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# Synthesis of Shrimp shell-derived Biochar@starch/$CoFe_2O_4$NPs and Its Applications as a Eco-friendly and Effective Adsorbent for Removal of Cd(II) ion from Aqueous Environments: Isotherms, Kinetics, and Thermodynamics Analysis

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**Abstract**
This study explores the potential of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs for heavy metals and toxic pollutants removal from aqueous environments. The adsorption of Cd(II) ion was studied under the various conditions, including pH, time, adsorbent dose, and temperature. The adsorption process was best described by the Langmuir isotherm and pseudo-second-order kinetic models, indicating monolayer adsorption and chemisorption-dominated interactions. The maximum adsorption capacity was determined to be 56.6 $mgg^{-1}$ at 298 °K. Thermodynamic results indicated that the process was spontaneous and exothermic. The calculated thermodynamic parameters, such as ΔG°, ΔH° and ΔS° for Cd(II) ion uptake on the adsorbent surface, come out to be -3.45 kJ $mol^{-1}$, -17.06 kJ $mol^{-1}$ and -41.26 J $mol^{-1}$. $K^{-1}$, respectively. The removal efficiency Cd(II) ion from actual water samples higher reached 90.0 %, although the efficiency decreased with increasing salt concentration. These findings demonstrate that shrimp shell-derived biochar modified with starch/$CoFe_2O_4$NPs is a sustainable, low-cost, and environmentally friendly adsorbent with significant potential for Cd(II) ion remediation in contaminated water systems.

**Keywords**
Cadmium, $CoFe_2O_4$ nanoparticles, Shrimp shells, Aqueous environments.

## 1. Introduction

Monitoring pollution is one of the most critical priorities in society today. Contamination of water and soil by toxic substances has become a significant environmental challenge. Rapid technological advancement, industrialization, and population growth have all been identified as major contributors to environmental pollution [1-3]. Therefore, to have a safe and clean environment, removing unacceptable amounts of heavy metals and synthetic organic dyes entering wastewater is essential for pollution control and operational safety [4, 5]. Cadmium (Cd) in particular is a heavy metal that requires special attention due to its significant toxicity and environmental persistence [6, 7]. This hazardous heavy metal infiltrates ecosystems via soil and water systems, subsequently bioaccumulating in flora and fauna, including those ingested by humans, altering food chains [8, 9].

Cadmium contamination in water systems poses serious risks to both human health and environmental safety. The WHO has also set recommended limits for Cd(II) ion in water at 5 $mgL^{-1}$, respectively [10-12]. With limited freshwater resources and increasing global demand, the removal of heavy metals and toxic pollutants from water has become a major focus of scientific research [13-15].

Various methods has been investigated for Cd ion removal, including such as electrochemical processes [16], flotation [17], ionic liquids [18], and chemical precipitation [19], activated carbon [20], zeolites [21], graphene oxide [22] have been reported. Initially, these materials attracted attention for their high adsorption capacities and availability, but limitations such as regeneration difficulty, low selectivity, and poor reusability have shifted focus toward new adsorbent families.

Adsorption methods have been reported to be more effective than other physical and chemical treatments for removing pollutants from wastewater [23-25]. However, the technical and economic limitations of conventional treatment methods have driven the search for alternative, innovative solutions. In this context, adsorption using high-performance adsorbents particularly those modified with biopolymers and magnetic nanoparticles has gained significant attention as a promising and sustainable option. Numerous studies indicate that biochar and natural biopolymers efficiently adsorb metal ions through surface adsorption mechanisms. Biochar made from crustacean waste is cost-effective and environmentally beneficial, providing a greener alternative to harsh chemicals in water/wastewater treatment and promoting sustainable economic growth [26].

Biochar is one of the most widely used adsorbents, and its application for removing pollutants from both gaseous and liquid phases is increasingly gaining attention. It has shown great potential in the treatment of industrial wastewater, effectively removing a wide range ions. A key advantage of biochar in pollutant removal lies in its high specific surface area, which facilitates efficient adsorption [27]. While previous studies have explored the use of biochar as an adsorbent, there remains a significant gap in comprehensive research focused on the removal of heavy metals and certain synthetic dyes from various water sources and industrial effluents. The present study investigates biochar modified with magnetic nanoparticles materials that play a critical role in complex reaction mechanisms, including photocatalysis, electrochemical oxidation, ultrasonic treatment, and hybrid processes. Our results demonstrate a marked improvement in the adsorption of ions across diverse water matrices [28, 29].

Valuable adsorbent properties include high capacity, availability, recyclability, and cost-effectiveness. Recent attention has focused on magnetic nanoparticles for water purification. Ferrites ($MFe_2O_4$, M = divalent transition metal) with cubic spinel structures are widely used due to their stability and superparamagnetic behavior. Nanoparticles such as $Fe_3O_4$, $CoFe_2O_4$, $MnFe_2O_4$, and $NiFe_2O_4$ combine high chemical and thermal stability, hardness, low toxicity, and hydrophilicity. Their adsorption capacities vary with heavy metal cations, with cobalt ferrite ($CoFe_2O_4$) showing particularly high adsorption and superior magnetic properties [30, 31].

Additionally, $CoFe_2O_4$ exhibits varying adsorption capacities for different heavy metals, making it a versatile component in adsorbent systems [32]. Starch is a natural polymer that combines carbon dioxide and water through photosynthesis. It is also an important and interesting biological material in various fields because it has water absorption capacity, and wastewater bioremediation. Starch, owing to its non-toxicity, biodegradability, and low cost, presents an acceptable option as a stabilizing agent for various adsorbents and nanoadsorbents, as well as a coating material for magnetic nanoparticles to enhance their functional properties [33, 34].

**The main aim** of this research is to develop environmentally safe and sustainable adsorbent materials for the removal of Cd(II) from polluted wastewater. Adsorbents with specific characteristics like a large surface area, high porosity, and active functional groups significantly enhance their adsorption capabilities. These features leads to an increased removal rates, improved adsorption efficiency, and more effective target adsorption. In this regard, **a novel** adsorbent was developed by modifying shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs. The improved performance is attributed to the presence of reactive functional groups and abundant active sites on the adsorbent surface, which facilitate efficient interaction with pollutants.

This study focuses on the removing materials from aqueous environments, we investigated the potential of biochar derived from shrimp shells, modified with starch and $CoFe_2O_4$ nanoparticles for Cd(II) ion removal from aqueous environments, systematically varying contact time, pH, initial Cd(II) ion, adsorbent dose, and temperature. Equilibrium was fit with Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherms, and multi-cycle adsorption–desorption verified efficient, stable, reusable performance for environmental remediation.

## 2. Experimental

### *2.1. Materials*

Shrimp shell waste was collected from a local shrimp market in Mahshahr, Iran. Cadmium sulfate octahydrate salt ($CdSO_4$ .$8H_2O$, 99.0%), starch (99.0%), cetyltrimethylammonium bromide (CTAB, 99.0%), cobalt chloride ($CoCl_2 \cdot 4H_2O$, 98.0%), iron chloride salts ($FeCl_3 \cdot 6H$□O (99.0%), $FeCl_2 \cdot 4H$□O (98.0%)), ammonium hydroxide NH□OH (98.0%), and ethanol (98.0%) were purchased from Merck (Germany). All aqueous solutions were prepared using distilled or deionized water.

