

Study of Adsorption Characteristics of Co(II) on Eggshell Residue

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A comparative study was conducted to evaluate the adsorption performance of cobalt(II) ions using untreated chicken eggshell powder (ES) and sulfuric acid-treated eggshell (EST). X-ray diffraction (XRD) analysis revealed characteristic 2θ values of 29.578° for ES and 29.483° for EST, corresponding to CaCO_3 . Following Co(II) adsorption, a reduction in crystal spacing and an increase in d-spacing were observed, suggesting enhanced repulsion between native Ca(II) and adsorbed Co(II) ions, along with reduced crystal density and increased bond lengths. Scanning electron microscopy (SEM) images revealed irregular particle morphologies and the formation of spherical or ovoid clusters following adsorption. Adsorption equilibrium was reached within 90 minutes. The Co(II) removal efficiency improved with increasing adsorbent dosage for both ES and EST. Surface modification with H_2SO_4 and NaHCO_3 expanded the effective pH range for Co(II) removal from 2–4 (ES) to 2–8 (EST), attributed to a shift in the point of zero charge (pHpzc) toward weakly basic values. Thermodynamic analyses confirmed that the adsorption process was endothermic and governed by physical interactions. Adsorption isotherms were evaluated using Freundlich, Langmuir, and Temkin models, with the results indicating that the Freundlich and Temkin models provided the best fit to the experimental data.

Keywords: adsorption of cobalt (II), eggshell (ES), eggshell treatment (EST), adsorption isotherm, removal

Introduction

Industrial, agricultural, and military activities have significantly contributed to the contamination of ecosystems with heavy metals and radioactive substances. These pollutants pose serious risks to both environmental and human health due to their persistence and toxicity. Among them, heavy metals are particularly problematic due to their non-biodegradable nature and slow natural attenuation, which makes their accumulation in the environment a critical concern.

Various technologies have been developed for the removal of heavy metals from contaminated media, including ion exchange, chemical precipitation, and membrane filtration. However, these conventional methods often require high operational costs and the use of additional chemicals, which may generate secondary waste and complicate disposal procedures [1]. Consequently, the search for more economic, efficient, and sustainable alternatives remains an active area of research.

Adsorption has emerged as one of the most promising and widely used methods for removing heavy metals from wastewater. It offers several advantages, such as operational simplicity, low cost, and high efficiency even at low contaminant

concentrations. Numerous natural and synthetic adsorbents have been explored, including activated carbon, zeolites, and agricultural by-products such as sawdust [2].

In parallel, large quantities of chicken eggshells are generated as waste from households, food services, and food processing industries. Traditionally considered a non-utilizable solid waste, eggshells are primarily composed of calcium carbonate and have demonstrated potential as a low-cost and effective adsorbent for removing various pollutants, including dyes such as Congo red [3], and heavy metals like cadmium, copper [4], lead [5], and nitrophenol [6].

The present study examines the potential of untreated and acid-treated chicken eggshell powder as an environmentally friendly, cost-effective, and readily available adsorbent for removing cobalt(II) ions from aqueous solutions. This work aims to contribute to the development of sustainable waste valorization strategies while addressing the urgent need for efficient heavy metal remediation techniques.

Experimental part

Materials

Chicken eggshells (ES) were collected from local poultry farms in Iraq. Cobalt(II) chloride hexahydrate

($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), sulfuric acid (H_2SO_4 , 95–98%), and sodium bicarbonate (NaHCO_3 , $\geq 99\%$) were purchased from BDH Chemicals (UK) and used as received without further purification.

Preparation of adsorbent materials

The collected eggshells (ES) were thoroughly cleaned by repeated washing with distilled water to remove dirt and impurities. The cleaned shells were then dried in an electric oven at 100°C for 1 hour. After drying, the ES was ground using a mechanical mill and sieved to obtain particles of uniform size. A portion of this material was set aside for further chemical modification.

To prepare the acid-treated eggshell adsorbent (EST), a known amount of ground ES was immersed in a 1:1 (w/v) H_2SO_4 solution and left to react overnight at room temperature. The treated material was subsequently rinsed several times with distilled water to remove residual acid. To neutralize any remaining acidity and bring the pH closer to neutral, the material was soaked in a 2% sodium bicarbonate (NaHCO_3) solution. After additional washing with distilled water, the EST material was dried at 150°C and stored in an airtight container for subsequent use.

