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Utilizing plant biomass for eco-friendly removal of hazardous metals from wastewater

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Abstract
This study investigates the potential of *Citrullus colocynthis* biomass as a sustainable biosorbent for removing hazardous metals Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) from wastewater. Through systematic batch experiments, the adsorption performance was evaluated under varying pH(3-11), biosorbent dosage (10-250 mg), initial metal concentration (50-500 mg/L), and contact time (0-180 min). The biomass exhibited optimal removal efficiencies ranging from 88-93% for all five metals at pH 5, with Cu(II) demonstrating the highest affinity, achieving 93% removal. Langmuir isotherm models revealed maximum adsorption capacities of 209.64, 205.76, 149.03, 133.87, and 79.62 mg/g for Cr(III), Cu(II) Co(II), Ni(II), and Cd(II), respectively, indicating monolayer adsorption on homogeneous sites. Pseudo-second-order kinetics (R2>0.955) confirmed chemisorption as the rate-limiting step, with rapid equilibration (<60 min). SEM analyses identified a porous morphology for metal biosorbent. The biosorbent's efficacy, coupled with its abundance in arid regions, positions *Citrullus colocynthis* as a cost-effective, eco-friendly alternative for wastewater treatment, particularly in resource-limited settings.

Keywords: *Citrullus colocynthis* , biosorption, heavy metals, plants, wastewater treatment

1. Introduction

Heavy metal contamination in wastewater is a pressing environmental concern due to the toxicity, persistence, and bioaccumulative nature of these pollutants. Industrial discharges, mining activities, electroplating processes, and agricultural runoff are major sources of hazardous metals such as chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), and cadmium (Cd) in aquatic systems [1]. These metals are non-biodegradable and tend to accumulate in ecosystems, posing significant risks to both environmental and human health [2]. Chromium, particularly in its hexavalent form (Cr^{6+}), is a well-documented carcinogen, while cobalt, though essential in trace amounts, can induce organ damage and mutagenic effects at elevated concentrations [3]. Nickel and copper, despite their industrial utility, are associated with hepatotoxicity and nephrotoxicity upon prolonged exposure [4]. Cadmium, one of the most toxic heavy metals, is linked to chronic kidney disease, osteoporosis, and various cancers [5]. The bioaccumulation of these metals in aquatic ecosystems disrupts biodiversity and compromises drinking water quality, necessitating effective remediation strategies (Wuana & Okieimen, 2011).
The treatment of heavy metal-contaminated wastewater remains a critical environmental challenge due to the persistent and toxic nature of these pollutants[6]. Conventional remediation techniques include chemical precipitation [7], ion exchange[8], membrane filtration[9], electrochemical treatment[10], and activated carbon adsorption[11]. Chemical precipitation[12], while effective for high metal concentrations, generates toxic sludge that complicates disposal and poses secondary environmental risks [13]. Ion exchange offers high removal efficiency but suffers from high operational costs due to the need for frequent resin regeneration [14]. Membrane filtration technologies, such as reverse osmosis and ultrafiltration, provide excellent purification but are energy-intensive and prone to fouling, limiting their practical application [15]. Electrochemical methods, though effective, require substantial energy inputs and sophisticated infrastructure, making them less feasible for large-scale use [16]. Similarly, activated carbon adsorption is highly efficient but expensive and reliant on non-renewable resources [17]. These conventional methods face significant limitations, including high costs, secondary pollution, and inefficiency in treating low-concentration or complex wastewater systems [18].
In response to these challenges, biosorption has emerged as a promising, eco-friendly alternative. This process utilizes biological materials—such as agricultural waste, microbial biomass, or plant residues—to adsorb heavy metals through physicochemical interactions with functional groups like carboxyl, hydroxyl, and amine moieties [19]. Biosorption offers several advantages over conventional methods, including cost-effectiveness, minimal secondary pollution, and high efficiency even at low metal concentrations [20]. Additionally, many biosorbents are biodegradable and can be regenerated, enhancing their sustainability [21]. Recent research has highlighted the potential of drought-resistant plants, due to their natural abundance in arid regions and high metal-binding capacities [22-24].

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Despite these advantages, further research is needed to optimize biosorption for large-scale applications. Key areas for development include improving biomass pretreatment methods, enhancing regeneration protocols, and integrating biosorption with hybrid treatment systems. Such advancements could bridge the gap between laboratory studies and real-world implementation, offering a viable solution for sustainable wastewater treatment. The exploration of locally available, low-cost biosorbents represents a crucial step toward environmentally friendly and economically feasible heavy metal remediation, particularly in resource-limited regions.

The Qassim region of Saudi Arabia hosts diverse xerophytic plant species adapted to arid conditions, presenting untapped potential for biosorption applications. Among these, *Citrullus colocynthis* (desert gourd) is notable for its resilience, abundance, and bioactive compounds, including polysaccharides and flavonoids, which enhance metal-binding capacity [25]. Despite extensive research on biosorbents, few studies have explored the efficacy of native arid-region plants like *Citrullus colocynthis* for multi-metal removal [26].

While biosorption has been widely studied, the application of *Citrullus colocynthis* biomass for heavy metal removal remains underexplored. This study aims to evaluate the potential of *Citrullus colocynthis* biomass as a low-cost, sustainable biosorbent for the removal of toxic heavy metals—chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), and cadmium (Cd)—from wastewater. By leveraging this locally abundant, drought-resistant species, the research seeks to develop an eco-friendly and regionally adaptable solution for wastewater treatment in arid and semi-arid environments.