### *2.2. Apparatus*

UV–visible measurements were carried out using a Maya Pro 180 spectrophotometer (Shimadzu Company, Japan). Functional groups were examined by Fourier-transform infrared spectroscopy (FTIR). X- ray diffractometer (D5005, Siemens, Germany). Scanning electron microscopy (SEM, Phillips, PW3710, Netherland), used to study the morphology of samples. Additional laboratory equipment used in this study included a centrifuge (Gama Teb-X, 400 rpm, Iran).

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### *2.3. Fabrication of biochar shrimp shells*

Shrimp shell-derived biochar was prepared using a modified procedure based on previously reported methods [26]. The collected shells were first washed thoroughly with water to remove impurities and then air-dried. The dried shells were ground to reduce particle size to less than 4 mm and washed repeatedly with distilled water. The pretreated material was transferred to ceramic containers and heated at 400 °C for two hours under a nitrogen atmosphere (N2 flow rate:100 $cm^3$ $min^{-1}$). After cooling to room temperature, the resulting biochar was washed with deionized water, neutralized using dilute hydrochloric acid (0.01 mol $L^{-1}$) for 1 h, and dried. The final product was stored in sealed containers until further modification and adsorption testing.

### *2.4. Synthesis of $CoFe_2O_4$NPs*

$CoFe_2O_4$ nanoparticles were synthesized by mixing aqueous solutions of ferric chloride (0.4 mol $L^{-1}$) $FeCl_3·6H$□O (5.4 g in 50 mL) and cobalt chloride 0.2 mol $L^{-1}$ of $CoCl_2·6H$□O (2.38 g in 50 mL)). 3.0 mol $L^{-1}$ Sodium hydroxide (NaOH) was added drop wise until the pH reached approximately 11–12, leading to the formation of a black precipitate. 0.2 g CTAB was then added as a surfactant, and the mixture was heated to 80 °C under reflux for 1 h. The obtained magnetic product was separated, washed several times with warm deionized water, dried, and ground into a fine powder.

### *2.5. Synthesis of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs*

The synthesis process of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs is as follows: In a typical procedure, 1.0 g of starch was added to 100 mL of distilled water and heated on a magnetic stirrer. Then, 5.0 g of $CoFe_2O_4$NPs were added to the solution, which was subsequently placed in an ultrasonic bath for 15 minutes. This step is intended to facilitate the interaction and potential precipitation of the starch onto the nanoparticles. After ten minutes of centrifugation at 2000 rpm, the mixture was washed with distilled water. The collected shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs were then washed with ethanol and dried under vacuum at 60 °C for 2 hours, as shown in Figure 1.

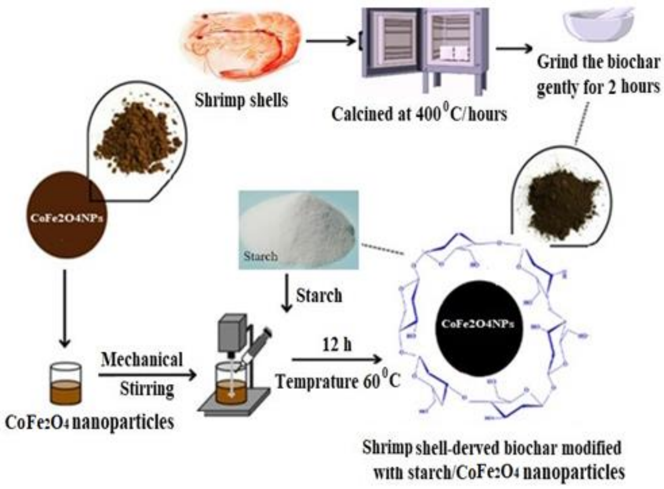


**Fig. 1.** Schematic of the synthesis of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs.

### *2.6. Application to real water samples*

Three water samples (tap water, surface water and industrial wastewater) were collected from an industrial site located in the Ahvaz industrial zone, situated in Khuzestan Province, Iran. A stock solution of 1000 $mgL^{-1}$ Cd(II) ion solution was prepared by adding metal salt (2.282 g of $CdSO_4$ .$8H_2O$ 99%) in a 1000 mL volumetric flask with deionized water. As well as, a known amount of Cd(II) ion (0.0, 5.0, and 10.0 $mgL^{-1}$) were spiked in each real sample, and 100 mL of this solution was transferred into a conical flask that contained 0.1 g of shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs and performed in batch mode for 60 min. After that, the solution of Cd(II) ion was separated, and the remaining concentration of Cd(II) ion was determined spectrophotometrically through calculating absorbance at 375 nm.

### *2.7. Adsorption experiments*

Batch adsorption experiments were carried out to determine the Cd(II) ion adsorption isotherm onto shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs was carried. To perform the 0.1 g of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs was dissolved in 100 mL of Cd(II) ion of concentration 10 ($mgL^{-1}$). The solution was agitated in an orbital shaking incubator at a speed of 180 rpm for 60 min, and Cd(II) ion concentration was recorded using a spectrophotometer at λmax = 375 nm. Similarly,

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pH study, adsorbent dosage, Cd(II) ion concentration, and the effect of temperature were studied. To calculate maximum adsorption capacity (qe), and adsorption percentages (% R), using the below equations (1) and (2) [15, 28, 34].

$$qe = \frac{V(C_0 - C_e)}{M} \times 100 \quad (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

$C_0$ (mg/L): Initial Cd(II) ion concentration
$C_e$ (mg/L): Final Cd(II) ion concentration
M (g): Amount of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs
V (L): Volume of the solutions

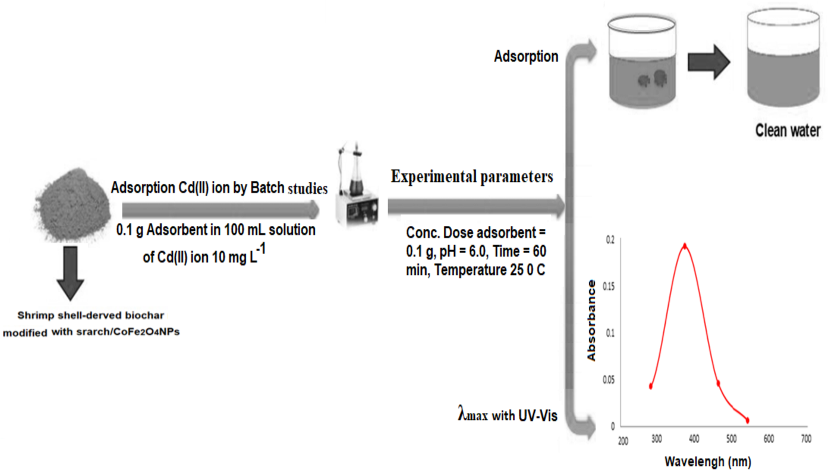
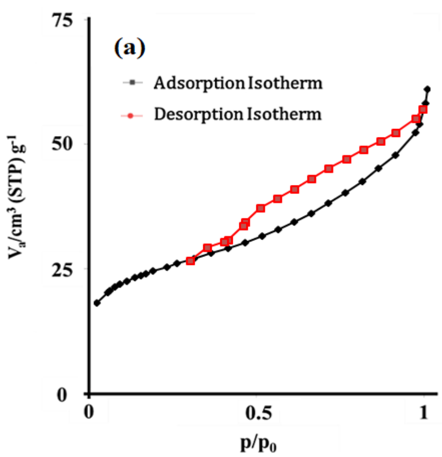



**Fig. 2.** Absorption of Cd(II) ion onto shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent in solution by batch studies.