Characterization of adsorbents

The crystalline structure of both ES and EST was analyzed using X-ray diffraction (XRD) with a LabX XRD-6000 (Shimadzu), recording diffraction patterns over the 2θ range of 0 – 80° . Surface morphology and particle geometry were examined by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). The residual concentration of cobalt(II) ions in solution after adsorption was quantified using an atomic absorption spectrophotometer (AA-6300, Shimadzu) at a wavelength of 240.7 nm.

Adsorption experiments

Batch adsorption experiments were performed to evaluate the Co(II) removal efficiency of ES and EST. In each experiment, 0.25 g of adsorbent was added to a 50 mL aqueous solution of Co(II) with an initial concentration of 10 mg/L. The mixture was agitated on a rotary orbital shaker for 90 minutes to reach equilibrium. After equilibration, the mixture was centrifuged, and the supernatant was analyzed to determine the residual Co(II) concentration.

The removal efficiency (E, %) was calculated using Equation (1):

$$E, \% = ((C_0 - C_t) / C_0) \times 100, \quad (1)$$

where C_0 and C_t (mg/L) represent the initial and time-dependent Co(II) concentrations, respectively.

The adsorption capacity at equilibrium (Q_e , mg/g) was calculated using Equation (2):

$$Q_e = ((C_0 - C_e) V) / m, \quad (2)$$

where C_e (mg/L) is the equilibrium Co(II) concentration, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent (ES or EST).

Results and Discussion

XRD Analysis

X-ray diffraction (XRD) was employed to investigate the crystalline structure and changes in the crystallinity of both untreated (ES) and acid-treated (EST) eggshell samples. As shown in Figures 1a and 1c, the predominant crystalline phase in both samples corresponds to calcium carbonate (CaCO_3), with characteristic diffraction peaks observed at $2\theta = 29.5784^\circ$ for ES and 29.4821° for EST [10]. The slight shift in the peak position for EST may be attributed to the incorporation or surface adsorption of sulfate ions from the acid treatment.

After the adsorption of Co(II) ions, further peak shifts were observed toward lower 2θ values: 29.405° for ES-Co and 29.306° for EST-Co (Figures S1b and S1d). These shifts indicate lattice distortion and the generation of internal stress within the crystal structure, likely resulting from the substitution or incorporation of Co(II) ions. Given that the ionic radius of Co(II) (0.709 Å) is smaller than that of Ca(II) (1.155 Å), this substitution leads to local strain and disruption in the CaCO_3 lattice [11]. Additionally, such stress may be further amplified by surface defects and grain boundaries introduced during treatment or adsorption [12].

A notable observation is the disappearance of Ca(OH)_2 peaks at approximately $2\theta \approx 25^\circ$, which were previously present in both ES and EST samples. This suggests a reduction in crystallinity following Co(II) adsorption, consistent with structural disorder induced by ion-exchange or surface-complexation processes [13].

As presented in Table 1, the d-spacing values of ES and EST increased after the adsorption of Co(II). This expansion of the crystal lattice may result from electrostatic repulsion between incoming Co(II) ions and native Ca(II), as well as the elongation of bond lengths. The increased interplanar spacing and lattice expansion are indicative of decreased crystal packing density [12]. Moreover, the higher d-spacing and accompanying decrease in average crystallite size observed for EST (compared to ES) suggest enhanced surface area and porosity, which likely contribute to the improved adsorption performance of the treated material.

Table 1. The d-spacing values of ES and EST before and after Co(II) adsorption.

Samples	d-spacing (Å)
ES before Co(II) adsorption	3.011
ES after Co(II) adsorption	3.034
EST before Co(II) adsorption	3.027
EST after Co(II) adsorption	3.045