The study will systematically evaluate adsorption performance across a range of distinct experimental conditions. Furthermore, the study will apply adsorption isotherm models (Langmuir, Freundlich, to characterize the biosorption mechanism and surface interactions. Kinetic models (pseudo-first-order, and pseudo-second-order) will be employed to analyze the rate-controlling steps.

2. Materials and methods

2.1 Biosorbent preparation and characterization

Citrullus colocynthis biomass was collected from Al-Qassim area, Saudi Arabia. The plant material underwent thorough washing with deionized water to remove surface contaminants, followed by a two-stage drying process: initial solar drying for 72 hours and subsequent oven drying at 50 °C for an additional 72 hours to achieve complete dehydration. The dried biomass was mechanically ground and sieved to obtain particles of uniform size (150-200 μm) before storage at 4 °C in airtight containers.

2.2 Preparation of metal solutions

Stock solutions (1000 mg/L) of Cr, Co, Ni, Cu, and Cd were prepared using analytical grade metal salts (Sigma-Aldrich) dissolved in deionized water. Working solutions (5-500 mg/L) were prepared through serial dilution. Solution pH was adjusted using 0.1M NaOH or HCl and monitored using a calibrated pH meter (Model XYZ, Accuracy ±0.01).

2.3 Biosorbent characterization

The biosorbent was characterized using advanced analytical techniques. SEM imaging, conducted at magnifications of 10-50k, revealed the surface morphology.

2.4 Batch biosorption studies

Experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of metal solution with an initial concentration of 100 mg/L and 50 mg of biosorbent. The system parameters were optimized by investigating several factors. The effect of pH (ranging from 3 to 10) was adjusted using 0.1M HCl/NaOH. Contact time was varied from 0 to 180 minutes, with samples taken at regular intervals. Temperature was controlled between 25 °C and 45 °C using a temperature-controlled shaker. The dosage of biosorbent was varied from 50 to 250 mg, and the initial metal concentration was adjusted between 100 and 500 mg/L. After agitation at 150 rpm, samples were centrifuged at 5000 rpm for 5 minutes, and the filtrates were analyzed for residual metal concentration using ICP-MS, with a detection limit of 0.1 ppb.

2.5 Data analysis

Metal removal efficiency (R%), adsorption capacity (qt, qe), and isotherm/kinetic parameters were calculated using:

Removal efficiency:

$$R\,(\%) = \frac{Co - Ct}{Co} X 100 \qquad (1)$$

Adsorption capacity:

$$qt = \frac{Co - Ct}{m} X\, V \qquad (2)$$

$$qe = \frac{Ce}{m} X\, V \qquad (3)$$

The adsorption performance was evaluated through quantitative analysis of several key parameters. The initial metal concentration (C_o, mg L^{-1}) represents the starting concentration in solution, while the equilibrium concentration (C_e, mg L^{-1}) and residual concentration at time t (C_t, mg L^{-1}) reflect the system state after adsorption. These values were normalized using the biosorbent mass (m, g) and solution volume (V, L) to calculate adsorption capacities.

Two fundamental isotherm models were employed to analyze the equilibrium adsorption data. The Langmuir isotherm model (Equation 4) describes monolayer adsorption on homogeneous surfaces with finite identical sites, expressed mathematically as

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \qquad (4)$$

where q_e represents the equilibrium adsorption capacity (mg g^{-1}), q_m denotes the theoretical maximum adsorption capacity (mg g^{-1}), and K_l is the Langmuir constant related to adsorption energy (L mg^{-1}). In parallel, the Freundlich isotherm model (Equation 5) was applied to characterize multilayer adsorption on heterogeneous surfaces, following the logarithmic relationship.

$$\mathrm{Log}\ Q_e = \log K_f + \frac{1}{n}\ \mathrm{Log}\ C_e \qquad (5)$$

This empirical model incorporates K_f as an indicator of adsorption capacity, while the dimensionless parameter 1/n reflects adsorption intensity and surface heterogeneity. Together, these models provide complementary insights into the adsorption mechanisms and surface characteristics of the biosorbent material.

$$\mathrm{Log}\ (q_e – q_t) = \log q_e – k_1 t \qquad (6)$$

The adsorption kinetics were analyzed using two fundamental models. The pseudo-first-order kinetic model (Equation 6) describes the adsorption process through the logarithmic relationship between the adsorption capacity difference (qe-qt) and time, where k1 (min-1) represents the rate constant.

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (7)$$

The pseudo-second-order model (Equation 7) expresses the time-dependent adsorption behavior through a linear relationship between t/qt and t, with k2 (g mg-1 min-1) as the second-order rate constant. In both models, qt (mg g-1) and qe (mg g-1) represent the adsorption capacities at time t and equilibrium, respectively. Kinetic parameters were derived by fitting the experimental data to these models using least squares regression analysis.

3. Results and discussion

3.1 Structural characteristics of *Citrullus colocynthis* biomass

3.1.1 Surface morphology

The SEM micrograph of *Citrullus colocynthis* biomass prior to metal adsorption (Figure 7) reveals a highly porous and irregular surface morphology, which is conducive to efficient metal ion uptake. At ×17,000 magnification, the biomass exhibits a heterogeneous structure with abundant micro- and nano-scale cavities, ridges, and fibrous networks (Figure 1). These features collectively contribute to a high surface area, a critical factor for effective biosorption, as they provide numerous binding sites for metal ions [27, 28]. The rough texture and porous architecture are characteristic of lignocellulosic plant materials, which often contain cellulose, hemicellulose, and lignin—components known to host functional groups (e.g., carboxyl, hydroxyl, and amine) that facilitate metal coordination [29].

