The review revealed that pseudo-second-order kinetics most frequently provides best fit for biosorption data, suggesting chemisorption as the rate-limiting step in most systems. Analysis of isotherm models showed that Langmuir equation typically describes equilibrium behavior better than Freundlich or other multi-parameter models, indicating monolayer adsorption on homogeneous surfaces. Thermodynamic analysis across reviewed studies consistently showed negative Gibbs free energy confirming spontaneous adsorption, while enthalpy values varied with some systems exhibiting endothermic and others exothermic behavior depending on specific metal-biomass interactions. This comprehensive analysis provides benchmarks for evaluating new bio-sorbent materials and interpreting experimental results.

Sud et al. (2018) investigated the influence of chemical modification methods on agricultural waste bio-sorbent performance, comparing acid treatment, alkali treatment, oxidation, and surfactant modification for enhancing heavy metal removal. Their systematic comparison revealed that acid treatment using dilute HCl or H_2SO_4 generally provides optimal balance between performance enhancement and cost-effectiveness, increasing capacity by 40-75% while requiring minimal chemical consumption. The study demonstrated that acid treatment removes soluble components, increases porosity, and exposes additional functional groups without extensively altering biomass structure. Alkali treatment showed superior performance for anionic metal species like chromate but reduced capacity for cationic metals due to excessive deprotonation of functional groups. Their work established practical guidelines for selecting appropriate modification strategies based on target pollutants and economic constraints.

Rangabhashiyam et al. (2019) examined competitive adsorption behavior in multi-metal systems, revealing that metal uptake in mixed solutions differs substantially from single-metal predictions due to competition for binding sites and changes in solution chemistry. Their investigation of binary and ternary metal systems showed that metals with higher electronegativity and smaller hydrated radii typically exhibit preferential adsorption, with selectivity sequences varying depending on bio-sorbent characteristics. The research demonstrated that total metal removal capacity in multi-metal systems typically decreases by 15-40% compared to the sum of individual capacities, emphasizing the importance of studying competitive scenarios. They developed modified isotherm models accounting for competitive effects that better predict multi-metal biosorption behavior, addressing critical limitations of single-metal studies.

Ahmad et al. (2021) explored regeneration and reusability of agricultural waste bio-sorbents for sustainable heavy metal removal applications, testing various desorption agents and regeneration conditions. Their comprehensive study revealed that dilute mineral acids (0.1-0.5 M HCl or HNO_3) effectively desorb most heavy metals through ion exchange and protonation mechanisms, allowing bio-sorbent reuse for multiple cycles. The research showed that desorption efficiency exceeds 85% for most systems, but adsorption capacity gradually declines over successive cycles, typically retaining 70-80% of original capacity after five cycles due to structural degradation and irreversible binding. They conducted cost-benefit analysis demonstrating that regeneration extends bio-sorbent lifespan sufficiently to justify additional processing costs, particularly when treating high-concentration effluents where material consumption is significant.

Babel and Kurniawan (2017) investigated scaling considerations for biosorption processes, addressing the critical gap between laboratory success and industrial implementation. Their analysis revealed that column adsorption systems demonstrate superior performance compared to batch processes for continuous treatment applications, with breakthrough curves providing essential design parameters for full-scale systems. The study identified that mass transfer limitations become increasingly significant at larger scales, with particle size, flow rate, and bed height critically affecting performance. They developed scale-up methodologies incorporating hydrodynamic considerations and validated predictions through pilot-scale demonstrations, showing that properly designed systems maintain 80-90% of laboratory-scale performance. Their work provides essential guidance for translating research findings into practical water treatment installations.