SEM-EDX Analysis

Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) was employed to investigate the surface morphology and

elemental composition of the eggshell adsorbents (ES and EST) before and after Co(II) adsorption, as illustrated in Figure 1 and S2. Figures 1a and S2a show that the untreated eggshell (ES) surface exhibits an irregular texture with relatively large, unevenly distributed spherical pores. The corresponding EDX spectrum confirms that the major elemental constituents of ES are calcium (Ca), carbon (C), and oxygen (O), accounting for nearly 100% of the detected elements, consistent with the presence of calcium carbonate. After chemical treatment, the surface morphology of EST (Figures 1b and S2b) exhibits noticeable changes, characterized by the formation of semi-spherical clusters and irregular porous structures. These morphological features are likely the result of surface modifications induced by sulfuric acid and sodium bicarbonate treatment. EDX analysis further confirms the presence of sulfur (S), indicating successful incorporation or surface adsorption of sulfate groups during the treatment process. The adsorption of Co(II) onto both ES and EST surfaces is evident from the SEM images and EDX spectra presented in Figures 1c and S2c. The surface of the materials after adsorption shows a significant

reduction in pore visibility, with the appearance of aggregated sphere-like substructures covering large portions of the surface. This morphological transformation suggests that Co(II) ions were effectively adsorbed and distributed over the surface of the material, likely through surface complexation or ion-exchange mechanisms.

Effect of Contact Time

To determine the time required to reach adsorption equilibrium, a fixed concentration of cobalt(II) solution was contacted with both untreated (ES) and treated (EST) eggshell adsorbents. The experiments were conducted at successive time intervals (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 minutes), and the residual Co(II) concentration in the solution was analyzed accordingly. As shown in Figure S3, the removal efficiency of Co(II) increased progressively with contact time for both ES and EST, reaching equilibrium at approximately 90 minutes. Beyond this point, no significant enhancement in adsorption was observed; in fact, a slight decrease in removal efficiency occurred. This decline is likely due to the limited availability of active adsorption sites, as most of the accessible surface binding sites become saturated