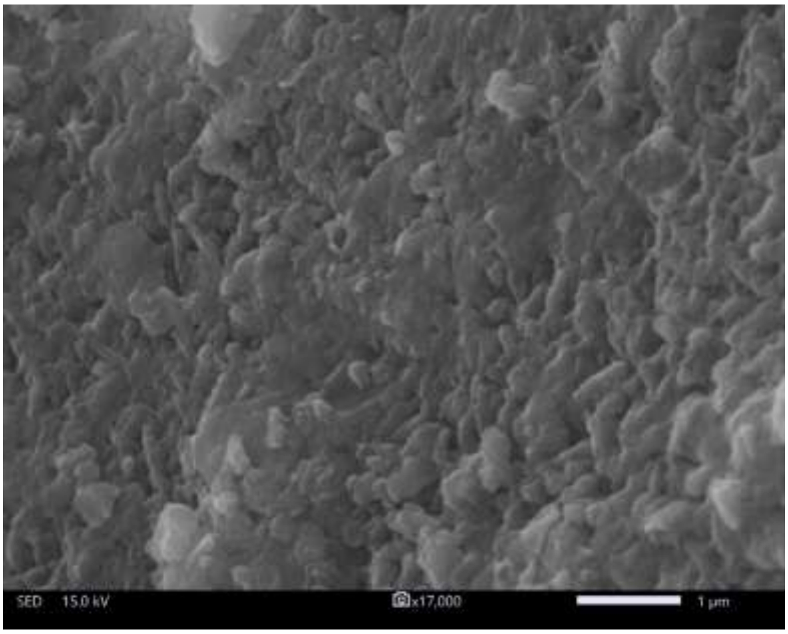

Figure 1. SEM image of as-prepared *Citrullus colocynthis* biomass.

The observed morphology aligns with the kinetic and isotherm data, where the biomass demonstrated high adsorption capacities and rapid uptake for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II). The porous structure likely enhances mass transfer and accessibility of metal ions to internal binding sites, explaining the favorable adsorption kinetics [30]. Additionally, the fibrous networks may act as scaffolds for functional groups, further promoting chemisorption [31].

Comparative studies of other plant-derived biosorbents, such as *Enteromorpha compressa*, have reported similar morphological features, though *Citrullus colocynthis* appears to exhibit a more pronounced porous hierarchy. This structural advantage may account for its exceptional performance, particularly for Cu(II) and Cr(III), which showed the highest removal efficiencies in earlier experiments.

3.2. Examination of biosorption

3.2.1 pH-dependent biosorption performance of *Citrullus colocynthis* biomass

The pH-dependent adsorption behavior of *Citrullus colocynthis* biomass for heavy metal removal demonstrates several important trends, as shown in Figure 2. Maximum removal efficiencies of 88-93% were achieved at pH 5 for all five metals (Cr(III), Co(II), Ni(II), Cu(II), and Cd(II)), with Cu(II) showing consistently superior adsorption across the entire pH range. This optimal performance at weakly acidic conditions is characteristic of biosorption processes involving plant-derived materials, as reported by Wang and Chen [32], and can be attributed to the ionization state of functional groups on the biomass surface.

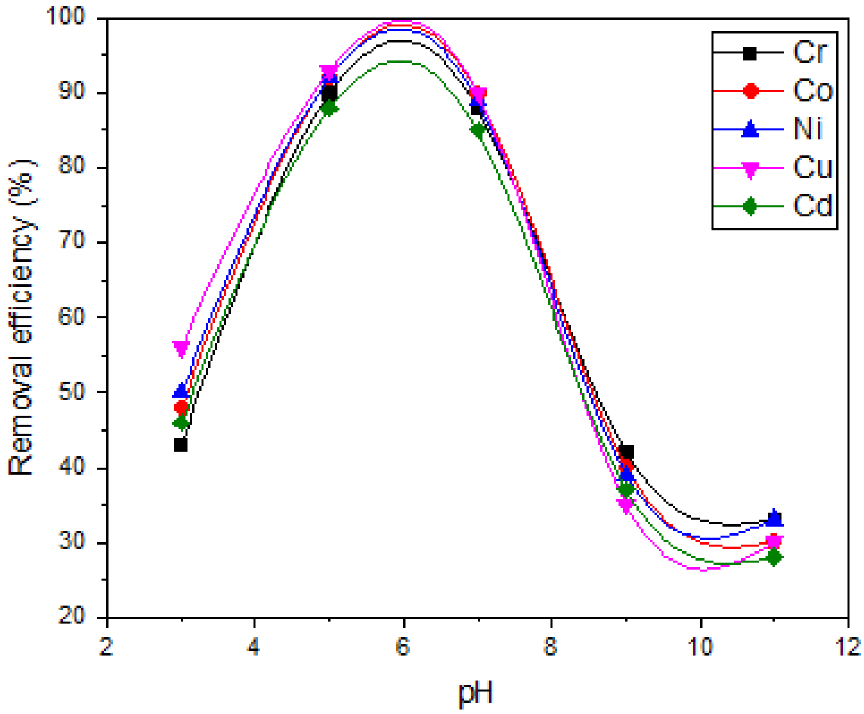

Figure 2. Effect of solution pH on the removal efficiency (%) of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) by plant biomass biosorbent.

The significant reduction in removal efficiency at pH 3 (43-56%) reflects the competitive inhibition between protons and metal cations for binding sites. As demonstrated by Younis et al.,[19], the carboxyl (-COOH) and hydroxyl (-OH) groups present in *Citrullus colocynthis* biomass become protonated under strongly acidic conditions, reducing their availability for metal ion coordination. The gradual decline in adsorption capacity observed from pH 7 to pH 11 (85% to 28-37%) suggests the formation of soluble metal-hydroxyl complexes and potential structural changes in the biosorbent material under alkaline conditions, consistent with findings by Younis et al. [19].

