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Cadmium Removal Using Egg and Peanut Shell

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ABSTRACT

This work studies the adsorption efficiency of a biochar composite derived from egg and peanut shells for the removal of cadmium (Cd) from synthetic wastewater. The biochar is prepared by combining equal proportions of egg and peanut shells. The removal capacity of Cd(II) ions from aqueous solutions has been evaluated using a batch adsorption test, and a UV-VIS spectrophotometer to determine the equilibrium concentration. Results demonstrate a maximum adsorption capacity of 3.013 mg/g under conditions of 5 g/L adsorbent dosage, an initial Cd(II) concentration of 5.0 mg/L, and a contact time of 180 minutes. Isotherm modeling indicates that the adsorption process is best fitted by the Freundlich model ($R^2 = 0.9800$), implying multilayer adsorption on a heterogeneous surface. The high density of functional groups in the biochar made it more convenient for Cd(II) to attach through surface complexation and electrostatic interactions. These data imply that egg and peanut shell-derived biochar is a promising, sustainable, and effective adsorbent for the removal of cadmium contaminated aqueous environments.

Keywords: Cadmium, Egg Shell, Peanut Shell, Adsorption Isotherm.

1. Introduction

The ecosystem and human health are at risk from heavy metal-induced water pollution, with cadmium contamination being particularly dangerous because of its high toxicity and persistence. According to World Health Organization (WHO) regulations, cadmium discharge must not exceed 0.003 mg/L [1]. Chronic cadmium toxicity endangers multiple organs, including the nervous system, liver, kidneys, and cardiovascular system, with severe cases potentially resulting in death [2, 3]. Conventional methods for removing heavy metals are costly and environmentally harmful, particularly for low concentration wastewater, due to high chemical consumption and the production of toxic sludge [4-8]. Adsorption provides an efficient alternative, delivering high capacity, low cost, and simple regeneration [9-11], while organic adsorbents further enhance waste reduction and resource recovery [12]. In this context, biochar has gained substantial attention as a stable, carbon rich substance with a highly aromatic structure formed by heating biomass in low or no oxygen conditions (pyrolysis) [13-15]. Its high surface area, porous structure, and acidic functional groups, particularly oxygen-containing ones, enable significant electrostatic interactions with metal ions such as cadmium [16]. Biochar not only has a wide range of raw material sources but also generates less secondary contamination when used to treat metal-containing wastewater [17]. Among these materials, eggshells stand out for their ability to effectively absorb organic compounds and highly toxic heavy metals, due to their porous structure. They have functional groups such as carbonyl, carboxylic, and hydroxyl, which are essential for the adsorption of heavy metals [18]. Calcium carbonate makes up 94% of their weight, followed by organic matter (4%), magnesium carbonate (1%), and calcium phosphate (1%). Eggshells are a promising biological sorbent since 94% of their chemical makeup is calcium carbonate [19]. Both reversible and non-reversible processes contribute to heavy metal sorption by eggshells, with ion exchange and precipitation functioning as the main mechanisms [20]. The effectiveness of eggshell biochar in removing As(V) was assessed by examining parameters such as contact time, pH, concentration, and sorbent dose [21]. The outcomes demonstrated a maximum sorption of 6.3 $mg.g^{-1}$ at a pH of 4.5, a 96% removal rate at a concentration of 0.6 $mg.L^{-1}$, and a sorbent dosage of 0.9 $g.L^{-1}$. Several studies have shown that chicken eggshells can adsorb heavy metals such as cadmium [20, 22], chromium [23, 24], nickel [25], lead [26], cobalt [27], and boron [28], as well as dyes [29, 30], primarily due to their calcium carbonate-based composition. Biochar made from peanut shells has a higher adsorption capacity than biochar produced from corn cobs and conta pulp, which enhances the process of treating wastewater containing Cd(II) [31]. Research comparing maximum Cd(II) adsorption capacity between peanut shell biochar (PBc) and chitosan-modified peanut shell biochar (CBc) indicated that biosorption depends on factors like biochar dosage, pH, and contact time [32]. The study found that CBc exhibited a higher removal effectiveness (95%) compared to PBc (49%), with corresponding maximum adsorption capacities of 58.82 mg/g and 40 mg/g, respectively. Peanut shells are rich in cellulose and polymer materials with reactive functional groups. They are lignocellulosic materials composed of three main components: cellulose (46.66%), hemicellulose (5.80%), and lignin (37.31%). These residues contain several functional groups suitable for adsorbing cationic ions [33]. Ash-free peanut shell biochar exhibited the best Cd(II) adsorption performance, reaching equilibrium within 6 hours with an adsorption capacity of 34.2 mg/g. The optimized conditions achieved a 91.7% Cd(II) removal efficiency [34]. $KMnO_4$ and KOH were used to modify the biochar produced from used peanut shells. Adsorption tests on modified biochar for Ni(II) demonstrated an adsorption capacity of 87.15 mg/g for modified peanut biochar [17]. This study aims to investigate the effectiveness of composite biochar derived from egg and peanut shells in removing cadmium from contaminated water. While these organic compounds have been previously studied individually for adsorption, their combined use as a composite biochar has not been explored. Due to the diverse chemical and physical properties of different adsorbents, the composite biochar is expected to exhibit enhanced adsorption capability. Batch tests were conducted, and the acquired data were analyzed using adsorption isotherm models to determine cadmium absorption behavior.