## 3. Results And Discussion

### *3.1. BET analysis*

Fig. 3a shows the adsorption/desorption isotherm of the shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs. Also, by using the adsorption/ desorption isotherm, we will be able to BET results of shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs surface area 62.11 $m^2g^{-1}$, average pore diameter 2.23 nm, and pore volume 0.096 $cm^3g^{-1}$, respectively. With increasing $CoFe_2O_4$ loading, the relative partial-pressure range of the adsorption isotherms contracts because nanoparticles infiltrate and constrict the biochar channels, reducing pore volume. The concomitant decreases in BET area and most probable pore diameter confirm successful nanoparticle incorporation into the shrimp-shell biochar (Fig. 3).



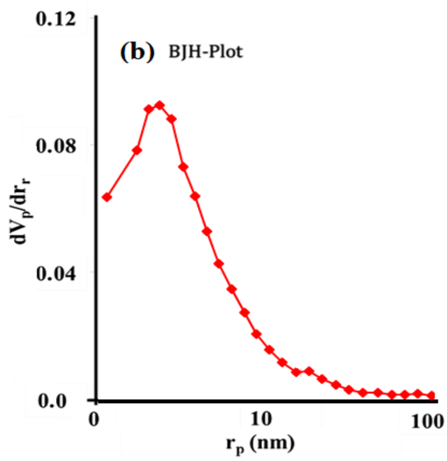
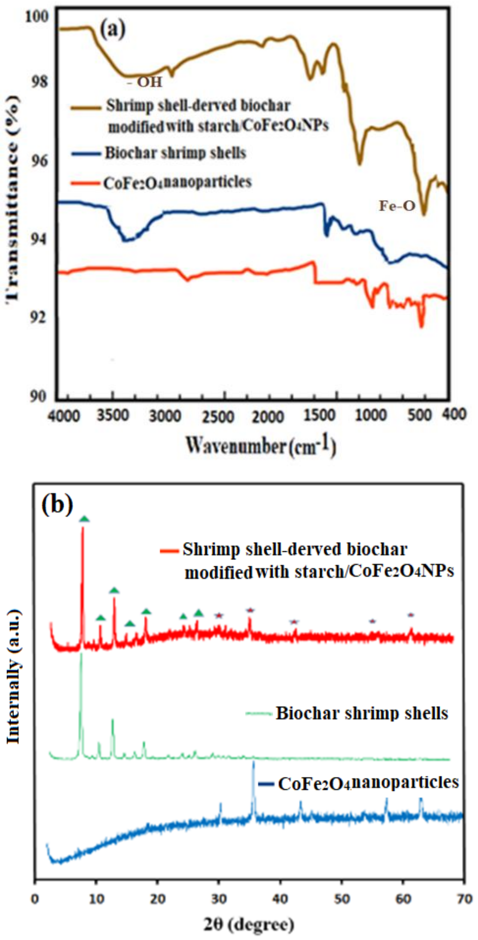




**Fig. 3.** (a) N2 adsorption–desorption isotherms (b) Pore size distributions of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs.

### *3.2. FT-IR, XRD, and SEM images of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs*

The surface functional groups of the fabricated nanocomposite were characterized via FT-IR spectroscopy (Figure 4a). The spectrum of the modified biochar exhibits a prominent, broad transmittance band centered between 3400-3300 $cm^{-1}$, which is assigned to the stretching vibrations of the -OH groups arising from surface-adsorbed moisture. The absorption band observed at 1731 $cm^{-1}$ indicates the presence of carboxylic acid groups and ester functionalities intrinsic to the biomatrix framework [30, 32]. Crucially, the successful co-functionalization of the biochar matrix with the ferrite phase is verified by the emergence of a distinctive band at 574 $cm^{-1}$, which corresponds directly to the characteristic Fe–O tetrahedral stretching vibration, validating the anchoring of iron-based magnetic entities onto the carbonaceous network [32]. The XRD pattern of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs (Fig. 4b) exhibits several peaks at the 2θ = 30.3, 35.6, 43.4, 53.6, 57.4 and 63.1, corresponding to reflections from the (220), (311), (400), (422), (511), and (440) planes, respectively, which are in good agreement with the standard crystal planes of $CoFe_2O_4$NPs [26, 30]. The main peaks of the synthesized shrimp shell-derived biochar (Fig. 4b) at the 2θ values of 7.4, 10.4, 12.8, 14.8, 16.47,18.0, 22.2, 25.7, 26.7, 29.6, 30.5 and 31.6 are indexed to the (011), (002), (112), (023), (013), (222), (114), (233), (224), (134), (044), (244) and (235) planes of shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs. The surface morphology of shrimp shell-derived biochar before and after $CoFe_2O_4$NPs modification was examined and presented Fig. 4c, d. These aggregated features confirm the successful deposition of $CoFe_2O_4$NPs on the shrimp shell-derived biochar. As depicted in SEM micrographs, the various sizes, in the range of 20-50 nm are very close to those determined by XRD analysis.



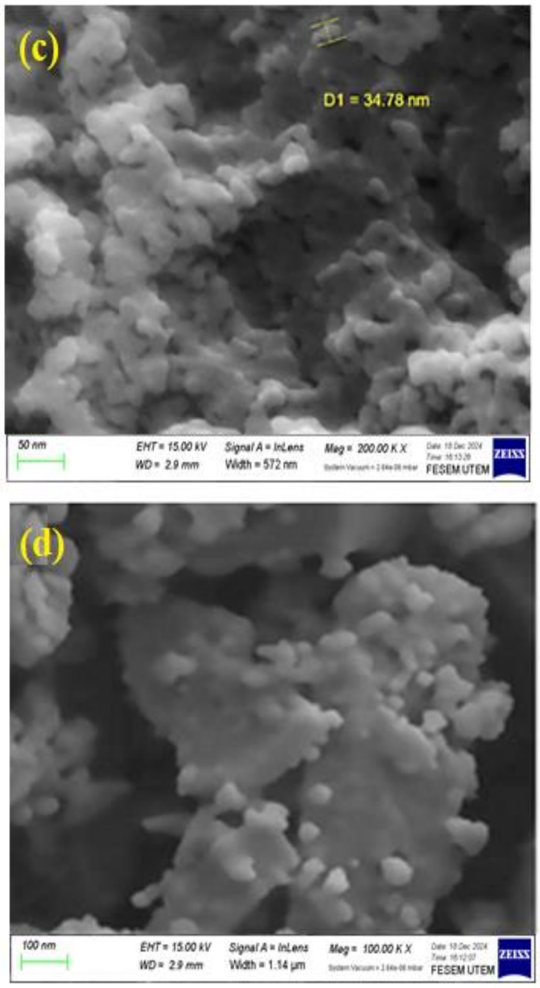




**Fig. 4.** (a) FT-IR spectrum (b) XRD patterns (c) SEM image of shrimp shell-derived biochar, (d) SEM image of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs.