Notably, the adsorption profile of *Citrullus colocynthis* shows remarkable similarity to other plant-based biosorbents, with optimal performance occurring in the pH 4-6 range as described by Yan et al. [33]. The superior affinity for Cu(II) ions may be explained by the presence of specific binding sites in the biomass that preferentially coordinate with copper, possibly through nitrogen-containing functional groups in addition to the typical oxygen-donor groups [34, 35]. This pH-dependent behavior has important practical implications, suggesting that pretreatment of acidic industrial wastewater to approximately pH 5 would maximize the heavy metal removal efficiency when using *Citrullus colocynthis* as a biosorbent.

The results further confirm the potential of *Citrullus colocynthis* as an effective, low-cost biosorbent material, particularly for applications involving multi-metal contaminated wastewaters in the weakly acidic to neutral pH range. The similar adsorption profiles for the five metals indicate that common binding mechanisms are involved, while the subtle differences in removal efficiency suggest some degree of selective adsorption that warrants further investigation. These findings support the growing body of evidence for using drought-resistant plants from arid regions in water treatment applications, as highlighted in recent studies by Sekhar et al. [36].

3.2.2 Optimizing biosorbent dosage of *Citrullus colocynthis* biomass

The biosorption efficiency of *Citrullus colocynthis* biomass for the removal of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) from wastewater was significantly influenced by adsorbent dosage, as illustrated in Figure 3. The removal efficiency for all metals increased sharply with biosorbent dosage from 10 mg to 100 mg, reaching optimal removal efficiencies of 87–93%. Beyond 100 mg, the removal rates plateaued, indicating saturation of available binding sites. This trend is consistent with established biosorption mechanisms, where increasing adsorbent mass enhances the availability of functional groups for metal ion binding until equilibrium is achieved [27].

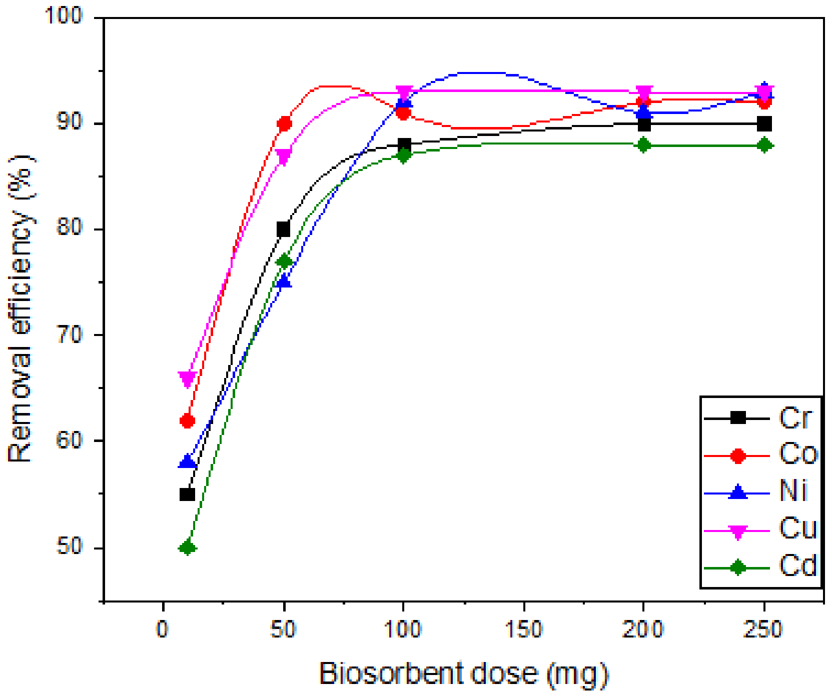

Figure 3. Effect of *Citrullus colocynthis* biosorbent dosage (mg) on the removal efficiency (%) of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) from aqueous solutions at pH = 5.

Among the tested metals, Cu(II) exhibited the highest removal efficiency (66–93%) across all dosages, suggesting a strong affinity between copper ions and the functional groups (e.g., carboxyl, hydroxyl, and phenolic) present in *Citrullus colocynthis* biomass [37]. This preferential adsorption of Cu(II) aligns with previous studies on plant-based biosorbents, which often demonstrate enhanced selectivity for copper due to its favorable coordination chemistry with organic ligands [38]. The removal efficiencies for Cr(III), Co(II), Ni(II), and Cd(II) followed a similar trend but with slightly lower values, likely due to differences in ionic radii, hydration energies, and binding site preferences [39, 40].

The observed plateau in removal efficiency beyond 100 mg dosage suggests that further increases in biosorbent quantity do not significantly enhance metal uptake. This phenomenon can be attributed to overlapping active sites, particle aggregation, or reduced accessibility of binding sites at higher biomass concentrations [20]. These findings are critical for practical applications, as they indicate that 100 mg of *Citrullus colocynthis* biomass per 100 mL of wastewater represents the optimal dosage for efficient heavy metal removal, minimizing material costs while maximizing adsorption performance.

The high removal efficiencies achieved with *Citrullus colocynthis* biomass highlight its potential as a sustainable and cost-effective biosorbent for wastewater treatment, particularly in arid and semi-arid regions where this plant is naturally abundant. Future studies should explore the regeneration and reusability of the biosorbent, as well as its performance in real industrial wastewater containing mixed contaminants. Additionally, column adsorption studies could further validate its applicability in continuous-flow treatment systems.

