Sustainable Conversion of Shrimp Shell Waste into Bio-adsorbent for Cd(II) and Ni(II) Removal from Industrial Wastewater

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ABSTRACT

This study *explores the modification of shrimp shell waste (SSW) using NaOH and H_2O_2 to enhance its adsorption efficiency for Cd(II) and Ni(II) removal from industrial wastewater. At pptimized conditions (pH 6 for Cd, pH 5 for Ni), maximum adsorption capacities of 33.62 mg/g and 13.70 mg/g were achieved, respectively. SEM and FT-IR confirmed structural changes improving adsorption performance. Langmuir isotherm model indicated monolayer adsorption. The findings highlight chitin's potential as a cost-effective, sustainable adsorbent for wastewater treatment.*

Keywords: **Shrimp shell waste, Chitin, Adsorption, Heavy metal removal, Wastewater treatment, Sustainable adsorbent**

1. *INTRODUCTION*

The global seafood industry generates substantial waste, with shellfish waste alone reaching 6–8 million tons annually [1], [2]. The FAO projects fishery and aquaculture production to hit 202 million tons per year by 2030, increasing seafood demand and marine waste [1]. Crustacean shells, rich in chitin, calcium carbonate, and proteins, offer a sustainable biomass source for chitin extraction, supporting the circular economy [1], [3]. The extraction process involves demineralization and deproteinization, where acids like lactic, citric, or hydrochloric dissolve minerals, and alkaline treatments (typically NaOH) remove proteins [4]. While effective, environmental concerns drive research into greener extraction methods [5].

Chitin is a structurally robust polysaccharide with applications in various industries, including wastewater treatment, agriculture, and biomedicine [3]. Its ability to form strong hydrogen bonds contributes to its high stability and resistance to degradation, making it suitable for environmental applications such as heavy metal adsorption [1], [5]. The extraction of chitin from fishery waste not only provides an alternative to synthetic polymers but also aligns with the principles of sustainable resource management by converting marine waste into valuable materials [5].

Water resources contamination by heavy metals is a critical environmental issue as they are non-biodegradable and persist in aquatic environments, leading to bioaccumulation and toxicity in marine life and humans [6], [7]. The World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) have set strict permissible limits for heavy metals in drinking water, underscoring the necessity of effective removal methods [6]. Adsorption has emerged as a highly efficient and cost-effective method for removing heavy metals from wastewater, particularly when utilizing bio-based adsorbents such as chitin [8], [9]. For example, Boddu et al. [2] studied the removal of copper ions (Cu(II)) and Pb(II) from electroplating wastewater using H_2O_2-treated shrimp shells and reported a maximum biosorption efficiencies of 96.42% for Cu at pH 5 in 40 minutes and 89.77% for Pb at pH 6 in 30 minutes under conditions of 20 mg/L concentration, 0.1 g adsorbent loading, and 303 K temperature.

The main goal of this study was to treat shrimpshell waste (SSW) with NaOH and H_2O_2 to enhance its physicochemical properties and improve its effectiveness in removing Cd(II) and Ni(II) from aqueous solutions. The proposed adsorbent's effectiveness was assessed under various pH and adsorbent dosage, to identify the optimal parameters for efficient metal removal. SEM analysis was performed to examine the surface morphology and porosity of chitin and SSW before and after heavy metal loading.

2. MATERIALS AND METHODS

Wastewater samples were simulated in the laboratory using standard heavy metal solutions, including Cd standard (1000 ppm in 2% HCl) for AAS and Ni standard (10,000 ppm in 3% v/v HNO_3) for ICP. The initial heavy metal concentration was set at 25 mg/L to evaluate other experimental factors. Test solutions of 25 ppm were prepared by diluting stock solutions with distilled water. The pH of the test solutions was adjusted to the desired level using 0.1 M HCl and 0.1 M NaOH, with an initial pH of 4, which closely matches the natural pH of the solutions. All chemicals used in this study were of analytical grade.

