


## Research Article

# Adsorption of Cd (II) Using Chemically Modified Rice Husk: Characterization, Equilibrium, and Kinetic Studies

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Cadmium (Cd) is a highly toxic heavy metal considered carcinogenic to humans. The adsorption behavior of cadmium adsorption using untreated and chemically modified rice husk was investigated. Experimental tests were carried out to evaluate the influence of the variables pH, initial concentration of cadmium, and dosage of adsorbent in the adsorption process. In optimal experimental conditions, the maximum adsorption efficiency was 92.65%. Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were used allowing the identification of the main functional groups and morphology of rice husk and treated rice husk, and the results showed an improvement of adsorption characteristics after rice husk treatment with NaOH. The optimum adsorption pH for both types of rice husk was 7. The maximum adsorption capacities of RH and treated RH fitted by the Langmuir model were 5.13 mg/g and 11.06 mg/g, respectively. The pseudosecond order kinetics has the best coefficients of determination for untreated ( $R^2 = 0.992$ ) and treated ( $R^2 = 0.999$ ) rice husk. The adsorption process was found to be endothermic in nature with enthalpy of 14.08 kJ/mol and entropy of 170.98 J/mol.K. The calculated activation energy was 24 kJ/mol. The results showed the potential of rice husk as a low-cost, easily managed, and efficient biosorbent for Cd removal from waters.

## 1. Introduction

Some of the most important characteristics that should be considered when choosing a bioadsorbent are, its nontoxic, abundant, and a large surface area [1, 2] and low-cost adsorbent [2–4]. Rice husk is an organic waste and is produced in large quantities as an important by-product of the rice production industry [5] and is predominantly composed of silica [6] and lignocellulose [1].

Rice husk is insoluble in water, has good chemical stability, and has functional groups in its structure such as OH, Si-

OH, C–H, C=O, C=C, CH<sub>2</sub>, CH<sub>3</sub>, CO, Si–O–Si, C–C, Si–H, and –O–CH<sub>3</sub> [Ferreira,2020]. These adsorption properties can be improved with chemical treatment, by example [7], reported that NaOH-treated soyabean and cottonseed hulls improved sorption capacity for Zn (II) as opposed to untreated materials. It was explained by an increase in the amount of galactouronic acid groups produced upon hydrolysis of O-methyl ester groups present in pectic substances. In addition, [8] showed that soyabean hulls treated with sodium hydroxide had an enhanced copper adsorption capacity. Then, rice husk can be a low-cost and good



FIGURE 1: Rice husk dried (a) and sieved (b).

adsorbent material for pollutant removal [9, 10]. Properly treated, this material can be used to remove heavy metals from water, as well as organic compounds. Heavy metals have a high atomic weight and a density at least 5 times greater than that of water [11–14]. They are naturally occurring elements that comprise essential (e.g., Fe, Cu, and Zn) and nonessential metals (e.g., Cd, Hg, and Pb) [15, 16]. Heavy metals are persistent in the environment [17], can be toxic, carcinogenic, mutagenic, or teratogenic even in low concentrations [16, 18], and cause different health problems due to their toxicity. They can also contaminate the food chains [19, 20]. Cadmium is a heavy metal with a density  $8.6 \text{ g/cm}^3$  [21]. It is used to produce alloys, pigments, plastics as a stabilizer in PVC products, and anticorrosive agent, and it can be found in batteries [22–25]. It is widely distributed by natural processes such as volcanic activities [26, 27] and by anthropic activities such as mining, metal refining, burning of fossil fuels, and the use of tobacco [28]. Approximately 30,000 tons of cadmium are released into the atmosphere every year; an estimated 4000–13,000 tons are the result of human activities [29]. Cadmium is an extremely toxic element and nonessential for human health [30–32] naturally present everywhere in water, air, soils, and foodstuffs [33] and poses a severe risks to human health [27]. It is accumulated mainly in the liver and the kidneys [34, 35] and has an extremely protracted biological half-life (approximately 20–30 years in humans) [36].