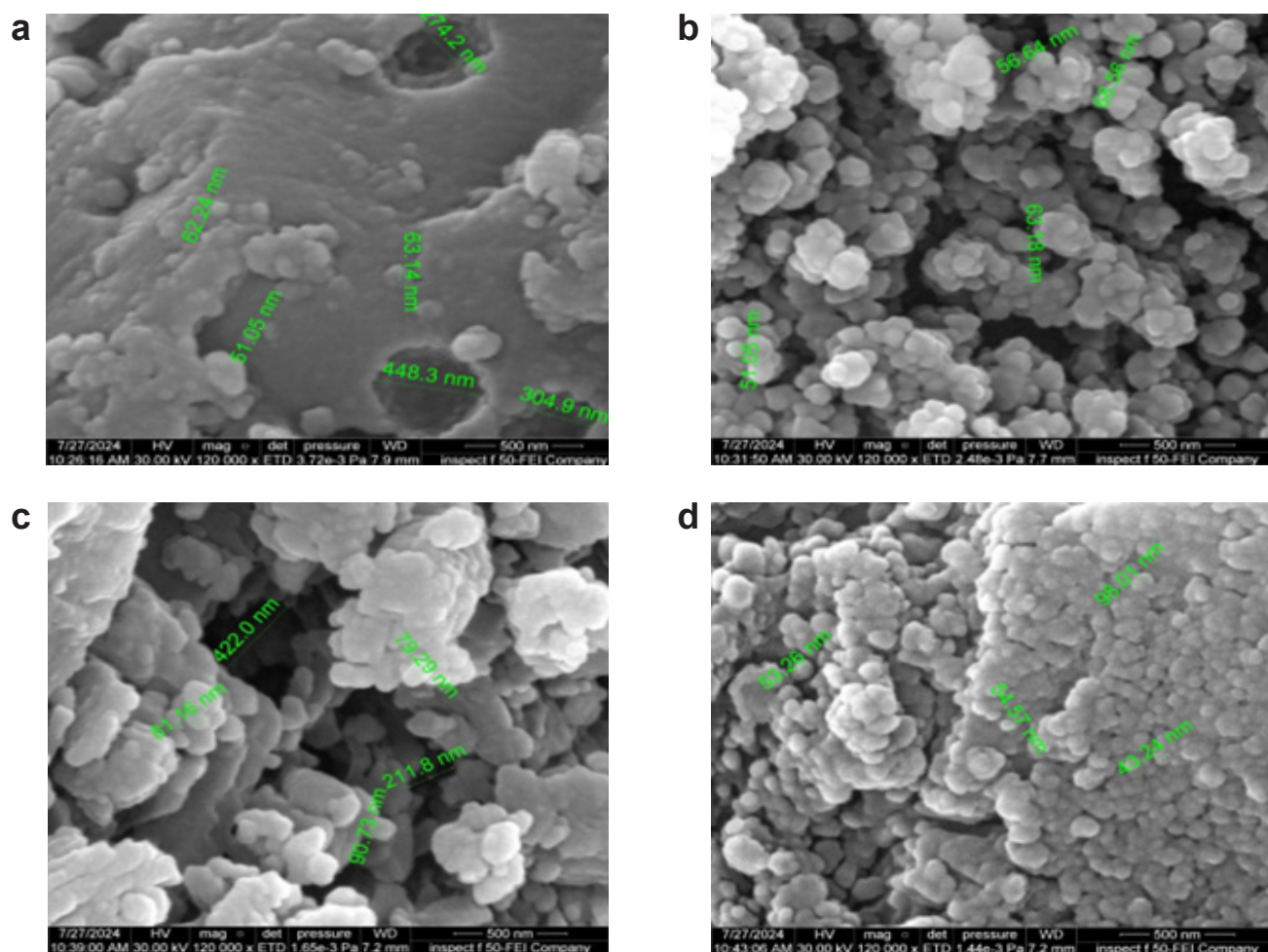


Figure 1. SEM micrographs of eggshell samples: (a) untreated eggshell (ES) before Co(II) adsorption; (b) ES after Co(II) adsorption; (c) acid-treated eggshell (EST) before adsorption; (d) EST after Co(II) adsorption.

over time [14]. Although both adsorbents exhibited the same equilibrium time, the overall adsorption capacity of EST was notably higher than that of ES. This enhancement is attributed to the surface modification during acid-base treatment, which increased porosity and surface functionality, thereby improving the material's affinity for Co(II) ions. These results indicate that 90 min is the optimal contact time for achieving maximum Co(II) removal under the given conditions, with EST exhibiting superior performance due to its modified physicochemical properties.

This morphological transformation suggests that Co(II) ions were effectively adsorbed and distributed over the surface of the material, likely through surface complexation or ion-exchange mechanisms. To further investigate the adsorption behavior and performance of both untreated (ES) and acid-treated (EST) eggshells, a series of batch adsorption experiments were conducted. These included studies on the effect of contact time, adsorbent dosage, initial Co(II) concentration, solution pH, and temperature. Each of these parameters plays a crucial role in determining the adsorption efficiency and mechanism, and their systematic evaluation provides a comprehensive understanding of the adsorbent's potential under varying environmental conditions.

Effect of Adsorbent Dosage

Adsorbent dosage is a crucial parameter that significantly influences adsorption capacity and removal efficiency. At a constant initial concentration of Co(II), an increase in the adsorbent dosage leads to a corresponding increase in the percentage of metal ion removal, as illustrated in Figure S4. This enhancement is attributed to the greater available surface area and a higher number of active binding sites provided by the increased amount of adsorbent [15].

In this study, varying doses of both ES and EST were tested within the range of 0.05 to 0.30 g. The results demonstrate a positive correlation between

adsorbent dosage and Co(II) removal efficiency up to a certain threshold. The optimum dosage for both ES and EST was determined to be 0.25 g, beyond which further increases in dosage resulted in minimal improvement. This plateau effect is likely due to the saturation of available Co(II) ions in solution, leading to a reduced adsorbent–adsorbate interaction per unit mass. Notably, the treated eggshell (EST) exhibited superior performance at all dosages compared to untreated ES, owing to its improved surface properties and higher affinity for Co(II) ions following chemical modification.

Effect of Initial Co(II) Concentration

The initial metal ion concentration plays a crucial role in overcoming mass transfer resistance between the aqueous phase and the solid adsorbent surface [16]. Figures 2a and 2b illustrate the effect of varying initial Co(II) concentrations (10–50 ppm) on the adsorption efficiency of both ES and EST. As the initial Co(II) concentration increases, the removal efficiency also increases for both adsorbents. This behavior is attributed to the enhanced driving force for mass transfer, which facilitates a more efficient interaction between metal ions and active sites on the adsorbent surfaces. Notably, at all tested concentrations, the acid-treated eggshell (EST) consistently demonstrated a higher Co(II) removal efficiency compared to the untreated eggshell (ES). This improvement is likely due to the increased porosity, surface area, and the introduction of functional groups resulting from acid treatment, which enhance the material's affinity toward Co(II) ions.

Effect of Temperature

The influence of temperature on the adsorption of Co(II) ions was evaluated over a range of 15 °C to 60 °C. As illustrated in Figure S5, the adsorption capacity of both untreated (ES) and treated eggshells (EST) increased with rising temperature. This trend indicates that the adsorption process is endothermic in nature.