2. Materials and Methodology

2.1 Preparation of Biochar

Peanut shells were cleaned with distilled water, air dried, and then pyrolyzed at 400 °C for 2 hours to produce biochar, which was subsequently ground into a fine powder. Similarly, eggshells were pyrolyzed at 550 °C for 2 hours to make eggshell-derived biochar. The two biochars were then combined in a 1:1 ratio to prepare the composite biochar.

2.2 Preparation of Stock Solution

A stock solution was prepared by dissolving 1000 grams of Cadmium Chloride ($CdCl_2 \cdot H_2O$) in 1 liter of distilled water. This stock solution was further diluted to obtain cadmium ion concentrations of 5, 5.5, 6, 6.5, and 7 mg/L.

2.3 Batch Adsorption Analysis

Equations Batch adsorption experiments were carried out with initial cadmium concentrations ranging from 5 to 7 mg/L. In each conical flask, 100 mL of cadmium chloride solution was mixed with 0.5 grams of biochar. The mixture was stirred with a magnetic stirrer on a heated plate at room temperature for 180 minutes. After stirring, the mixture was filtered through Whatman filter paper to separate the residual solution from the biochar. Residual cadmium concentrations were then measured using a UV-VIS spectrophotometer (DR-6000). Following adsorption, the solution containing cadmium was disposed of safely through the laboratory's hazardous waste management system.

2.4 Adsorption Equilibrium Studies

To compute the adsorption capacity and the percentage of metal ions removed by the adsorbent, equation (1) and (2) was used [12]:

$$q_e = \frac{(C_o - C_e) \cdot V}{m} \tag{1}$$

$$Removal\ \% = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

Where: C_o and C_e are initial and final metal concentrations (mg/l); q_e is the adsorption capacity (mg/g); V is the volume of the solution (L); m is the mass (g) of the adsorbent.

2.5 Isotherm Models

Equilibrium isotherms describe the interaction between sorbate and adsorbent. As a monolayer approach, the Langmuir isotherm suggests that the adsorbent's active surface can only absorb one adsorbate molecule at a time. The Freundlich isotherm employs a multilayer approach, in which the active surface adsorbent can absorb multiple adsorbate molecules. The Temkin isotherm model explains how the interaction between the adsorbate molecules and the solid surface causes the adsorption heat to decrease as coverage increases [35]. The Langmuir isotherm relationship is

$$q_e = \frac{q_{max} K_l C_e}{1 + K_l C_e} \tag{3}$$

Where: K_l is the Langmuir constant (L/mg), which indicates the affinity of metal ions to the adsorbent; C_e is the metal ion concentrations (mg/L) at equilibrium; q_{max} (mg/g) is the maximum amount of metal ion per unit mass of biosorbent; q_e is the adsorbent metal's uptake capacity (mg/g); and K (L/g) is the equilibrium adsorption constant.