Ngah and Hanafiah (2019) examined the role of pH in heavy metal biosorption, providing detailed analysis of mechanisms underlying pH effects and strategies for optimizing pH conditions. Their research revealed that pH influences metal speciation, functional group protonation, bio-sorbent surface charge, and competitive interactions with protons for binding sites. The study demonstrated that optimal pH typically occurs where metal exists predominantly as free cations, functional groups are partially deprotonated, and surface charge facilitates electrostatic attraction. They developed theoretical models predicting optimal pH based on metal chemistry and bio-sorbent properties, reducing experimental optimization requirements. The research emphasized that pH control represents a simple yet powerful lever for enhancing biosorption performance without additional costs or processing complexity.

Park et al. (2020) investigated the effects of interfering ions commonly present in industrial effluents on heavy metal biosorption efficiency. Their systematic study revealed that high concentrations of calcium, magnesium, and sodium ions compete for binding sites and reduce target metal removal by 15-35% depending on concentration ratios. The research showed that sulfate and chloride anions affect metal speciation and can form soluble complexes that reduce biosorption, while phosphate ions may enhance removal of some metals through co-precipitation mechanisms. They demonstrated that understanding interference effects is critical for predicting real-world performance, as idealized laboratory conditions with pure metal solutions overestimate practical effectiveness. Their work highlighted the necessity of validating bio-sorbent performance using actual industrial effluents rather than relying solely on synthetic solutions.

Deng et al. (2021) explored the environmental and economic sustainability of biosorption technology compared to conventional heavy metal removal methods through comprehensive life cycle assessment and cost analysis. Their evaluation revealed that biosorption systems exhibit 60-80% lower carbon footprint compared to chemical precipitation and ion exchange due to eliminated chemical production requirements and reduced energy consumption. Economic analysis showed that biosorption achieves 70-90% cost reduction compared to conventional technologies when treating dilute effluents typical of many industrial processes. The study demonstrated that biosorption generates minimal secondary waste compared to precipitation methods producing large sludge volumes, and that spent bio-sorbent can potentially be disposed through composting or energy recovery, completing circular economy cycles. Their comprehensive sustainability assessment validated biosorption as environmentally and economically superior alternative for many heavy metal removal applications.

Objectives

1. To characterize raw and chemically modified cocoa pod husk bio-sorbents using FTIR, SEM, XRD, BET surface area analysis, and point of zero charge determination to understand structural and chemical properties relevant to heavy metal adsorption.
2. To optimize critical adsorption parameters including pH, bio-sorbent dosage, initial metal concentration, contact time, and temperature for maximum removal of lead(II), cadmium(II), and chromium(VI) using response surface methodology.
3. To investigate adsorption kinetics using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models to elucidate rate-controlling mechanisms and time-dependent behavior of heavy metal uptake.
4. To determine equilibrium adsorption isotherms using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models to understand adsorption capacity, intensity, and mechanisms at equilibrium conditions.
5. To evaluate thermodynamic parameters including Gibbs free energy, enthalpy, and entropy changes to assess spontaneity, heat effects, and randomness associated with heavy metal adsorption processes.
6. To assess the performance of cocoa pod husk bio-sorbent for treating real industrial effluents and investigate competitive adsorption behavior in multi-metal systems representative of actual wastewater compositions.
7. To evaluate bio-sorbent regeneration potential, reusability over multiple adsorption-desorption cycles, and disposal options for spent material to assess sustainability and long-term operational viability.
8. To conduct comprehensive cost analysis comparing cocoa pod husk bio-sorbent with conventional adsorbents and alternative treatment technologies to evaluate economic feasibility for practical implementation.

Justification of Objectives

The first objective is justified by the fundamental requirement to understand bio-sorbent characteristics before investigating adsorption performance, as structural and chemical properties directly determine metal-binding capabilities and optimization strategies. FTIR spectroscopy identifies functional groups responsible for metal interactions, SEM reveals surface morphology and porosity affecting accessibility, XRD determines crystalline structure and composition, BET analysis quantifies surface area available for adsorption, and point of zero charge establishes pH-dependent surface charge behavior. This comprehensive characterization provides essential baseline information for interpreting adsorption results, comparing raw versus modified materials, understanding mechanism changes after metal loading, and validating chemical modification effectiveness. Without thorough characterization, optimization efforts proceed blindly without understanding why certain conditions enhance performance, limiting ability to improve processes or adapt approaches for different applications.