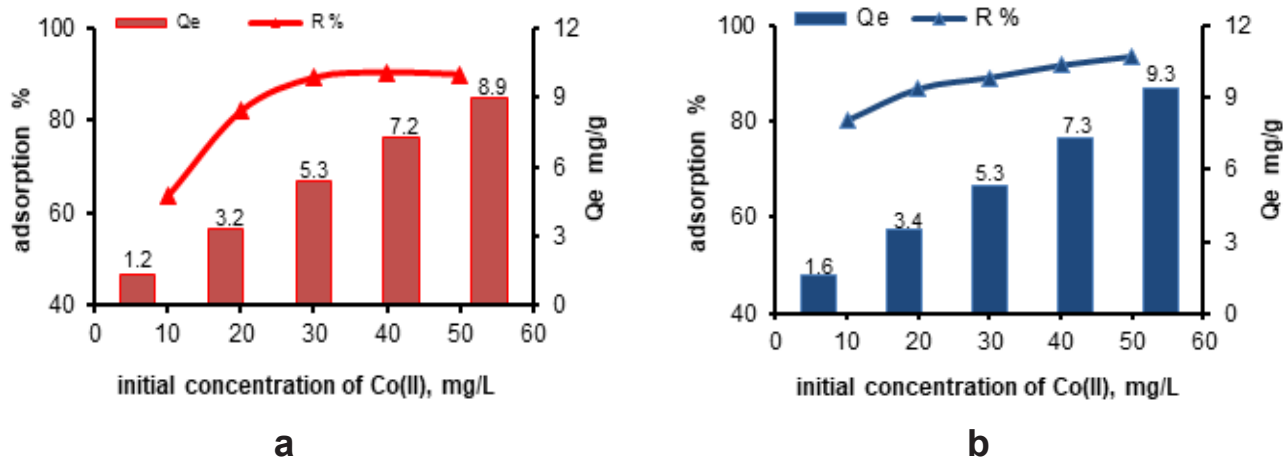


Figure 2. Effect of initial Co(II) ion concentration on (a) percentage removal and (b) adsorption capacity (Q_e) using untreated eggshell (ES) and acid-treated eggshell (EST) as adsorbents.

The enhancement in adsorption at elevated temperatures can be attributed to the increased mobility of Co(II) ions in solution and the greater accessibility of active sites resulting from the expansion of pore structures. Additionally, higher temperatures may facilitate bond disruption at the adsorbent surface, thereby enhancing the interaction between Co(II) ions and functional groups on the adsorbent [17]. The observed temperature dependence suggests that the adsorption mechanism involves both physical and weak chemical interactions, and that thermal energy contributes positively to the adsorption efficiency.

The thermodynamic characters - enthalpy (ΔH°), free energy (ΔG°), and entropy (ΔS°) were calculated depending on equilibrium constant (k_d) values using the following equations [18,19]:

$$k_d = C_{\text{ads}}/C_e \quad (3)$$

$$\log k_d = \Delta S^\circ/(2.303 R) - \Delta H^\circ/(2.303 RT) \quad (4)$$

where: C_{ads} is the amount of adsorbate (C_0 ion) on the solid surface (mg/L), C_e is the amount of adsorbed C_0 ion in (mg/L) at equilibrium, R is the gas constant equal to (8.314 J/mol K), and T (K) is the absolute temperature of the solution.

The ΔG° can be obtained by using the following relation [20]:

$$\Delta G^\circ = -2.3030 RT \log k_d \quad (5)$$

Based on Figures S6 and S7, the thermodynamic parameters for the adsorption of Co ion on ES and EST surface set out in Table S1, the positive ΔH referring to the adsorption process was endothermic with values 11.970 kJ. mol⁻¹ and 12.508 kJ. mol⁻¹ for adsorption on ES and EST, respectively. These magnitudes enhance the physical adsorption between 2.1 and 20.9 kJ/mol [21]. The negative values of ΔG° refer to the adsorption process that occurs spontaneously in nature [20], and the adsorption process on the EST surface is faster than the adsorption process on the ES surface with increasing temperature. The ΔG° values observed

ranged between (-20 kJ/mol and 40 kJ/mol), which ensured the adsorption is physical sorption [22]. The small positive values of ΔS° offered the alliance of the adsorbent for adsorbate and the rise of randomness at the solid-solution interface through the adsorption process [23].