The Langmuir parameters can be found by plotting C_e/q_e vs. C_e, using a linearized form of Eq. (3), which is shown as follows:

$$\frac{C_e}{q_e} = \frac{1}{K q_{max}} + \frac{C_e}{q_{max}} \tag{4}$$

The Freundlich equation is:

$$q_e = K_f C_e^{1/n} \tag{5}$$

Where: K_f is the Freundlich constant (mg/g). $(L/mg)^{1/n}$; n is the Freundlich constant, which represents the biosorption intensity.

By linearizing Eq. (5) in logarithmic form, a plot of log q_e against log C_e can be used to estimate the unknown parameters:

$$log q_e = log K_f + \frac{1}{n} log C_e \tag{6}$$

The nature of the equilibrium data mostly determines whether to use the Freundlich or Langmuir isotherms [36]. The linear form of the Temkin isotherm model is shown in Eq. (7) below.

$$q_e = \frac{Rt}{b} \ln K_T + \frac{Rt}{b} \ln C_e \tag{7}$$

Where: K_T is the Temkin isotherm constant (L/g), and the heat of sorption is associated with the Temkin constant, b (J/mol) [37].

3. Results and Discussion

The data for this study were collected from the experiment, and the relevant parameters from the batch adsorption are illustrated in Table 1.

Table 1 Initial and equilibrium concentration of Cd

Sample	Initial conc. C_0 (mg/L)	Equilibrium Conc. C_e (mg/L)	% Removal	Adsorption q_e (mg/g)
1	5	0.199	96.0200	2.8806
2	5.5	0.247	95.5090	3.1518
3	6	0.278	95.3667	3.4332
4	6.5	0.310	95.2308	3.7140
5	7	0.340	95.1429	3.9960

3.1 Effect of Initial Cd (II) Ion Concentration

The biosorption efficiency and adsorption capacity of cadmium ions were assessed across a range of initial concentrations (5.0–7.0 mg/L). Figures 1 and 2 illustrate the percentage removal and equilibrium adsorption capacity (q_e)

of Cd(II) as functions of initial concentration. As summarized in Table 1, the maximum removal efficiency was 96.02% at an initial Cd(II) concentration of 5.0 mg/L. With increasing initial concentration of Cd(II), there is a slight rise in equilibrium concentration, while the adsorption capacity increased from 2.88 mg/g to 3.996 mg/g. As the concentration of Cd(II) ions increases, the available binding sites become increasingly occupied, reducing the number of sites accessible for additional ions.

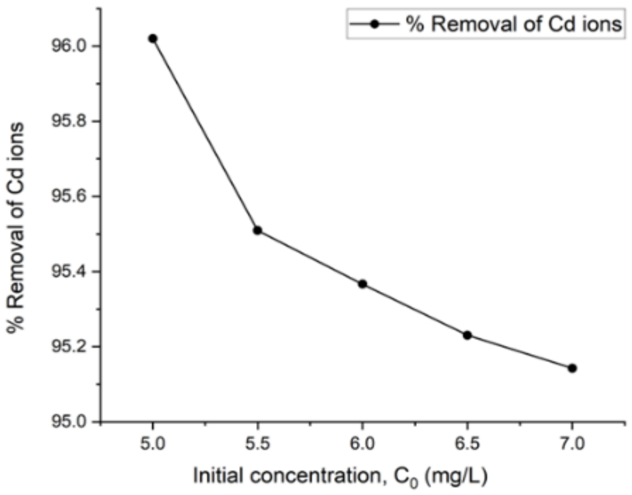

Fig.1 Initial concentration vs removal of Cd (II)