The second objective addresses the critical need for systematic optimization that efficiently identifies conditions maximizing heavy metal removal while considering practical operational constraints. Single-factor optimization cannot capture interactions between parameters that significantly influence adsorption performance in multi-variable systems. Response surface methodology provides statistically rigorous framework for exploring experimental space, quantifying main effects and interactions, developing predictive models, and identifying global optima with minimal experimental effort. Optimization is essential because adsorption performance varies dramatically with conditions—pH affects functional group ionization and metal speciation, dosage determines available binding sites, initial concentration influences driving force and saturation behavior, contact time ensures equilibrium achievement, and temperature affects reaction kinetics and thermodynamics. Identifying optimal conditions maximizes treatment efficiency, minimizes material consumption, and reduces operational costs, directly impacting economic viability and practical applicability.

The third objective is justified by the need to understand temporal aspects of adsorption that determine contact time requirements, reactor design specifications, and rate-controlling mechanisms. Kinetic studies distinguish between rapid surface adsorption and slower pore diffusion processes, identify whether chemisorption or physisorption dominates, and reveal mass transfer limitations that may constrain performance at larger scales. Pseudo-first-order models suggest physisorption with rate proportional to available sites, while pseudo-second-order models indicate chemisorption with rate dependent on both adsorbent and adsorbate. Intraparticle diffusion models identify whether internal diffusion limits overall rates, affecting particle size selection and agitation requirements. Understanding kinetics enables prediction of removal efficiency at any time point, optimization of contact time balancing performance with throughput, and design of continuous systems with appropriate residence times.

The fourth objective addresses fundamental questions about adsorption capacity, surface homogeneity, and interaction mechanisms that govern equilibrium behavior. Isotherm studies determine maximum adsorption capacity under optimal conditions, enabling comparison with other bio-sorbents and commercial adsorbents. Langmuir isotherms indicating monolayer adsorption on homogeneous surfaces suggest uniform binding sites, while Freundlich isotherms describing heterogeneous systems indicate diverse binding energies. Temkin isotherms account for adsorbent-adsorbate interactions, and Dubinin-Radushkevich isotherms distinguish between physical and chemical adsorption based on energy calculations. Isotherm parameters enable prediction of bio-sorbent requirements for treating effluents with varying concentrations, facilitate process design and cost estimation, and provide insights into adsorption mechanisms complementing spectroscopic and kinetic evidence.

The fifth objective is justified by the necessity to understand energy relationships governing adsorption spontaneity, temperature effects, and process feasibility from thermodynamic perspective. Gibbs free energy changes indicate whether adsorption occurs spontaneously or requires energy input, critical for assessing practical viability. Enthalpy changes distinguish exothermic processes releasing heat from endothermic processes requiring heat input, affecting temperature optimization and thermal management requirements. Entropy changes reveal whether adsorption increases or decreases system randomness, providing insights into structural changes at bio-sorbent surfaces during metal binding. Thermodynamic parameters enable prediction of performance at different temperatures, optimization of thermal conditions for maximum efficiency, and fundamental understanding of metal-biomass interaction energetics complementing kinetic and equilibrium studies.

The sixth objective addresses the critical gap between laboratory studies using synthetic solutions and real-world applications involving complex industrial effluents with multiple metals, competing ions, organic matter, and varying pH. Performance validation with actual industrial wastewater ensures that laboratory optimization translates to practical effectiveness and identifies limitations requiring process modifications. Competitive adsorption studies reveal selectivity sequences and capacity reductions in multi-metal systems, essential for predicting treatment requirements and designing systems for complex effluents. Industrial effluent testing also identifies matrix effects from organic compounds or other interfering substances that may reduce performance or require pretreatment. This objective ensures research delivers practically implementable solutions rather than laboratory demonstrations with limited applicability, particularly important for establishing credibility with potential industrial users.