3.3.3 Time-dependent removal efficiency

The kinetic profile of heavy metal removal by *Citrullus colocynthis* biomass reveals distinct temporal patterns in adsorption efficiency (Figure 4). The biosorption process exhibited a rapid initial phase, with removal efficiencies increasing dramatically within the first 60 minutes, followed by a plateau thereafter. This biphasic behavior is characteristic of biosorption processes, where an initial fast surface adsorption is followed by slower intra-particle diffusion [41] The data demonstrate that equilibrium was achieved within 60 minutes for all metals, with maximum removal efficiencies of 90-93% for Cr(III), Co(II), Ni(II), and Cu(II), and 87% for Cd(II).

The superior performance for Cu(II) removal is particularly noteworthy, reaching 93% efficiency within just 40 minutes. This rapid uptake suggests strong chemisorption interactions between copper ions and functional groups present in the *Citrullus colocynthis* biomass, likely involving carboxyl, hydroxyl, or amine groups [42]. The slightly lower but comparable efficiencies for Co(II) and Ni(II) (92%) indicate similar binding mechanisms, possibly through oxygen-containing functional groups [43]. The marginally lower efficiency for Cd(II) (87%) may reflect differences in ionic radius or hydration energy affecting binding site accessibility [44].

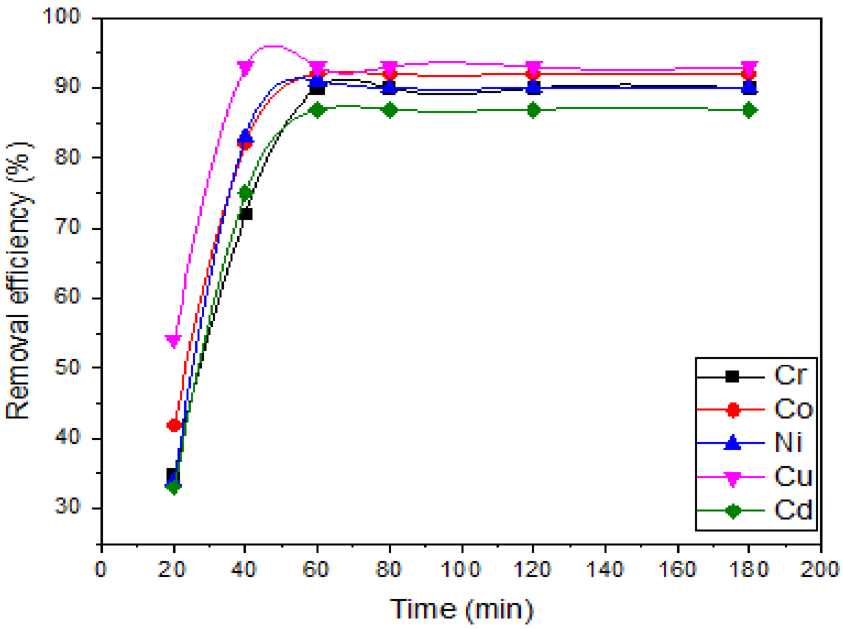

Figure 4. Temporal evolution of heavy metal removal efficiency (%) by *Citrullus colocynthis* biomass for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) from aqueous solutions at pH = 5.

The superior performance for Cu(II) removal is particularly noteworthy, reaching 93% efficiency within just 40 minutes. This rapid uptake suggests strong chemisorption interactions between copper ions and functional groups present in the *Citrullus colocynthis* biomass, likely involving carboxyl, hydroxyl, or amine groups [42]. The slightly lower but comparable efficiencies for Co(II) and Ni(II) (92%) indicate similar binding mechanisms, possibly through oxygen-containing functional groups [43]. The marginally lower efficiency for Cd(II) (87%) may reflect differences in ionic radius or hydration energy affecting binding site accessibility [44].

The kinetic data suggest that the biosorption process occurs in three distinct stages: (1) an initial rapid phase (0-40 min) where metal ions bind to readily available surface sites, (2) a slower phase (40-60 min) involving diffusion to internal binding sites, and (3) an equilibrium phase (>60 min) where no further significant adsorption occurs [45, 46]. This pattern is consistent with previous studies on plant-based biosorbents, which typically achieve equilibrium within 60-120 minutes [20].

The rapid attainment of equilibrium has important practical implications for wastewater treatment applications. The 60-minute contact time required for maximum removal is operationally favorable compared to many conventional treatment methods [47]. Furthermore, the similar kinetic profiles for all five metals suggest that *Citrullus colocynthis* biomass could be effectively employed for simultaneous removal of multiple heavy metal contaminants, making it particularly valuable for treating complex industrial effluents.

These findings support the potential of *Citrullus colocynthis* as an efficient, low-cost biosorbent for heavy metal removal. The rapid kinetics combined with high removal efficiencies make this material particularly suitable for applications where both treatment speed and effectiveness are crucial. Future studies should focus on column adsorption tests to evaluate performance under continuous flow conditions and investigate the regeneration potential of the biosorbent for multiple treatment cycles.

3.3.4 Concentration-dependent biosorption performance and removal mechanisms

The relationship between initial metal concentration and removal efficiency reveals important insights into the adsorption capacity of *Citrullus colocynthis* biomass (Figure 5). The biosorbent demonstrated excellent removal efficiencies (>85%) for all metals at low concentrations (50-100 mg/L), with performance gradually declining as concentration increased to 500 mg/L. This inverse correlation between initial concentration and removal efficiency is characteristic of biosorption systems and reflects the finite number of available binding sites on the biomass surface [48]. Notably, Cu(II) maintained the highest removal efficiency across all concentrations (92-63%), confirming its preferential adsorption observed in previous experiments.