Shrimp shells were collected, rinsed with tap water to remove impurities, and thoroughly washed with distilled water. They were air-dried for 24 hours, then mechanically ground to a fine powder and sieved (#100). To remove biological pigments and proteins, the powdered shrimp shells were treated with a 5 wt.% NaOH and 1 wt.% H_2O_2 solution (L/S = 20), stirred at 303 K for 72 hours. The resulting residue was washed with distilled water until neutral, filtered using an EZFlow membrane filter (47 mm, 0.45 µm pore size), and oven-dried at 70°C overnight. The dried chitin was then stored in an airtight container for further use [2].

The adsorption of Cd(II) and Ni(II) using chitin was studied in batch mode under varying experimental conditions, including pH levels (4 to 7) and adsorbent dosages (0.1, 0.2, 0.3, 0.4, and 0.5 g per 100 mL solution). Batch adsorption experiments were conducted for 24 hours to ensure equilibrium [2]. After each experiment, the chitin loaded with heavy metals was separated from the aqueous phase through filtration. Each experimental run was performed in triplicate, and the average values were reported. The residual concentrations of heavy metals were determined using Atomic Absorption Spectroscopy (AAS) (PinAAcle 500, Perkin Elmer, Canada). The detection wavelengths were 228.8 nm for Cd(II) and 232 nm for Ni(II). The initial and equilibrium metal concentrations in solution were denoted as Ci and Ce, respectively.

The adsorption removal efficiency (%) was calculated using equation 1:

$$Adsorption\ Removal\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

The adsorption capacity of chitin (q_e) was evaluated from the Eq. (2);

$$Adsorption\ Capacity\ (mg/L) = \frac{(C_i - C_e)\,V}{chitin\ dosage} \quad (2)$$

where V represents the volume of the solution (L), Ci and Ce are the initial and equilibrium heavy metal concentrations (mg/L), and chitin dosage is given in grams.

In order to identify the surface topography and surface elemental composition of adsorbent, Scanning Electron Microscopy (SEM) (JEOL JSM-7500F) was used and observe the images at 3.0 kV acceleration voltage. To measure pH, a HACH (HQ40D) Instrument pH Meter was applied. Functional groups existing in chitin was analyzed with Fourier Transform Infrared Spectroscopy (FT-IR) using an attenuated total reflectance (ATR) sampling method within 400–4000 cm^{-1} range (Thermo Fischer, Nicolet 6700).

3. *RESULTS AND DISCUSSION*

3.1 Chitin Characterization

SEM analysis was performed to examine the morphology and porosity of chitin under studied adsorption conditions. The experimental parameters were set at an initial metal concentration of 25 ppm, 24-hour contact time, room temperature, and pH 6 for Cd(II) and pH 5 for Ni(II). The studied chitin dosage was 0.25 g per 100 mL solution. The obtained SEM images are presented in Figure 1. The SEM micrographs

revealed that chitin exhibits a highly heterogeneous, porous, and rough surface morphology, which contributes to its adsorption capacity. SEM imaging was also conducted after the adsorption of Ni(II) and Cd(II) (Figure 1). The post-adsorption images showed that the porous surface of chitin was covered with Ni(II) and Cd(II) ions, confirming the high removal efficiency of chitin for heavy metal adsorption (section 3.2).