After an extensive bibliographic search, it has been observed that works using rice husk to remove cadmium from water had been predominantly carried out in Asia [37–42]. This is why it is relevant to study biosorbents made out of South American rice husk, since the composition of rice husk varies in different regions according to its geographical characteristics and type of rice, among other factors. The resulting biosorbent after chemical treatment would also be different, and this could influence the efficiency of its contaminant removal capacity.

In Peru, rice production in 2018 was 3,557,900 tons [43], and in consequence, large amounts of rice husk waste were produced. The Peruvian standard regulates the maximum

admissible value for discharge to the sewer system for cadmium with a value of  $0.2 \text{ mg/L}$  (Supreme Decree No. 010-2019-Housing).

The objective of this work was to study the bioadsorption of Cd (II) ions from synthetic waters using raw and chemically modified rice husk taken from crops grown in the South America region, specifically from Peru, employing the smallest amount of chemical reagent to prepare the biosorbent.

## 2. Materials and Methods

**2.1. Preparation of the Bioadsorbent.** The rice husk (*Oryza sativa*) was collected from northern part of Peru, Lambayeque Department, an arid region on the coast of Peru. The place of growth influences the physicochemical and biochemical properties of the rice husk [1, 44].

Figure 1 shows the conditioned raw rice husk (a) and the sieved rice husk after milling (b) to be used as bioadsorbent.

The rice husk was milled then classified according to the following particle size sieves: ASTM E11-17 number 20 ( $850 \mu\text{m}$ )-S2, 30 ( $600 \mu\text{m}$ )-S2, and 40 ( $425 \mu\text{m}$ )-S1. It was washed using distilled water until the water did not show any color, indicating that dirt and water-soluble substances were removed, and then it was dried in an oven at  $70^\circ\text{C}$  for 24 h. To chemically treat the RH, a solution of NaOH 0.3 M was prepared. 3 grams of RH was mixed with 100 mL of solution then stirred during 17 h at 150 rpm, to be, later, left to rest for 12 h. Finally, the RH was separated and washed several times until it reached pH of 7.

**2.2. Preparation of the Synthetic Solution.** Solutions of 10, 20, and 50 mg/L of Cd (II) using  $\text{Cd}(\text{NO}_3)_2$  (Merck Millipore) were prepared by diluting a standard solution of 1000 mg/L of Cd (II). The pH was adjusted with a 0.70M caustic soda solution in all cases. Then, all adsorption tests were carried out using a pH range from 2.5 to 7, because it was experimentally determined that a white precipitate of cadmium hydroxide ( $\text{Cd}(\text{OH})_2$ ) forms at pH 8.

**2.3. Moisture and Ash Content.** The moisture in the rice husk samples was determined using the oven drying method. Two grams of untreated rice husk was placed in a Petri dish and placed in an oven at 105°C. Weight was controlled hourly until reaching a constant. Ash is the total measure of inorganic components in the sample, and the ash content was determined following the AOAC 930.05-1965 ash of plants method [45]. Both analyses were made in duplicate. The results obtained were  $9.50 \pm 0.66\%$  and  $11.90 \pm 0.02\%$ , respectively.

**2.4. Surface Characterization of the Rise Rusk.** The surface of the untreated and NaOH (0.3 M)-treated rice husk was analyzed with a scanning electron microscope (SEM, HITACHI, model SU8230). A semiquantitative determination of the elements present on the untreated and treated surface was carried out using energy dispersive X-ray spectroscopy (EDS), an analysis technique that is incorporated into SEM. The analysis conditions were as follows: distance (8.1 mm), magnification ( $\times 200$ ,  $\times 500$ , and  $\times 1200$ ), acceleration potential (3.0 kV), and current emission (1500-1900 nA). The chemical treatment of the rice husk in other studies was carried out with NaOH (1 M) [46].