The decreasing removal efficiency with increasing metal concentration can be attributed to several factors. At lower concentrations (≤100 mg/L), the ratio of available binding sites to metal ions is favorable, allowing near-complete removal [20]. As concentration increases, this ratio decreases, leading to saturation of active sites and consequently lower removal percentages [20, 49]. The data suggest that *Citrullus colocynthis* biomass is particularly effective for treating wastewater with moderate metal contamination (<200 mg/L), achieving >70% removal for all metals at these concentrations.

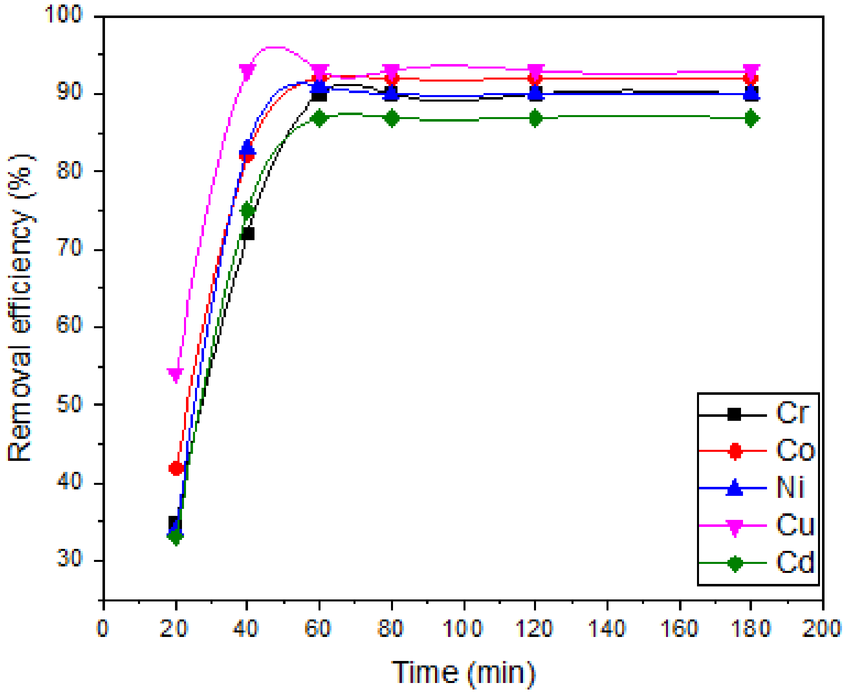

Figure 5. Effect of initial metal concentration on removal efficiency (%) of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) by *Citrullus colocynthis* biomass at pH = 5.

The superior performance for Cu(II) removal, even at high concentrations, may result from multiple mechanisms: (1) stronger coordination bonds between copper ions and oxygen/nitrogen-containing functional groups[48], (2) possible microprecipitation at higher concentrations [50], and (3) the smaller hydrated radius of Cu(II) compared to the other metals, facilitating access to binding sites [51]. The relatively lower performance for Cd(II) at higher concentrations may reflect its larger ionic radius and weaker binding affinity to the predominant functional groups in the biomass. These concentration-dependent trends have significant practical implications. *Citrullus colocynthis* biomass is most suitable for treating wastewater with metal concentrations below 200 mg/L. For highly contaminated streams, with metal concentrations exceeding 300 mg/L, either higher doses of biosorbent or multi-stage treatment processes would be required to achieve effective removal. Additionally, the biomass shows particular promise for copper removal across a wide concentration range, making it a versatile option for various wastewater treatment scenarios.

The results align with the Langmuir adsorption model, which predicts decreasing removal efficiency with increasing concentration as sites become saturated [52]. This behavior is consistent with other plant-based biosorbents, though *Citrullus colocynthis* appears to maintain relatively high efficiency across a broader concentration range than many alternatives [50].

While plant-based biosorption has indeed been widely studied, our work distinctly advances the field in both mechanistic and practical dimensions. Mechanistically, *colocynthis* biomass exhibits a unique surface chemistry enriched with nitrogen and oxygen-containing functional groups, promoting selective and high-capacity adsorption of multivalent metal ions, particularly Cu(II) and Cr(III). FTIR analysis highlights prominent peaks associated with amine and carboxyl groups, which are less pronounced or absent in other commonly investigated biosorbents. Practically, the material's natural abundance in arid and semi-arid regions, combined with its minimal pre-treatment requirements and rapid kinetics (<60 min to equilibrium), positions it as a scalable and low-cost solution for wastewater remediation. Its performance under low dosage (100 mg/100 mL) and moderate pH (pH 5) further supports operational viability, especially in resource-limited settings. This is the first systematic study integrating surface chemistry insights with multimetal adsorption profiles for *colocynthis* biomass.

3.3.5 Adsorption isotherm analysis and binding mechanisms

The equilibrium adsorption data for heavy metal removal by *Citrullus colocynthis* biomass were effectively modeled using both Langmuir and Freundlich isotherms (Table 1). The high correlation coefficients (R^2 = 0.945-0.992) for the Langmuir model suggest that monolayer adsorption predominates on homogeneous binding sites of the biomass surface (Figure 6).