### *3.3. TGA, and DTG analysis*

Thermogravimetric analysis is a thermal method employed to measure changes in a sample's weight as a function of increasing temperature. This technique is commonly used to quantify the amount of water lost during heating. The thermal stability of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs was investigated using TGA, and the results are presented in Figure 5a. The TGA study revealed a two-stage weight loss occurring at approximately 80-100 °C and 600-1000 °C. The Derivative DTG curve exhibits a significant peak in the first stage, corresponding to an 8% weight loss. This initial loss is attributed to the temperature-induced desorption of absorbed water molecules. The subsequent absence of any further significant weight loss indicates that the support material remains stable up to 700 °C.

### *3.4. Determination Point-of-Zero Charge ($pH_{PZC}$)*

To determine the point of zero charge ($pH_{PZC}$) the pH at which there is zero electric charge on the surface of synthesized shrimp shell-derived

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biochar@starch/$CoFe_2O_4$NPs, 10 mL of 0.1 M NaCl solution was added in 100 mL Erlenmeyer flasks, and pH was adjusted from 3 to 9 using 0.1 M NaOH, 0.05 g of the modified biochar was added to the flasks, and the solutions were agitated at 180 rpm for 12 h at 25 °C using a laboratory rotatory shaker. The PZC was determined from the graphical plot of $pH_i$ vs. ΔpH ($pH_f - pH_i$), and pH of 7.0, the surface of modified shrimp shell-derived biochar has a point of zero charge (PZC), as shown in (Fig. 5b).

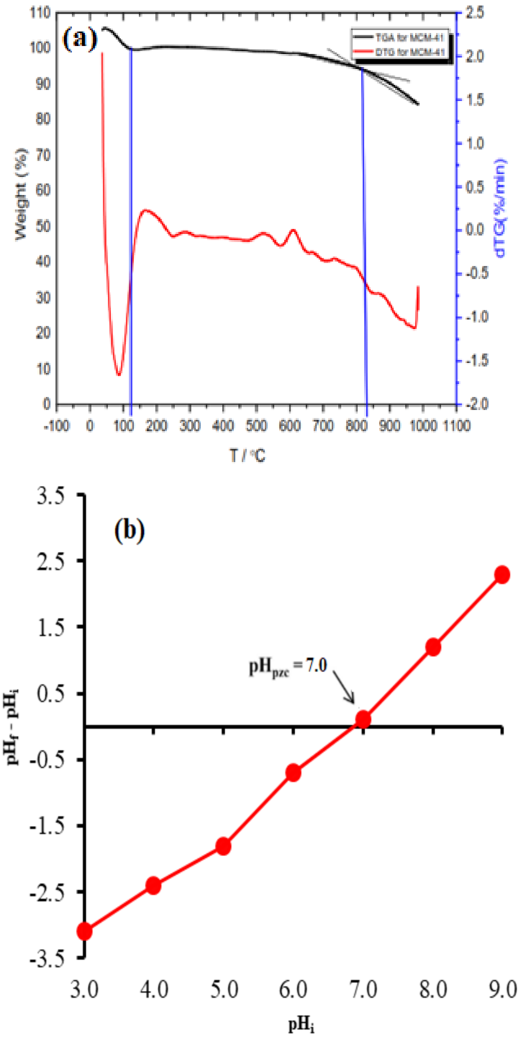


**Fig. 5.** (a) TGA, and DTG diagram. (b) $pH_{ZPC}$ on the adsorption of shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs.

## 3.5. Optimized parameters

### *3.5.1. Effect of pH*

The effect of pH on Cd(II) ions adsorption by shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs was examined in the range of pH 2-10 was investigated in 100 mL of Cd(II) ion concentration 10 $mgL^{-1}$, and the results are presented in Figure 6a. According to suggest value of $pH_{PZC}$ (i.e.) the high efficiency of Cd(II) ion reducing in acidic pH, (especially pH = 6.0) occur due to electrostatic attraction among molecules of adsorbent and compounds related to Cd(II) ion lead to clean up of waste water. Based on this trend, pH 6.0 was identified as the optimal condition for subsequent adsorption experiments involving Cd(II) ions using shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs [28, 35, 36].

### *3.5.2. Effect of adsorbent dose*

Adsorbent dose is a critical factor in surface adsorption processes. Following the optimization of pH, the influence of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent dose was investigated (Figure 6b). Experiments were conducted with doses ranging from 0.01 to 2.0 g, while maintaining constant conditions (pH = 6, initial Cd(II) ion concentration of 10 $mgL^{-1}$, time = 60 min). Increasing the adsorbent dose provides more active and accessible sites for Cd(II) ion adsorption, leading to improved removal. However, beyond a certain point, the adsorption rate plateaus. The optimal adsorbent dose for Cd(II) ion removal was found to be 0.1 g, resulting in a removal efficiency of 88.4%. However, further increasing the adsorbent dosage beyond this point may lead to reduced mixing efficiency and disturbances in mass transfer, potentially hindering the adsorption process due to particle aggregation or diffusion limitations [37, 38].

### *3.5.3. Effect of time and temperature*

The combined effects of time and temperature on Cd(II) ion adsorption by shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent were investigated to determine the time required to reach equilibrium (Figure 6c, d). The effect of time was studied over a range of 10 to 80 min, and effect of temperatures in range 298 to 348 K for Cd(II) ion adsorption onto adsorbent in pH = 6, initial Cd(II) ion concentration of 10 $mgL^{-1}$, and adsorbent dose 0.1 g. The results indicate that at all tested temperatures, over 91.0% of Cd(II) ion was removed within the first minute. Furthermore, no significant improvement in removal was observed after 60 minutes [1, 36].