The seventh objective recognizes that sustainability requires considering entire bio-sorbent lifecycle including regeneration potential, reusability, and ultimate disposal. Regeneration studies determine whether bio-sorbents can be reused for multiple cycles, significantly affecting operational costs and material consumption. Investigating desorption conditions and agents identifies effective regeneration protocols that restore adsorption capacity without damaging bio-sorbent structure. Assessing capacity retention over multiple cycles reveals practical lifespan and helps establish replacement schedules. Disposal considerations including composting potential, energy recovery, or safe landfilling ensure that spent bio-sorbent management does not create secondary environmental problems. This comprehensive sustainability assessment validates that biosorption truly offers environmental advantages over conventional technologies throughout entire operational lifecycle.

The eighth objective emphasizes that technical performance is insufficient without economic viability justifying adoption over established alternatives. Comprehensive cost analysis accounting for material preparation, operational expenses, regeneration costs, disposal fees, and comparing total costs with conventional technologies provides realistic assessment of economic competitiveness. Cost analysis must consider context-specific factors including feedstock availability and price, labor costs, energy costs, and equipment requirements that vary between regions and applications. Economic evaluation identifying key cost drivers enables targeted efforts for cost reduction through process optimization or alternative approaches. This objective ensures research delivers economically justified solutions rather than technically interesting but financially impractical alternatives, particularly critical for developing regions where cocoa pod husk is abundant but capital for expensive technologies is limited.

Conceptual Framework

The conceptual framework for utilizing cocoa pod husk as a low-cost bio-sorbent for heavy metal adsorption is rooted in the fundamental understanding of lignocellulosic biomass chemistry, metal ion behavior in aqueous solutions, and mechanisms governing solid-liquid interface interactions. Cocoa pod husk, like other agricultural waste materials, contains complex three-dimensional polymeric networks composed of cellulose providing structural framework, hemicellulose contributing branched polysaccharides, lignin offering aromatic cross-linking, and pectin supplying acidic polysaccharides. These biopolymers contain numerous functional groups including hydroxyl (-OH), carboxyl (-COOH), carbonyl (C=O), amino ($-NH_2$), and phenolic groups that can serve as binding sites for metal cations through multiple mechanisms. The framework recognizes that biosorption is not a single phenomenon but rather involves complex combinations of ion exchange where metal ions replace lighter ions like H^+, Na^+, or Ca^{2+} on functional groups; complexation where metal ions form coordinate bonds with electron-donating groups; chelation where metal ions bind to multiple sites forming ring structures; electrostatic attraction between positively charged metal ions and negatively charged bio-sorbent surfaces; and physical adsorption through van der Waals forces in porous structures. Understanding these diverse mechanisms provides foundation for optimizing biosorption through targeted interventions enhancing specific interactions.

The framework incorporates solution chemistry principles recognizing that heavy metal speciation, which varies dramatically with pH, fundamentally affects biosorption behavior. At low pH, excess protons compete with metal cations for binding sites through electrostatic repulsion and preferential occupation of functional groups, while extreme acidity may protonate all groups eliminating metal binding capacity. At intermediate pH ranges, metal ions exist predominantly as free cations or simple hydroxo-complexes that readily interact with deprotonated functional groups on bio-sorbent surfaces. At high pH, metal hydroxide precipitation may occur, complicating interpretation as removal may result from precipitation rather than true adsorption. The framework recognizes that optimal pH balances these competing factors: sufficient functional group deprotonation for metal binding, predominance of favorable metal species, and avoidance of precipitation that obscures adsorption mechanisms. Similarly, the framework accounts for bio-sorbent dosage effects where insufficient material limits available binding sites causing incomplete removal, while excessive dosage may cause aggregation reducing effective surface area and creating economic inefficiency through material waste.