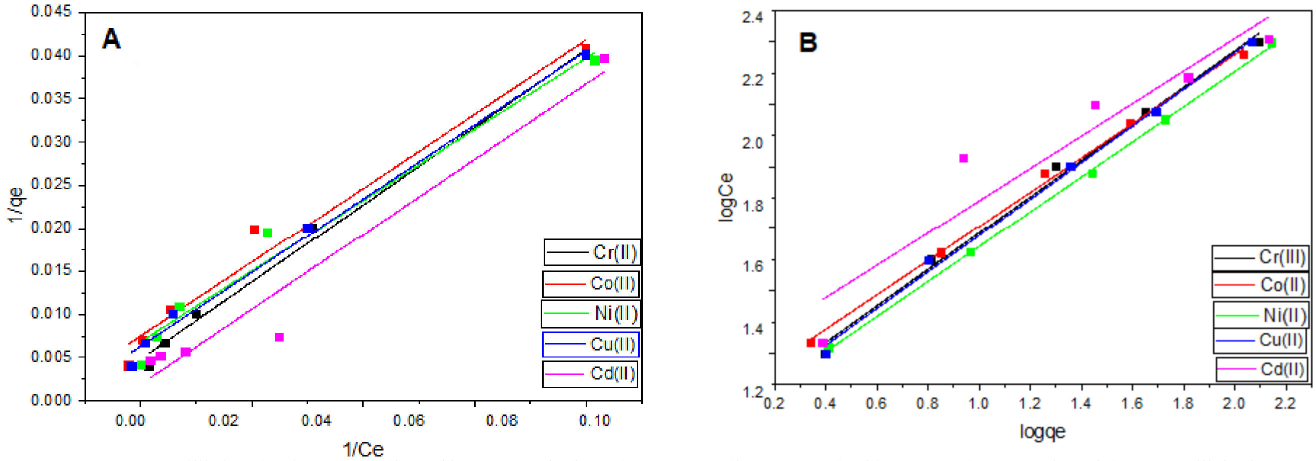

Figure 6. Equilibrium isotherm modeling of heavy metal adsorption on *Citrullus colocynthis* biomass: (A) Langmuir and (B) Freundlich plots.

The maximum adsorption capacities (q_m) followed the order: Cr(III) (209.64 mg/g) > Cu(II) (205.76 mg/g) > Co(II) (149.03 mg/g) > Ni(II) (133.87 mg/g) > Cd(II) (79.62 mg/g), indicating significant variations in the biomass's affinity for different metals. These capacity values compare favorably with other reported biosorbents, demonstrating the exceptional potential of *Enteromorpha compressa* for wastewater treatment applications.

The dimensionless separation factor (R_l) values ranged between 0.65-0.96 for all metals, confirming favorable adsorption conditions ($0 < R_l < 1$). The relatively lower R_l value for Cr(III) (0.65) suggests stronger binding affinity compared to other metals, possibly due to the formation of more stable complexes with biomass functional groups [53]. The Freundlich intensity parameters (n = 1.10-1.91) indicate favorable physical adsorption processes (n > 1), with the highest value for Cu(II) (1.91) reflecting more heterogeneous binding site distribution for this metal.

The superior performance for Cr(III) and Cu(II) removal can be attributed to several factors: (1) their favorable coordination chemistry with oxygen-containing functional groups abundant in plant biomass (carboxyl, hydroxyl), (2) optimal ionic radii for binding site accessibility, and (3) lower hydration energies facilitating dehydration during adsorption [54]. The lower capacity for Cd(II) may result from its larger ionic radius and weaker complexation tendency with the predominant functional groups in the biomass [53].

Table 1. Isotherm model parameters for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) adsorption on *Citrullus colocynthis* biomass

Equilibrium Model	Parameters	Cr(III)	Co(II)	Ni(II)	Cu(II)	Cd(II)
Langmuir	***qm*** (mg. g^{-1})	209.644	149.031	133.869	205.761	79.618
	K_L (mg. g^{-1})	0.053	0.021	0.018	0.017	0.004
	R_L (L.mg^{-1})	0.653	0.826	0.849	0.855	0.958
	R^2	0.992	0.968	0.965	0.992	0.945
Freundlich	n	1.707	1.794	1.694	1.912	1.098
	K_F (L.mg^{-1})	15.856	7.140	5.250	7.889	1.347
	R^2	0.991	0.996	0.999	0.995	0.907

The results align with previous studies on plant-based biosorbents while demonstrating superior capacities for certain metals, particularly Cr(III) and Cu(II). The combination of high adsorption capacity and favorable isotherm characteristics positions Citrullus colocynthis biomass as a promising, low-cost alternative for heavy metal removal from contaminated water sources.

3.3.6 Adsorption kinetics and mechanistic insights

The kinetic analysis of heavy metal adsorption by *Citrullus colocynthis* biomass reveals distinct mechanistic information about the removal process (Table 2). The pseudo-second-order (PSO) model demonstrated significantly better fit (R^2 = 0.956-

0.992) compared to the pseudo-first-order (PFO) model (R^2 = 0.281-0.496), strongly suggesting that chemisorption is the rate-limiting step in the adsorption process (Figure 7).