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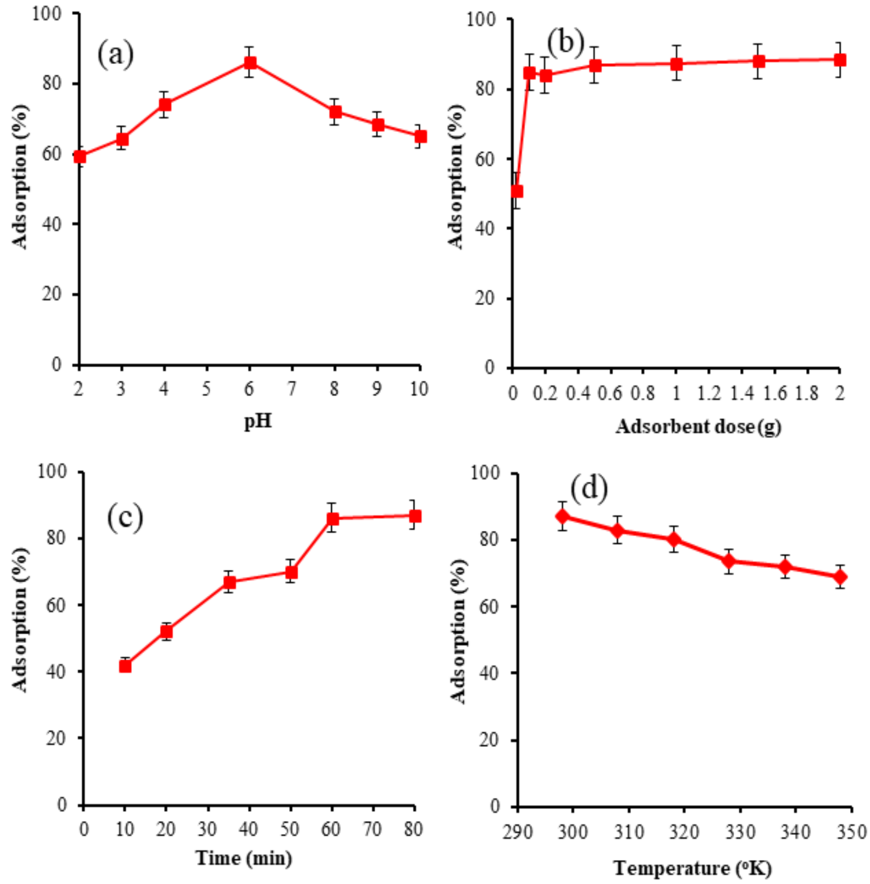


**Fig. 6.** (a) Effect of pH (adsorbent dose 0.1 g, time 60 min). (b) Effect of adsorbent dose (pH 6.0, time 60 min). (c) Effect of contact time (pH 6.0, adsorbent dose 0.1 g). (d) Effect of temperature for Cd(II) ion (pH 6.0, adsorbent dose 0.1 g, time 60 min).

### *3.6. Adsorption isotherms*

The maximum adsorption mechanism is evaluated using adsorption isotherms. The described the best behavior of the adsorption process between the Cd(II) ion adsorbed on the shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs surface in solution was investigated using widely used Isotherm studies were conducted at 298 K at a time interval of 60 min using isotherm Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherms [15, 36, 39]. The estimated using Eqs. (3), (4), (5), and (6), respectively. The respective equations for these models are as follows:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad \text{Langmuir} \quad (3)$$

$$q_e = q_m K'_F + C_e^{\frac{1}{n}} \quad \text{Freundlich} \quad (4)$$

$$q_e = q_m (B'_T \ln A_T\, C_e) \quad \text{Temkin} \quad (5)$$

$$E = 1/(2B_D)^{1/2} \quad \text{D–R model} \quad (6)$$

In these models, $q_m$ is ($mgg^{-1}$), and $K_L$: Langmuir constant ($L\ mg^{-1}$). $K_F$is Freundlich constant, and n: Surface heterogeneity factor. $A_T$ and $B_T$ are experimentally determined Temkin constants. Dubinin–Radushkevich (D–R) isotherm, where E ($kJ\ mol^{-1}$), and $B_D$ are experimentally determined D–R constants.

The goodness-of-fit for these adsorption models was further validated using the Chi-square ($X^2$) statistic, calculated as given in Equation (7).

$$X^2 = \sum \frac{(q_e - q_{e.m})^2}{q_{e.m}} \quad (7)$$

Here,"$q_{exp}$" and "$q_{cal}$" represent the experimental and calculated adsorption capacities ($mgg^{-1}$), respectively.

The experimental results indicate that the Langmuir model provides the best fit for the adsorption data. This model yielded a maximum adsorption capacity ($q_m$) of 56.6 $mgg^{-1}$, and a high correlation coefficient ($R^2$=0.984). that the Langmuir isotherm is the best model to explain the Cd(II) ion adsorption onto shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs, which quantitatively describes the formation of a monolayer of adsorbate on the outer surface of the shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs. The result is shown in (Fig. 7, and Table 1).

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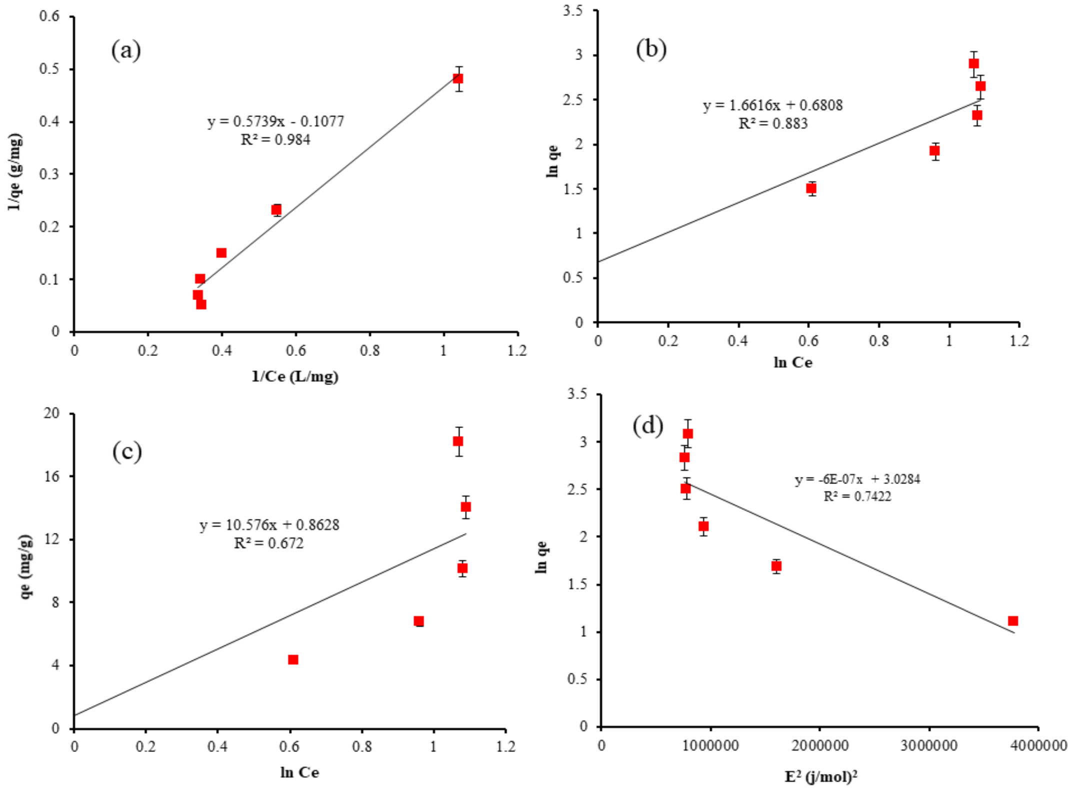


**Fig. 7.** (a) Langmuir (b) Freundlich (c) Temkin (d) Dubinin–Radushkevich isotherms for Cd(II) ion adsorption onto shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent (pH 6.0, adsorbent dose 0.1 g, time 60 min).