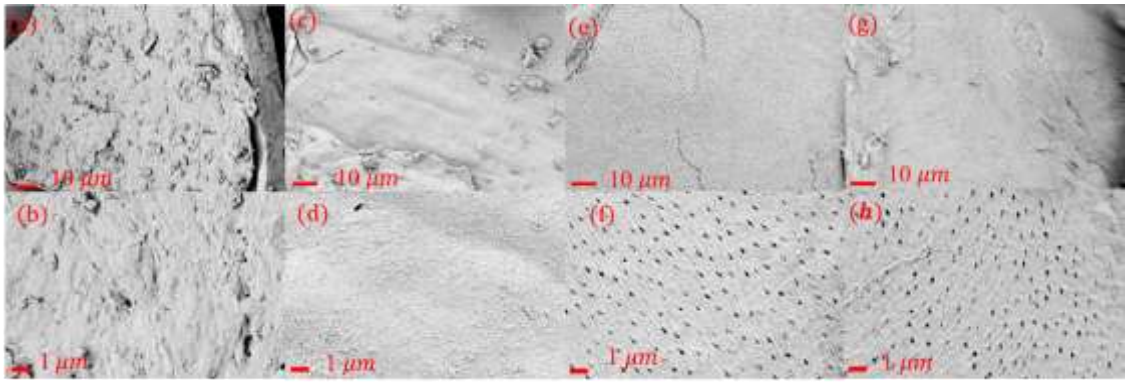

Figure 1. SEM analysis (a) and (b) original SSW; (c) and (d) chitin (before adsorption process); (e) and (f) chitin loaded with Ni(II); (g) and (h) chitin loaded with Cd(II).

FT-IR analysis was conducted to investigate the functional groups of SSW and unloaded and metal-loaded chitin, assessing their role in heavy metal binding. The analysis was performed under 25 ppm initial concentration, 24-hour contact time, room temperature, pH 6 for Cd(II), and pH 5 for Ni(II).

As shown in Figure 2, significant differences between SSW and purified chitin (Figure 2A) indicate chemical changes during extraction. In untreated SSW, the broad O-H/N-H stretching band (~3263 cm^{-1}) becomes sharper in chitin, confirming the removal of proteins and enhanced hydroxyl group presence [2]. The weakening of Amide I (1627 cm^{-1}) and Amide II (1515 cm^{-1}) bands further validates successful deproteinization and demineralization [10]. Additionally, the carbonate-related band (~1400 cm^{-1}) strengthens, highlighting increased carbonate exposure after purification. The C-O stretching band (1014 cm^{-1}) also becomes more pronounced in chitin, indicating a well-defined structure [10].

Upon Cd(II) and Ni(II) adsorption (Figure 2B), the O-H stretching bands (3420 and 3260 cm^{-1}) remain weak, suggesting hydroxyl involvement in metal binding [10]. Notable shifts in the C-O stretching region (1014 cm^{-1}), particularly with Cd(II), indicate strong coordination with oxygen-containing functional groups. The emergence of metal-ligand bands (543 cm^{-1} and ~871 cm^{-1}) further confirms metal-chitin complex formation [2]. These findings demonstrate that purified chitin, with its well-defined structure and available hydroxyl and carboxyl groups, exhibits superior heavy metal adsorption.

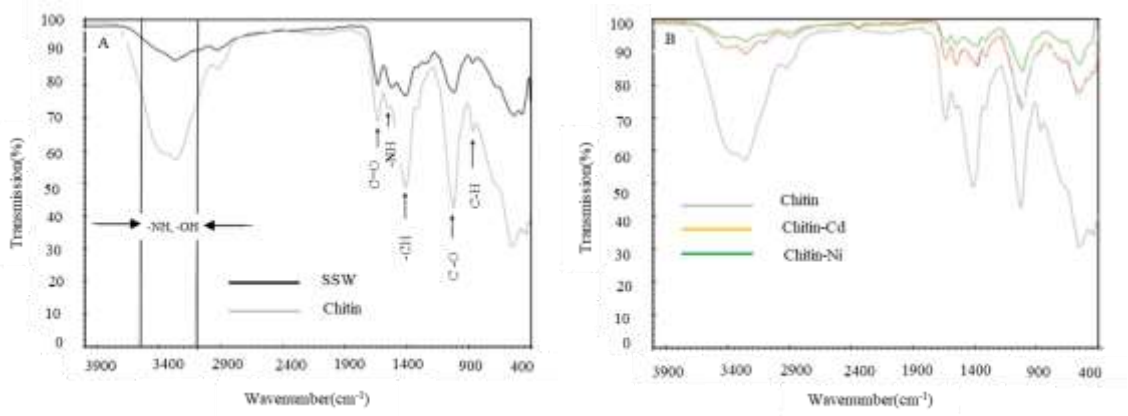

Figure 2. FT-IR analysis on (A) SSW and chitin;(B) chitin and chitinn loaded with Cd(II) and Ni(II)