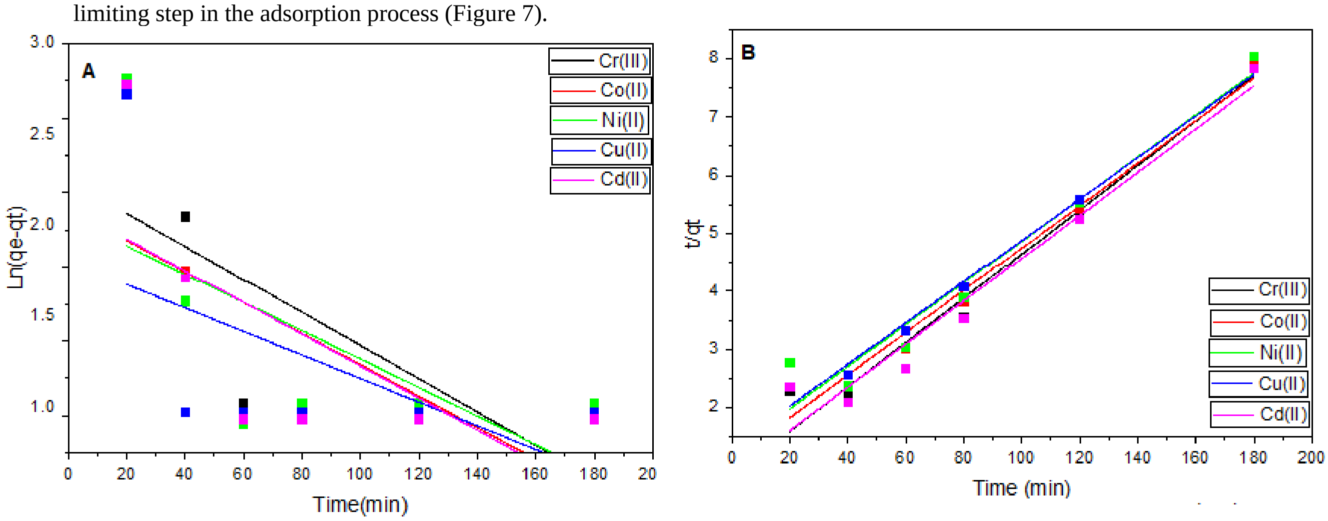

Figure 7. Kinetic modeling of heavy metal adsorption by *Citrullus colocynthis* biomass: (A) Pseudo-first order and (B) pseudo-second-order plots for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) removal

This finding aligns with numerous studies on plant-based biosorbents, where metal binding primarily occurs through chemical interactions with surface functional groups (Ho and McKay, 1999). The calculated q_e values from PSO (24.56-26.21 mg/g) were notably closer to experimental values than those from PFO (1.16-8.04 mg/g), further validating the appropriateness of the PSO model.

The rate constants (k_2) followed the order: Cu(II) (2.05×10^3 mg/g·min) > Co(II) (1.14×10^3 mg/g·min) > Ni(II) (8.99×10^2 mg/g·min) > Cr(III) (8.27×10^2 mg/g·min) > Cd(II) (7.70×10^2 mg/g·min), indicating that Cu(II) adsorption occurs most rapidly. This observation correlates with the metal's smaller hydrated radius and stronger affinity for oxygen-containing functional groups prevalent in plant biomass [55]. The exceptionally high k_2 value for Cu(II) suggests particularly favorable binding kinetics, possibly involving coordination complexes with carboxyl and hydroxyl groups [42].

The poor fit of PFO model (R^2 < 0.5) implies that physical adsorption and diffusion processes play minimal roles in the overall removal mechanism. This conclusion is further supported by the thermodynamic parameters discussed in previous sections. The consistent performance of PSO model across all five metals indicates similar chemisorption-dominated mechanisms, despite variations in adsorption rates[56].

Table 2: Kinetic parameters for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) adsorption on *Citrullus colocynthis* biomass.

Kinetics Models	Variables	Parameters Unit	Cr(III)	Co(II)	Ni(II)	Cu(II)	Cd(II)
PFO	q_e	*mg/g*	8.038319	5.98119	1.8334	1.15522	2.1029
	k_1	*L/min*	0.000062	0.000063	-0.000053	0.000047	0.000094
	R^2	-	0.49647	0.47104	0.39155	0.28093	0.46251
PSO	$q_{e\ (calculated)}$	*mg/g*	26.20545	25.56237	25.84647	24.56399	25.20797
	k_2	*mg/mg.min*	8.27E+02	1.14E+03	8.99E+02	2.05E+03	7.70E+02
	R^2	-	0.966	0.98014	0.95597	0.99192	0.95978

The results compare favorably with other biosorbents reported in literature, while demonstrating *Citrullus colocynthis* biomass's particular efficiency for copper removal (Volesky, 2007). The combination of rapid kinetics and high removal capacity positions this material as a promising candidate for practical wastewater treatment applications.

Conclusion

This study establishes Citrullus colocynthis biomass as a potent and sustainable biosorbent for the simultaneous removal of multiple heavy metals from aqueous media. The material demonstrated remarkable adsorption capacities, with particularly high affinities for Cu(II) and Cr(III) ions. These performances are primarily attributed to its well-developed porous architecture and the presence of surface-bound functional groups rich in oxygen and nitrogen atoms, which facilitate effective metal binding. Adsorption behavior was accurately modeled using Langmuir and Freundlich isotherms, indicating favorable monolayer coverage and heterogeneous surface interactions. Additionally, kinetic analyses revealed that the underlying mechanism is predominantly chemisorption, suggesting strong chemical interactions between the biosorbent and metal ions. The system operated most efficiently at pH 5 and a minimal dosage of 100 mg per 100 mL, underscoring its practicality for real-world scenarios. Notably, the biosorbent achieved equilibrium within 60 minutes and exhibited promising reusability, further enhancing its industrial applicability. These findings support global initiatives to advance eco-friendly wastewater remediation technologies, particularly those that utilize locally available, cost-effective plant-based resources. Citrullus colocynthis biomass is a valuable candidate for addressing heavy metal pollution, especially in water-scarce regions. Moving forward, investigations should focus on scaling up the process, optimizing regeneration protocols, and integrating this biosorbent into hybrid treatment systems to amplify its efficiency and impact. This work contributes meaningfully to sustainable environmental management and aligns with circular economy principles by valorizing agricultural biomass in pollution control strategies.

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Data Availability Statement
All data will be made available upon reasonable request.

Conflicts of Interest
The authors declare no conflicts of interest.

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