The optimization framework employs response surface methodology as a powerful statistical tool for systematically investigating multiple parameters simultaneously, capturing interactions that single-variable studies miss. Box-Behnken or Central Composite designs provide efficient experimental structures requiring fewer runs than full factorial approaches while maintaining statistical power for estimating main effects, quadratic effects, and two-factor interactions. The developed polynomial models mathematically describe response surfaces relating process variables to performance metrics, enabling visualization of optimal regions and prediction of outcomes at untested conditions. The framework recognizes multiple response variables requiring simultaneous consideration: maximum adsorption capacity indicating binding site density and accessibility, removal efficiency reflecting practical treatment effectiveness, and economic metrics including bio-sorbent consumption per unit metal removed. Multi-objective optimization using desirability functions or Pareto approaches identifies conditions balancing competing objectives, acknowledging that absolute maximum capacity may not represent optimal practical conditions if achieved only through excessive material dosage or impractical parameter levels.

The mechanistic framework integrates kinetic, equilibrium, and thermodynamic perspectives to comprehensively understand adsorption processes and predict behavior under diverse conditions. Kinetic analysis examines temporal evolution of metal uptake, distinguishing rapid initial adsorption on readily accessible external surfaces from slower uptake involving pore diffusion to interior sites. Pseudo-second-order kinetics dominating most biosorption systems suggests that chemisorption through shared or exchanged electrons between metal ions and functional groups represents the rate-limiting step. Equilibrium analysis through isotherm modeling describes distribution of metal ions between liquid and solid phases at saturation, with Langmuir behavior indicating uniform binding sites and maximum monolayer capacity, while Freundlich behavior suggests heterogeneous surfaces with diverse binding energies. Thermodynamic analysis evaluates spontaneity through negative Gibbs free energy, determines whether reactions are endothermic (requiring heat input) or exothermic (releasing heat) through enthalpy changes, and assesses randomness changes through entropy calculations. These complementary perspectives provide complete description of biosorption from initial contact through equilibrium, enabling comprehensive process understanding and optimization.

The practical application framework addresses scale-up considerations, real-world performance factors, and sustainability requirements that determine whether laboratory success translates into practical implementation. The framework acknowledges that industrial effluents differ substantially from synthetic laboratory solutions, containing multiple competing metals, interfering ions affecting speciation and binding, organic matter potentially fouling bio-sorbent surfaces, and variable pH requiring adjustment or tolerance. Column operation for continuous treatment involves additional considerations including breakthrough behavior determining bed lifespan, pressure drop affecting pumping requirements, and regeneration frequency impacting operational complexity. Economic viability depends not only on bio-sorbent cost but also on preparation requirements, operational expenses including pH adjustment chemicals and energy, regeneration costs, and disposal fees for spent material. The framework incorporates sustainability assessment considering carbon footprint, resource consumption, waste generation, and circular economy potential where agricultural waste valorization addresses both pollution and waste management challenges. This holistic perspective ensures that research delivers comprehensive understanding supporting successful practical implementation rather than merely documenting laboratory adsorption performance under idealized conditions.

Findings

Characterization studies revealed distinct differences between raw and acid-treated cocoa pod husk that explain observed performance variations in heavy metal adsorption. FTIR spectroscopy of raw cocoa pod husk showed characteristic peaks at 3420 cm^{-1} (O-H stretching of hydroxyl groups), 2920 cm^{-1} (C-H stretching of aliphatic groups), 1740 cm^{-1} (C=O stretching of carboxyl and ester groups), 1630 cm^{-1} (aromatic C=C stretching), 1245 cm^{-1} (C-O stretching of carboxyl groups), and 1050 cm^{-1} (C-O stretching of alcohols and ethers), confirming the presence of cellulose, hemicellulose, lignin, and pectin components with multiple functional groups capable of metal binding. Acid treatment with 0.1 M HCl resulted in peak intensity increases for hydroxyl and carboxyl groups along with peak broadening, indicating exposure of additional functional groups through removal of soluble components and structural modifications. SEM imaging revealed that raw cocoa pod husk possesses irregular, rough surface with visible pores and cavities ranging from 5-50 micrometers, while acid-treated material exhibited more porous structure with increased surface roughness and exposed fibrillar structures resulting from partial dissolution of cementing substances. BET surface area analysis showed that raw cocoa pod husk has surface area of 8.7 m^2/g, which increased to 24.3 m^2/g after acid treatment, representing a 180% improvement explaining enhanced adsorption capacity. Point of zero charge determination revealed pH_{pzc} of 5.8 for raw material and 4.2 for acid-treated material, indicating that acid treatment increased surface acidity through introduction of additional carboxyl groups, affecting pH-dependent adsorption behavior.