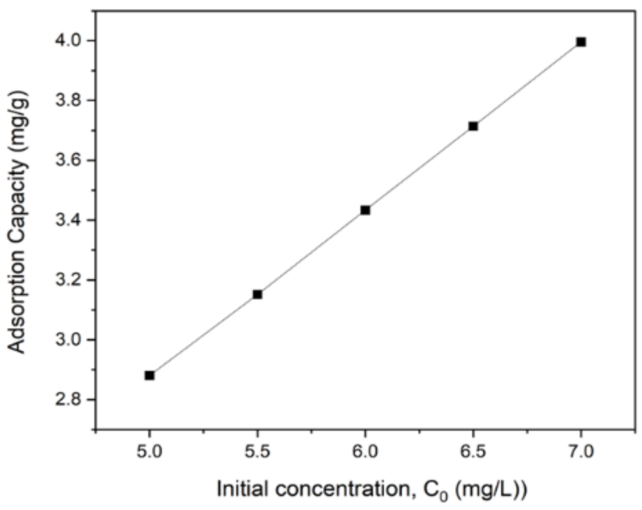

Fig. 2 Adsorption Capacity of Adsorbent

Table 2 q_e of peanut and egg shell biochar

Adsorbent	Adsorbate	Adsorption Capacity, q_e
Eggshell biochar [21]	As(V)	6.3 mg/g
Peanut shell biochar [31]	Cd(II)	0.314 mg/g
Peanut shell biochar [31]	Pb(II)	0.271 mg/g
Chont pulp biochar [31]	Cd(II)	0.155 mg/g
Corn cob biochar [31]	Cd(II)	0.049 mg/g
Peanut shells biochar [33]	Cd(II)	0.39 mmol/g
Peanut shells biochar [33]	Cu	0.48 mmol/g
Ash-free peanut shell biochar[34]	Cd(II)	34.2 mg/g

Although the adsorption capacity increases with elevated initial concentrations, the overall removal efficiency decreases due to the limited availability of binding sites. When compared to the values of other natural adsorbents previously published in Table 2, the adsorption capacity values found in the current study are highly significant.

3.2 Adsorption Isotherms

Biosorption isotherms illustrate the relationship between the amount of adsorbate retained per unit mass of biosorbent and its concentration in the solution. To describe the adsorption behavior of metal ions onto the biomass surface, three well known isotherm models were applied: Langmuir, Freundlich, and Temkin, which are shown in Figures 3, 4, and 5.