**Table 1.** Isotherms for Cd(II) ion adsorption on to shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent under identical experimental conditions (pH 6.0, adsorbent dose 0.1 g, time 60 min).

| Isotherm | Parameters | Ad% Cd(II) ion |
|---|---|---|
| Langmuir | $q_m$ ($mgg^{-1}$) | 56.6 |
| | $K_L$ (L $mg^{-1}$) | 0.19 |
| | $R^2$ | 0.984 |
| | $X^2$ | 1.16 |
| Freundlich | 1/n | 0.59 |
| | $K_F$ $(mg)^{1-n}$ $L^n g^{-1}$ | 1.92 |
| | $R^2$ | 0.883 |
| | $X^2$ | 1.58 |
| Temkin | $B_T$ (J $mol^{-1}$) | 10.55 |
| | $K_T$ (L $mg^{-1}$) | 1.08 |
| | $R^2$ | 0.672 |
| | $X^2$ | 1.76 |
| Dubinin–Radushkevich (D–R) | $q_m$ ($mgg^{-1}$) | 49.6 |
| | E (kj $mol^{-1}$) | -873.4 |
| | $R^2$ | 0.742 |
| | $X^2$ | 1.63 |

### *3.7. Adsorption kinetic equation*

The adsorption kinetics of Cd(II) ion by the shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs was investigated by applying pseudo-first-order, pseudo-second-order, and Elovich kinetic models. These models can be described by the differential forms represented in Equations (8), (9), and (10), respectively [40-42].

Pseudo-first-order model

$$\log(q_{e/\exp} - q_t) = \log q_{e/cal} - \frac{K_1}{2.303}t \quad (8)$$

In these models, qt: Adsorption capacity at time (t) ($mgg^{-1}$), and $k_1$: first order rate constant ($min^{-1}$).

Pseudo- second-order model

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$$\frac{t}{q_t} = \frac{1}{K_2 q_{e/cal}^2} + \frac{t}{q_{e/cal}} \quad (9)$$

Where, t: time in min, and $k_2$: second order rate constant (g $mg^{-1}$. $min^{-1}$).

Elovich model

$$q_t = \frac{1}{\beta} Ln\alpha\beta + \frac{1}{\beta} Lnt \quad (10)$$

Here, $\alpha$ : Initial adsorption speed (mg $g^{-1}$. $min^{-1}$), and $\beta$ : Desorption constant (g $mg^{-1}$).

To clarify the adsorption mechanism of Cd(II) ion on the shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs, the results show that pseudo-second-order kinetics best describe the adsorption, with equilibrium capacities closely matching experimental values. Initially, adsorption is rapid due to physical diffusion as Cd(II) ions occupy surface sites, while later stages are dominated by slower chemical adsorption, reaching equilibrium in ~60 minutes as ions penetrate the biochar interior. These findings confirm that chemical adsorption is the primary removal mechanism, consistent with previous studies. The results are shown in (Fig. 8, and Table 2).

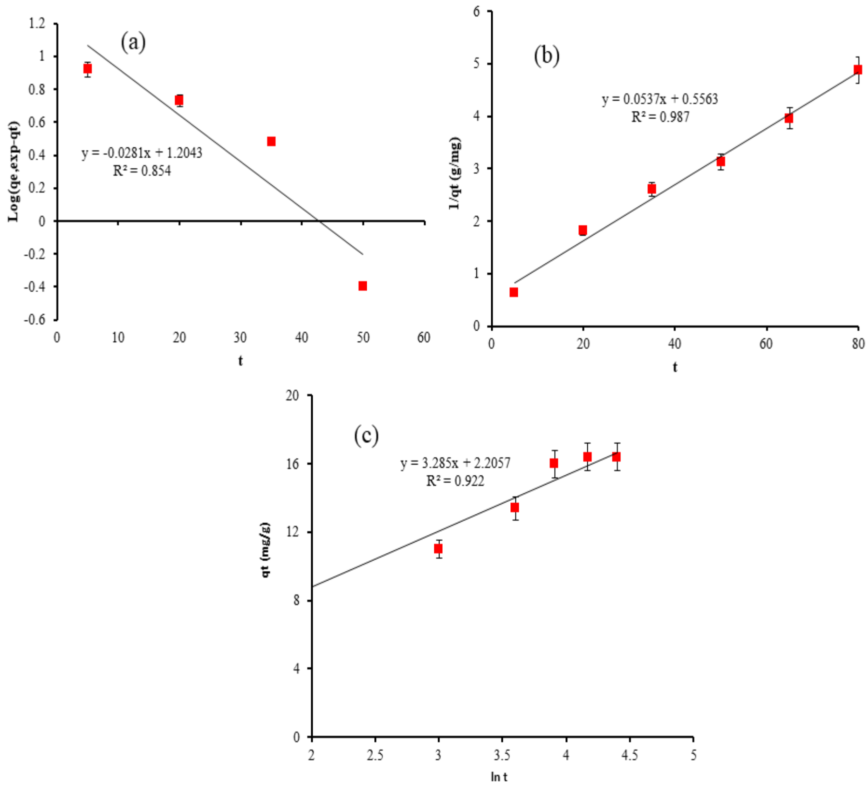


**Fig. 8.** (a) First-order model (b) Second-order model (c) Elovich model for adsorption of Cd(II) ion onto shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent (pH 6.0, adsorbent dose 0.1 g, time 60 min).

### *3.8. Thermodynamic adsorption*

Temperature is one of the most important factors in ions removal efficiency by focusing on change in nature of the reaction (exothermic or endothermic) to reveal spontaneous and non-spontaneous reaction. Thermodynamic parameters can be using the Eqs. (9) and (10) (11) and (12) [24, 43].

$$\ln K_c = \frac{\Delta S^{\circ}_{ad}}{R} - \frac{\Delta H^{\circ}_{ad}}{RT} \quad (11)$$

$$\Delta G^{\circ}_{ad} = -RT \ln K_c \quad (12)$$

Evaluating the energetic variations summarized in Table 2 helps clarify the underlying mechanisms driving the extraction of Cd(II) ions from polluted aqueous streams. The negative values recorded for Gibbs free energy (ΔG) across the investigated thermal spectrum (298–338K) confirm that the target ions undergo an entirely spontaneous accumulation pathway. The declining magnitude of these values alongside a negative enthalpy reading ΔH= -17.06 kJ $mol^{-1}$) confirms an exothermic process. Furthermore, the negative entropy changes ΔS= - 41.26 J $mol^{-1}$. $K^{-1}$) indicates a reduction in structural disorder at the solid-liquid boundary, showing that the Cd(II) ions encounter restricted mobility upon binding to the adsorbent.