Effect of Initial pH on Co(II) Adsorption

The pH of a solution is one of the most influential parameters governing the adsorption behavior of metal ions, as it directly affects both the adsorbent surface charge and the speciation of metal ions. In this study, the adsorption of Co(II) ions was investigated across a pH range of 2 to 10. The pH was adjusted using a few drops of 0.1 N HCl or NaOH to achieve the desired value prior to adsorption. The results are presented in Figure 3. For the untreated eggshell (ES), the maximum Co(II) removal was observed under acidic conditions, particularly in the pH range of 2–4. This can be attributed to the surface characteristics of CaCO₃, the main component of eggshells, which has a relatively low point of zero charge (pHpzc), typically in the acidic range [10, 24]. Under these conditions, the surface bears a net negative charge, facilitating electrostatic attraction with positively charged Co(II) ions. As the pH increases beyond this range, the surface charge becomes less favorable for Co(II) adsorption, leading to a decline in removal efficiency.

In contrast, the acid/base-treated eggshell (EST) exhibited enhanced Co(II) adsorption over a broader pH range, from 2 to 8. This improved performance is attributed to the chemical modification of the surface during treatment, which increases surface functionalization and shifts the pHpzc to near-neutral or slightly basic values (around pH 7–8) [25]. As a result, the EST surface remains negatively charged over a wider pH range, improving its affinity for Co(II) ions via electrostatic interactions. However, at pH values above 8, a decline in Co(II) removal was observed for both ES and EST. This reduction is likely due to increased electrostatic repulsion between negatively

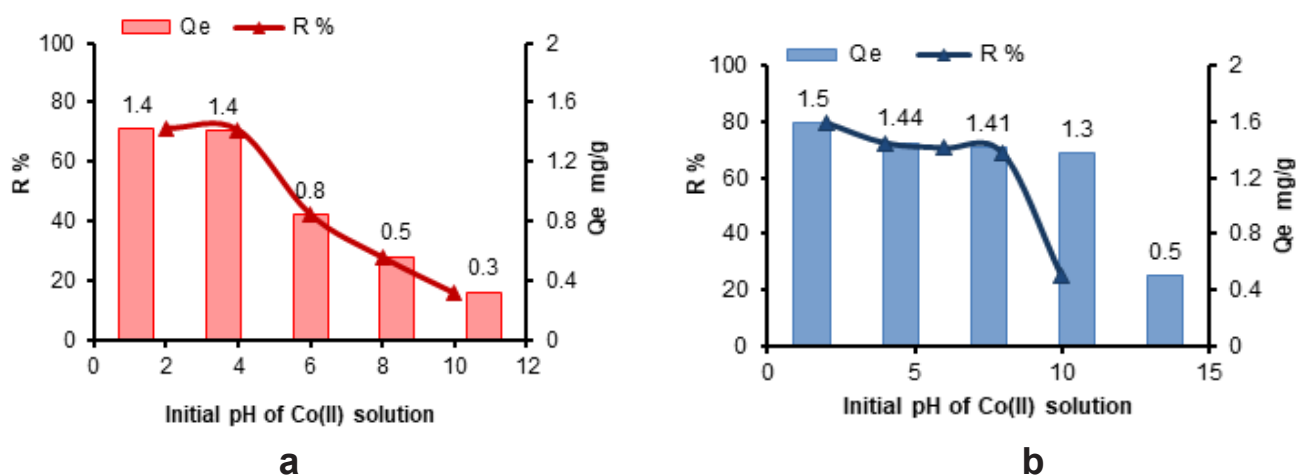


Figure 3. Effect of initial pH on (a) percentage removal and (b) adsorption capacity (Q_e) of Co(II) ions onto untreated eggshell (ES) and acid/base-treated eggshell (EST) surfaces.

charged Co(II) species (e.g., $[\text{Co}(\text{OH})]_2$ or $\text{Co}(\text{OH})_2$) and the negatively charged adsorbent surface [26]. Additionally, several studies have reported that eggshell materials may undergo flocculation or structural destabilization at high pH values (>8 or >10), which further hinders the adsorption process [27–29]. Furthermore, the precipitation of Co(II) as $\text{Co}(\text{OH})_2$ under alkaline conditions may also contribute to the observed decrease in removal efficiency.