3.2 Effect of Experimental factors on Adsorption

3.2.1 Effect of pH

The pH of the solution plays a crucial role in adsorption efficiency by influencing chitin-adsorbate interactions, including ionization, protonation/deprotonation of active sites, surface properties, and metal ion speciation. The effect of initial pH (4.0–8.0) on the adsorption efficiency of Cd(II) and Ni(II) at an adsorbent dosage of 2.5 mg/L was investigated. The results indicate that removal efficiency increased from pH 4 to 5 for both metals due to the presence of amino groups in chitin. However, beyond pH 5, the efficiency gradually declined. For Cd(II), adsorption remained relatively constant, with the highest removal at pH 6. Based on these findings and previous studies [11], [12], the optimal pH for adsorption was determined to be pH 5 for Ni(II) and pH 6 for Cd(II). Under these conditions, the maximum removal efficiencies achieved were 99.75% for Cd(II) and 99.83% for Ni(II), demonstrating the effectiveness of chitin in weakly acidic environments.

3.2.2 Chitin dosage

Determining the optimal adsorbent dosage is crucial for maximizing interactions between metal ions and adsorption sites while maintaining high removal efficiency. The effect of chitin dosage (0.1–0.5 g/L) on Cd(II) and Ni(II) adsorption was examined at 25 mg/L metal concentration, pH 4, and 293 K, with a 24-hour contact time. Figure 3 illustrates the impact of varying chitin dosages on adsorption capacity and removal efficiency. For Cd(II), removal increased sharply from 54.36% to 99.83% as dosage increased from 1 to 5 mg/L, before reaching a plateau, consistent with previous studies [13]. However, adsorption capacity (mg/g) followed a reverse trend [14], decreasing from 13.59 to 4.99 mg/g, likely due to incomplete saturation of binding sites. A similar pattern was observed for Ni(II), where removal increased from 77.80% to 97.91%, while adsorption capacity declined from 19.45 to 4.89 mg/g. The optimal dosage for maximum removal efficiency and adsorption capacity was determined to be 0.25 g (2.5 mg/L), which was used for further experiments.

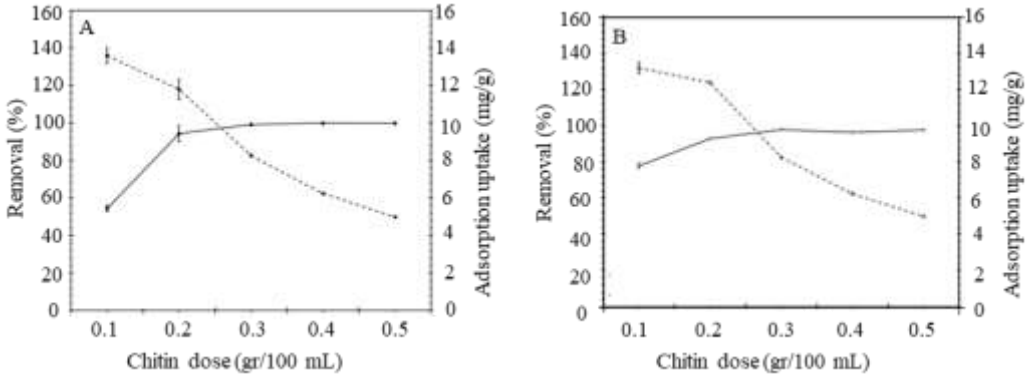

Figure 3. Effect of chitin dosage on removal and adsorption uptake: (A) Cd; (B) Ni