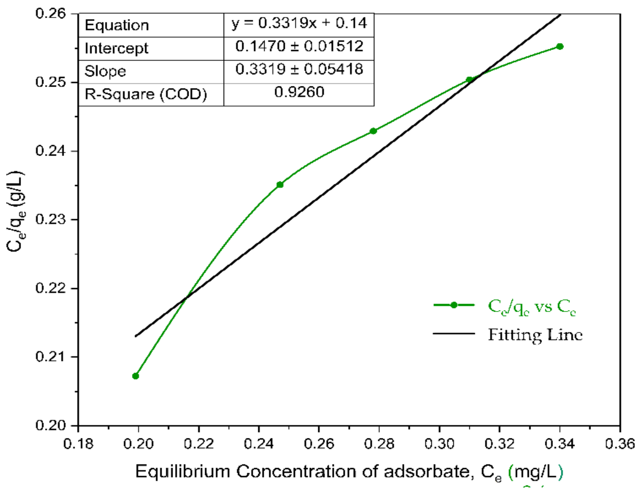

Fig. 3 Langmuir Isotherm

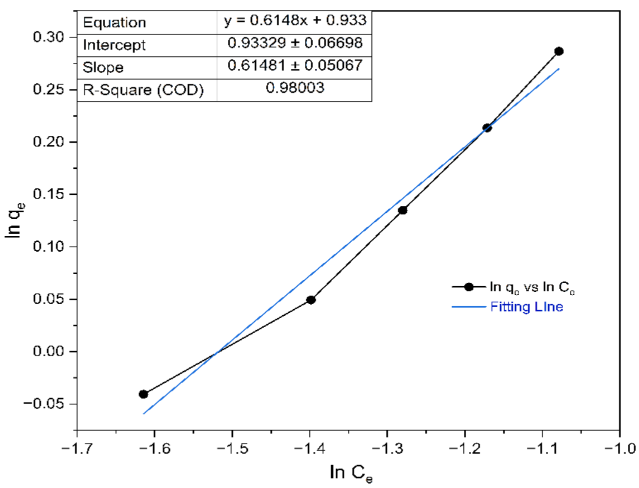

Fig. 4 Freundlich Isotherm

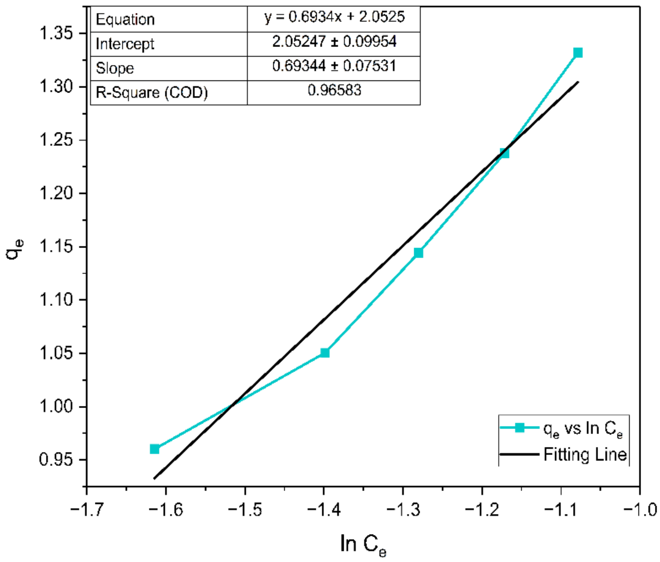

Fig. 5 Temkin Isotherm

These models were selected to describe the complex nature of the process, which involves multiple physical and chemical interactions. The isotherm parameters for these models are obtained through linear regression analysis, as detailed in Figures 3, 4, and 5, with corresponding constants listed in Table 3.

Table 3 Isotherm Parameter

Isotherm Model	Parameter	value
Langmuir Isotherm	q_{max} (mg/g)	3.013
	K_l (L/mg)	0.4428
	R^2	0.9622
Freundlich Isotherm	n	1.62652
	K_f (L/mg)	2.54286
	R^2	0.9800
Temkin Isotherm	b (J/mol)	0.6934
	K_T (L/mol)	19.2989
	R^2	0.9658

Among the models, the Freundlich isotherm model exhibited a stronger correlation to the experimental data, with an R^2 value of 0.9800 for the investigated metal ions. In comparison, the Langmuir and Temkin models showed comparatively lower R^2 values of 0.9622 and 0.9658, respectively. Despite this, the Langmuir isotherm still revealed a relatively good fit, suggesting monolayer adsorption on a homogeneous surface. It yielded a maximum adsorption capacity (q_{max}) of 3.013 mg/g and a Langmuir constant (K_l) of 0.443 L/mg, indicating a moderate binding affinity between Cd(II) ions and the biochar surface. This implies that chemisorption may partially influence the binding process. The value of n acts as an index of adsorption favorability, with n values greater than 1 representing a favorable adsorption process [38]. The favorable adsorption behavior is further validated by the Freundlich constant n value of 1.63, which falls within the optimal range of 1 to 10. It also demonstrated a larger correlation coefficient, suggesting adsorption on a heterogeneous surface with varied energy sites. The Freundlich constant K_f of 2.54 L/mg indicates a moderately strong binding affinity and likely involves multilayer coverage, including both physical adsorption and surface complexation. With an R^2 of 0.9658, the Temkin model provided an adequate fit to the data and accurately represented the adsorbate–adsorbent interactions, characterized by a decreasing heat of adsorption as surface coverage increases. Moderate adsorption energies are suggested by the equilibrium constant (K_T) of 19.30 L/mol and the Temkin binding energy constant consistent with processes like electrostatic interactions and ion exchange.

4. Conclusion

Composite biochar prepared from egg and peanut shells is used as an adsorbent to remove Cadmium from aqueous solutions. The maximum removal effectiveness is 96.02% under optimum conditions, with an adsorption capacity of 3.013 mg/g. The adsorption process followed the Freundlich isotherm model, indicating multilayer adsorption on a heterogeneous surface. Cadmium adsorption occurs through surface complexation and electrostatic interactions involving functional groups on the biochar surface. Due to its high efficiency and sustainable origin, composite biochar exhibits significant potential for removing cadmium from contaminated water. Future studies should investigate adsorption kinetics, thermodynamics, and advanced analyses, such as SEM-EDS, BET surface area analysis, and XPS, to gain a better understanding of the mechanisms involved.

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