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**Table 2.** Kinetic, and Thermodynamic parameters for adsorption of Cd(II) ion onto shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent (pH 6.0, adsorbent dose 0.1 g, time 60 min).

| **Kinetic parameters** | | |
|---|---|---|
| Models | Parameters | Ad% Cd(II) ion |
| First-order model kinetic | $k_1$ ($min^{-1}$) | 0.047 |
| | $q_e$ ($mgg^{-1}$) | 43.7 |
| | $R^2$ | 0.854 |
| Second-order model kinetic | $K_2$ ($min^{-1}$) | 0.058 |
| | $q_e$ ($mgg^{-1}$) | 55.7 |
| | $R^2$ | 0.987 |
| Elovich | $\alpha$ (mg $g^{-1}$ $min^{-1}$) | 6.37 |
| | $\beta$ (g $mg^{-1}$) | 0.33 |
| | $R^2$ | 0.922 |

| **Thermodynamic parameters** | | | | |
|---|---|---|---|---|
| (Cd(II) ion =10 ($mgL^{-1}$) | T ($^OK$) | value of $\Delta G^o$ (kJ $mol^{-1}$) | value of $\Delta H^o$ (kJ $mol^{-1}$) | value of $\Delta S^o$ (J $mol^{-1}$. $K^{-1}$) |
| | 298 | -3.45 | -17.06 | -41.26 |
| | 308 | -2.39 | | |
| | 318 | -2.19 | | |
| | 328 | -1.94 | | |
| | 338 | -1.56 | | |

### *3.9. Adsorption mechanism of Cd(II) ions*

Adsorption of Cd(II) ions from wastewater using shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs is one of the effective and environmentally friendly methods. Under optimized background conditions (pH 6.0), the solid substrate is rich in reactive functional centers such as iron-oxygen bridging domains (Fe–O), carboxylic networks (COOH), and structural hydroxyl structural entities (OH). This means the core capture framework does not stem from plain electrostatic attraction between opposing charges; rather, the target pollutant bonds via interfacial coordination, electron sharing into empty Cd(II) ions orbitals, and intensive hydrogen-bonding connections with the active oxygenated linkages distributed throughout the starch-ferrite-biochar architecture. Moreover, the Cd(II) ion undergoes ion and/or proton exchange reactions with the reactive sites of shrimp shell-derived biochar@starch/CoFe2O4NPs with hydroxyl groups, as shown in Figure 9.

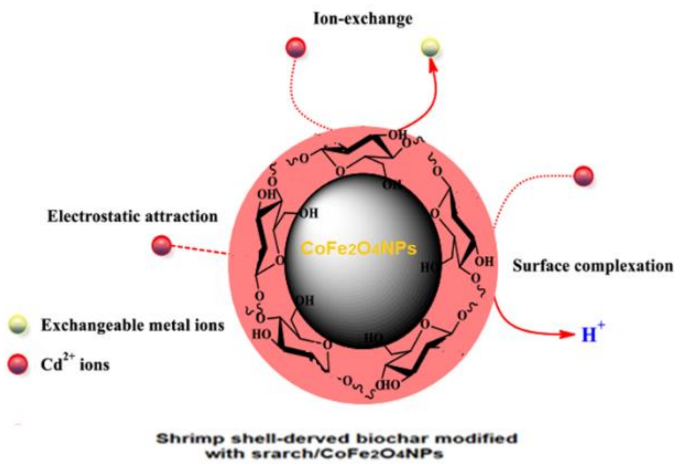


**Fig. 9.** The adsorption mechanism between shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs surface and Cd(II) ion in solutions.

### *3.10. Application to real samples*

To remove Cd(II) ion from actual water samples were spiked with varying concentrations of Cd(II) ion (0.0, 5.0, and 10.0 $mgL^{-1}$) were spiked separate in each real sample, and 100 mL of this solution was transferred into a conical flask that contained 0.1 g of shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs and performed in batch mode for 60

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min, and to assess the removal efficiency under realistic conditions. The tests were conducted in triplicate, and the results demonstrated that the synthesized shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs exhibited effective Cd(II) ion removal from both water and wastewater samples. Table 3 shows that the shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs can remove 96.0%, 97.0% and 94.0% Cd(II) ion from tap water, surface water, and industrial wastewater samples, respectively. These findings demonstrated the usefulness of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs in the removal of Cd(II) ions in actual water [35, 40].

**Table 3.** Removal of Cd(II) ion from real water samples using shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs (n = 3).

| Water samples | Added ($mgL^{-1}$) | Founded ($mgL^{-1}$) | RSD (%) | Recovery (%) |
|---|---|---|---|---|
| Tap water | 0.0 | N.D | ---- | ---- |
| | 5.0 | 4.70 | 1.5 | 94.0 |
| | 10.0 | 9.50 | 1.2 | 96.0 |
| Surface water | 0.0 | 0.25 | ---- | ---- |
| | 5.0 | 5.05 | 1.8 | 96.0 |
| | 10.0 | 9.90 | 1.4 | 97.0 |
| Industrial wastewater | 0.0 | 0.44 | ---- | ---- |
| | 5.0 | 5.10 | 1.2 | 93.2 |
| | 10.0 | 9.80 | 1.1 | 94.0 |

### *3.11. Impact of ion concentration on Cd(II) ion adsorption*

The impact of ionic strength on the adsorption of Cd(II) ion using shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs was investigated. The salts such (NaCl, $CaCl_2$, and $Na_2SO_4$) were used as the ionic strength agent, prepared at five distinct concentrations: 0.0, 0.6, 1.0, 1.5, and 2.0 g $L^{-1}$ in 100 mL solutions. The data presented in Table 4, indicate the Cd(II) ion adsorption on the adsorbent surface decreases as the salts concentration increases, that is attributed to competition between salts and Cd(II) ions in solution.

**Table 4.** The impact of ionic strength on the adsorption of Cd(II) ion using shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs (pH 6.0, adsorbent dose 0.1 g, time 60 min).

| Salts | Salts concentration (g $L^{-1}$) | Ad% Cd(II) ion |
|---|---|---|
| NaCl | 0.00 | 94.2 |
| | 0.06 | 94.1 |
| | 1.0 | 93.5 |
| | 1.5 | 92.4 |
| | 2.0 | 90.2 |
| $CaCl_2$ | 0.00 | 94.2 |
| | 0.06 | 93.4 |
| | 1.0 | 91.5 |
| | 1.5 | 88.8 |
| | 2.0 | 86.3 |
| $Na_2SO_4$ | 0.00 | 94.2 |
| | 0.06 | 90.4 |
| | 1.0 | 88.4 |
| | 1.5 | 86.2 |
| | 2.0 | 84.0 |

### *3.12. Reusability studies*

To determine the reusability of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs adsorbent was placed in NaOH solution and stirred for 180 min to desorb Cd(II) ion. Then washed with double distilled water followed drying and used for the next adsorption cycles. It was observed that the removal of Cd(II) ion decreases from 96.6% to 90.3% in the 4 cycle. The decrease in removal efficiency of Cd(II) ion may be due to the loss of some functionalities of shrimp shell-derived biochar modified by starch/$CoFe_2O_4$ nanoparticles adsorbent available for Cd(II) ion sorption. The results are illustrated in Figure 10.