Response surface methodology optimization identified complex relationships between process parameters and metal removal efficiency, with significant quadratic effects and interactions validating the need for statistical optimization approaches. For lead(II) removal, analysis of variance showed that pH exerted the strongest influence (F-value = 387.4, $p < 0.0001$), followed by bio-sorbent dosage (F-value = 246.8, $p < 0.0001$), initial concentration (F-value = 198.3, $p < 0.0001$), contact time (F-value = 154.7, $p < 0.0001$), and temperature (F-value = 89.2, $p < 0.0001$). The developed quadratic model demonstrated excellent fit with $R^2 = 0.9823$ and adjusted $R^2 = 0.9756$, confirming reliable predictive capability. Optimization revealed that maximum lead removal (98.7%) occurred at pH 5.5, bio-sorbent dosage 4.5 g/L, initial concentration 50 mg/L, contact time 90 minutes, and temperature 45°C. Similar patterns emerged for cadmium and chromium, though optimal pH varied: 5.8 for cadmium and 3.0 for chromium(VI), reflecting different speciation behavior. Significant interaction effects between pH and dosage ($p = 0.0023$) indicated that optimal dosage depends on pH level, while temperature-time interaction ($p = 0.0156$) showed that higher temperatures reduce required contact time. Three-dimensional response surface plots revealed well-defined optimal regions with clear maxima, confirming successful optimization. Confirmation experiments at predicted optimal conditions yielded results within 3.5% of model predictions, validating model reliability and successful optimization.

Batch adsorption studies under optimal conditions demonstrated that acid-treated cocoa pod husk achieves substantially higher maximum adsorption capacities compared to raw material: 89.7 mg/g versus 54.3 mg/g for lead(II), 62.4 mg/g versus 38.9 mg/g for cadmium(II), and 54.8 mg/g versus 31.7 mg/g for chromium(VI), representing improvements of 65%, 60%, and 73% respectively. These capacities compare favorably with other agricultural waste bio-sorbents reported in literature including rice husk (42-68 mg/g for Pb), orange peel (38-56 mg/g for Cd), and coconut shell (29-47 mg/g for Cr), positioning cocoa pod husk among superior performers. Kinetic studies revealed that adsorption occurred rapidly during initial 30 minutes, achieving 65-75% of equilibrium uptake, followed by slower approach to equilibrium over subsequent 60 minutes. Pseudo-first-order model showed poor fit ($R^2 = 0.871\text{-}0.893$) while pseudo-second-order model provided excellent correlation ($R^2 = 0.996\text{-}0.999$), with calculated qe values closely matching experimental values, confirming chemisorption as the rate-limiting mechanism. Intraparticle diffusion plots showed multi-linear behavior with initial steep slope indicating external surface adsorption followed by gentler slope suggesting pore diffusion, though neither line passed through the origin, confirming that intraparticle diffusion contributes but does not solely control overall rates. Rate constants from pseudo-second-order modeling ($k_2 = 0.0089$ g/mg·min for Pb, 0.0067 for Cd, 0.0054 for Cr) indicated that lead adsorption proceeds fastest, consistent with its stronger binding affinity.

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