Adsorption isotherms

Adsorption isotherms are essential for understanding the interaction between metal ions and the surface of an adsorbent, providing valuable insights into adsorption capacity, surface characteristics, and the underlying mechanism of the process. Isotherm modeling plays a critical role in predicting the performance of an adsorbent under various conditions and is vital for the design and optimization of adsorption systems [30]. In this study, three widely used isotherm models were employed to analyze the equilibrium data for Co(II) adsorption onto untreated (ES) and treated (EST) eggshells: the Langmuir, Freundlich, and Temkin models. These models were selected due to their relevance in describing both monolayer and heterogeneous surface adsorption mechanisms. The isotherm equations used are as follows [19,31] 6 & 7,8, and 9.

$$C_e/Q_e = 1/(Q_e k_L) + C_e/Q_m \quad (6)$$

$$R_L = 1/((1 + K_L C_0)) \quad (7)$$

$$\log Q_e = 1/n \log C_e + \log K_f \quad (8)$$

$$Q_e = B_1 \ln C_e + B_1 \ln k_e \quad (9)$$

where k_L is the sorption constant, k_f and n are the Freundlich constants. Q_e and Q_m are the amount of adsorbate per unit mass (mg/g) of adsorbent at equilibrium and at different times. C_0 and C_e are the initial and equilibrium concentrations of ions (mg/L), and B_1 is the Temkin constant.

Table S2 summarizes the linearized equations, correlation coefficients (R^2), and fitted parameters derived from the experimental data for all three isotherm models. The Freundlich and Temkin plots for Co(II) adsorption onto ES and EST are presented in Figures S8 and S10, respectively. These graphical representations provide further insight into the applicability and fit quality of each model to the experimental data.

The correlation coefficients (R^2) for both the Freundlich and Temkin isotherms were found to be relatively high, indicating good agreement with the experimental data. For the Freundlich model, the R^2 values were 0.914 and 0.997 for ES and EST, respectively, suggesting that Co(II) adsorption occurs via a multilayer process on heterogeneous surfaces [34,35]. Similarly, the Temkin isotherm produced R^2 values of 0.956 and 0.955 for ES and

EST, respectively, further supporting the suitability of this model for describing the adsorption behavior. In contrast, the Langmuir isotherm failed to adequately describe the adsorption process for either material. As shown in Figure S10 and Table S2, the Langmuir plots did not follow a consistent linear trend, consistent with previous findings reported by Amjad Hussain et al. [36]. Furthermore, the calculated dimensionless separation factor (RL) was equal to zero for both ES and EST, indicating that the adsorption process is irreversible [37]. Overall, the Freundlich and Temkin models demonstrated better fit to the experimental data compared to the Langmuir model, as evidenced by the higher correlation coefficients and linearity of the plots. These results suggest that the adsorption of Co(II) onto ES and EST occurs on energetically heterogeneous surfaces and likely involves a combination of physical and chemical interactions.

Conclusions

This study demonstrates that both untreated eggshell (ES) and acid-treated eggshell (EST) can serve as low-cost, environmentally friendly adsorbents for the removal of Co(II) ions from aqueous solutions. Structural characterization by XRD confirmed the presence of CaCO_3 as the main component, while SEM-EDX analyses revealed notable surface and morphological changes upon acid treatment and metal adsorption.

The optimal removal conditions were established at an initial Co(II) concentration of 50 ppm, with 0.25 g of adsorbent and 90 minutes of contact time. The EST material exhibited significantly higher adsorption efficiency than ES, primarily due to its enhanced surface properties, increased porosity, and a broader effective pH range (2–8), which is attributed to a shift in the point of zero charge.

Thermodynamic data confirmed that the adsorption process is endothermic and spontaneous, governed largely by physical interactions. The proposed adsorption mechanism involves several sequential steps: initial mass transfer of Co(II) ions from the bulk solution to the external surface of the adsorbents, partial desolvation of the hydrated ions, diffusion through the porous structure of ES and EST, and rapid binding of Co(II) to active sites within the adsorbent matrix. These interactions are facilitated by electrostatic attraction and the increased number of available binding sites in EST following acid treatment.

Overall, this work highlights the potential of modified biowaste materials, such as treated eggshells, for effective cobalt removal and provides a promising route toward sustainable wastewater treatment technologies.

Conflicts of Interest

The authors declare no conflicts of interest.

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