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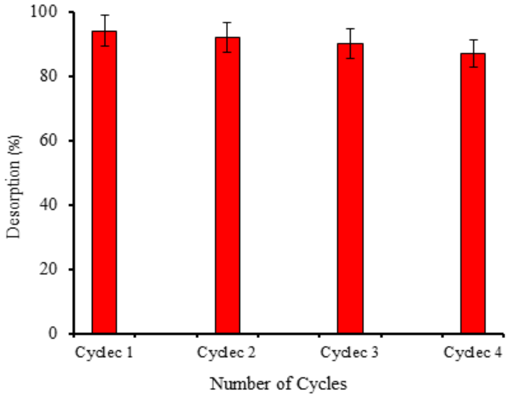


**Fig. 10.** Number of cycles of operation for adsorption of Cd(II) ion into shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs (pH 6.0, adsorbent dose 0.1 g, time 60 min).

### *3.13. Comparison of adsorption capacity*

To evaluate the treatment performance of shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs for Cd(II) ion removal, it is essential to compare its adsorption capacity with that of other adsorbents reported in the literature. The results showed the $q_{max}$ in this study was higher than some other adsorbents such (Luffa peels, Activated carbon, Cucumis melo Peel, Passion fruit shell, $TiO_2$NPs, Magnetic carbon aerogel), and respective results are reported in (Table 5).

**Table 5.** Comparison of various adsorbents for Cd(II) ion removal.

| Adsorbents | Dosage sorbent (g) | pH | Time (min) | Adsorption capacity ( $mgg^{-1}$) | Adsorption efficiency (%) | References |
|---|---|---|---|---|---|---|
| Luffa peels | 0.1 | 5.6 | 60 | 25.8 | (92.0% to 90.0%) | [7] |
| Coconut shell, Walnut shell | 0.15 | 6.5 | 150 | 32.4 | (100% to 83.7%) | [11] |
| $TiO_2$NPs | 0.7 | 4.3 | 120 | 45.5 | (89.45%) | [14] |
| Commercial activated carbon | 0.6 | 6.0 | 45 | 18.4 | (97.0% to 95.0%) | [15] |
| Cucumis melo Peel | 0.25 | 6.0 | 180 | 35.66 | (89.6% to 86.6%) | [20] |
| Passion fruit shell | 0.1 | 4.0 | 60 | 28.6 | (91.0% to 88.5%) | [25] |
| Magnetic carbon aerogel | 0.4 | 7.0 | 30 | 143.88 | (98.7% to 85.0%) | [43] |
| Shrimp shell-derived biochar@starch/$CoFe_2O_4$NPs | 0.1 | 6.0 | 60 | 56.6 | (96.6% to 90.3%) | This work |

## 4. Conclusion

Shrimp shell-derived biochar@starch/ $CoFe_2O_4$NPs was successfully prepared for heavy metals and toxic pollutants removal from aqueous environments. Characterization analyses confirmed the formation of a magnetic composite with functional surface groups, suitable morphology, and acceptable thermal stability. The adsorption process was strongly affected by pH, adsorbent dosage, contact time, temperature, and ionic strength. The optimum conditions were pH 6.0, 0.1 g adsorbent dose, and 60 minutes contact time. The Langmuir model best described the equilibrium data, with a maximum adsorption capacity of 56.6 $mgg^{-1}$, while the pseudo-second-order model best represented the adsorption kinetics. Thermodynamic results indicated that the process was spontaneous and exothermic. The adsorbent also showed strong performance in real water and wastewater samples and maintained good removal efficiency after three reuse cycles. The adsorbent with chemical structure shrimp shell biochar, starch and $CoFe_2O_4$NPs, all of which are compatible with the environment is very inexpensive, and non-toxic. These findings suggest that starch/$CoFe_2O_4$NPs-modified shrimp shell biochar is a promising, low-cost, and environmentally friendly material for Cd(II) ion and other pollutants removal from contaminated water.

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# سنتز بیوچار مشتق‌شده از پوسته میگو اصلاح‌شده با نشاسته/ نانوذرات $CoFe_2O_4$ و کاربرد آن به عنوان جاذبی مؤثر و سازگار با محیط زیست برای حذف یون کادمیم از محیط‌های آبی: تحلیل ایزوترم، سینتیک و ترمودینامیک

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**چکیده**
این مطالعه به بررسی پتانسیل بیوچار مشتق‌شده از پوسته میگو اصلاح‌شده با نشاسته/ نانوذرات $CoFe_2O_4$. برای جذب فلزات سنگین و آلاینده‌های سمی از محیط‌های آبی می‌پردازد. جذب یون کادمیم (II) تحت شرایط مختلف، از جمله pH، زمان تماس، دوز جاذب و دما مورد مطالعه قرار گرفت. فرآیند جذب به بهترین وجه توسط مدل‌های ایزوترم لانگمویر و سینتیک شبه درجه دوم توصیف شد که نشان‌دهنده جذب تک لایه و برهمکنش‌های غالب جذب شیمیایی است. حداکثر ظرفیت جذب ۵۶/۶ میلی‌گرم بر گرم در دمای ۲۹۸ درجه کلوین تعیین شد. آنالیزهای ترمودینامیکی نشان داد که فرآیند جذب خود به خودی و گرمازا است. پارامترهای ترمودینامیکی محاسبه‌شده، مانند $\Delta G°$، $\Delta H°$ و $\Delta S°$ برای جذب یون کادمیم (II) بر روی سطح جاذب، $kJ\ mol^{-1}$ ۳/۴۵–، $kJ\ mol^{-1}$ ۱۷/۰۶– و $J\ mol^{-1}.\ K^{-1}$ ۴۱/۲۶– به دست آمدند. راندمان حذف یون کادمیم (II) از نمونه‌های آب واقعی بالاتر از ۹۰ درصد بود، اگرچه راندمان با افزایش غلظت نمک کاهش یافت. این یافته‌ها نشان می‌دهد که بیوچار مشتق‌شده از پوسته میگو اصلاح‌شده با نشاسته/ نانوذرات $CoFe_2O_4$ یک جاذب پایدار، کم‌هزینه و سازگار با محیط زیست با پتانسیل قابل توجه برای حذف یون کادمیم در سیستم‌های آب آلوده است.

**کلید واژه‌ها**

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کادمیم، نانوذرات CoFe2O4، پوسته میگو، محیط‌های آبی.