3.2.3. Equilibrium isotherms

To enhance the design and efficiency of the adsorption process, it is essential to establish a correlation between equilibrium adsorption data and isotherm models. Adsorption isotherms describe the relationship between the adsorption capacity—the amount of adsorbate retained by the adsorbent—and the adsorbate concentration in solution at a constant temperature [15]. This study evaluated the Langmuir and Freundlich isotherm models for the removal of Cd(II) and Ni(II) from the solution. Figure 4 presents the isotherm curves generated using experimental data. The Freundlich isotherm model assumes adsorption occurs on a heterogeneous surface with non-uniformly distributed active sites, accommodating multilayer adsorption. In

contrast, the Langmuir isotherm model describes monolayer adsorption on a homogeneous surface, where adsorption takes place at a fixed number of identical and energetically equivalent sites, with no lateral interactions or steric hindrance between adsorbed molecules [16].

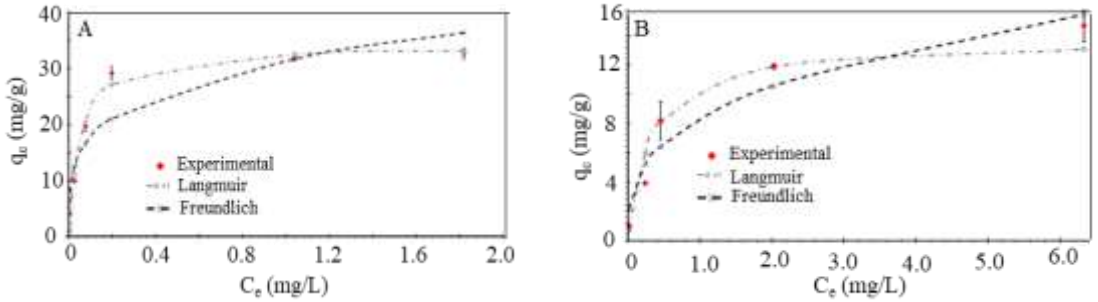

Figure 4 Langmuir and Freundlich isotherm models of the adsorption for A: Cd and B: Ni on chitin

Langmuir model (Table 1) described the adsorption behavior better, indicating a homogeneous surface with uniformly distributed adsorption sites. According to the Langmuir model, the maximum adsorption capacities were 33.616 mg/g for Cd(II) (at 20°C, pH 6, and 2.5 mg/L chitin) and 13.70 mg/g for Ni(II) (at pH 5 under the same conditions). The Langmuir constant (KL) was highest for Cd(II), suggesting a stronger affinity of chitin for Cd(II) ions, leading to greater adsorption at higher concentrations [17].

Table 1. Langmuir and Freundlich isotherm data for Cd(II), and Ni(II)

Model	*Constant*	*Cd*	*Ni*
Langmuir	q_{max} *(mg/g)*	*33.62*	*13.70*
	K_L *(L/mg)*	*18.86*	*3.18*
	E	*3.11*	*2.93*
	R^2	*0.996*	*0.975*

4. CONCLUSIONS

This study demonstrates the potential of shrimp shell-derived chitin as an effective, eco-friendly adsorbent for heavy metal removal from aqueous solutions. By modifying SSW with NaOH and H_2O_2, the physicochemical properties of chitin were enhanced, leading to improved adsorption efficiency for Cd(II) and Ni(II). The adsorbent's performance was systematically evaluated under varying pH and dosage conditions, identifying optimal parameters for maximum removal efficiency.

Characterization through SEM and FT-IR confirmed the structural and chemical modifications that contributed to improved adsorption. Isotherm analysis indicated that the Langmuir model best described the adsorption process, suggesting monolayer adsorption with well-defined binding sites. The high adsorption capacities achieved in this study highlight the feasibility of using chitin-based materials for water purification applications.

Overall, the findings contribute to sustainable waste valorization by repurposing marine biowaste into functional adsorbents for environmental remediation. Future work should explore large-scale applications and potential regeneration techniques to enhance the economic viability of this approach.

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