**2.5. Cd (II) Biosorption Test.** Cd adsorption tests were carried out in aqueous solution prepared with Cd (NO<sub>3</sub>)<sub>2</sub> using raw and chemically modified rice husk at different particle sizes according sieves ASTM E11-17 number 20 (850 μm)-S2, 30 (600 μm)-S2, and 40 (425 μm)-S1. The effect of pH was carried out at 2.5, 4, 5.5, and 7 adjusted with a solution of 0.7 M NaOH. After the adsorption tests, the flasks were shaken on a digital orbital shaker (SHO-2D) at a speed of 185 rpm, time of 18 hours, and room temperature. After stirring, the solution was centrifuged (Frontier 5000) at a speed of 5000 rpm and a time of 5 minutes. A 15 mL aliquot of centrifuged solution was taken to analyze the final concentration of Cd by atomic absorption spectrometry (CONTRAA 800-D). The samples for this assay were run in duplicate.

**2.6. Determination of Adsorption Capacity.** Adsorption capacity ( $q$ ) is the amount of adsorbate taken up by the adsorbent per unit mass (or volume) of the adsorbent [47]. The removal efficiency ( $R$ ) and the adsorption capacity ( $q_t$ ) were evaluated using the following mathematical expressions (Eqs. (1) and (2)). The adsorption capacity of an adsorbent depends on several parameters such as the particle size of the bioadsorbent, the structure of its inner surface area, and the concentration of the adsorbate [48].

$$R = \left( \frac{C_o - C_e}{C_o} \right) \times 100\%, \quad (1)$$

$$q_t = \frac{C_o - C_t}{m} \times V, \quad (2)$$

where  $q_t$  and  $q_e$  refer to the adsorption capacity of metal ions (Cd II) at  $t$  (min) and equilibrium time, respectively.  $C_o$  (mg/L) is the initial cadmium concentration, while  $C_e$  (mg/L) and  $C_t$  (mg/L) denote the equilibrium

and  $t$  time concentration of metal ions, respectively. Also,  $m$  (mg) and  $V$  (L) are the amount of adsorbent (rice husk) and volume of adsorbate solution (Cd (NO<sub>3</sub>)<sub>2</sub>).

**2.7. Kinetics of Cd (II) Biosorption.** To determine the kinetic model that describes the adsorption of Cd (II), solutions of 10 mg/L of Cd (II) were prepared using the standard solution 1000 mg/L of Cd (NO<sub>3</sub>)<sub>2</sub>, and the pH was adjusted to 7 using NaOH 0.7 M. 50 mL of solution and 150 mg of untreated rice husk with a size range of 425-600 μm were added to 100 mL flasks. Treated rice husk in the same size range was analyzed under the same conditions. The solutions were stirred at 185 rpm at room temperature at variable times. Then, the solutions were centrifuged at 5000 rpm for 5 minutes. Aliquots of 15 mL of centrifuged solution were taken to determine the remaining concentration of Cd (II).

**2.7.1. Pseudofirst Order Model.** The model was developed by [49] and has also been called the pseudofirst order kinetic equation, because it was intuitively associated with the model of one-site occupancy adsorption kinetics governed by the rate of surface reaction [50]. This model assumes that the uptake rate of adsorbate with time is proportional to the amount available active sites on the adsorbent surface [51]. The equation is expressed as equation (3).

$$\left( q_t = q_e e^{-k_1 t} \right), \quad (3)$$

where  $q_e$  is the amount of Cd (II) adsorbed at equilibrium (mg/g),  $q_t$  is the amount of Cd (II) adsorbed at time  $t$  (mg/g), and  $k_1$  is the equilibrium rate constant of pseudofirst order (min<sup>-1</sup>). [52].

**2.7.2. Pseudosecond Order Model.** The model is based on the assumption that the rate-limiting step is chemical sorption or chemisorption and predicts the behavior over the whole range of adsorption [51]. The equation for the model is given by equation (4) [53].

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \quad (4)$$

where  $k_2$  is the pseudosecond order adsorption rate constant (g/mg.h),  $q_e$  is the amount of Cd (II) adsorbed at equilibrium (mg/g), and  $q_t$  is the amount of Cd (II) adsorbed at time  $t$ .

**2.8. Adsorption Isotherms.** Adsorption isotherms are important because they help to understand the interactions between the adsorbate and the active sites present on the surface of the adsorbent. In this study, Langmuir, Freundlich, Hill, Redlich-Peterson, and Temkin isotherm models of solid-liquid phases (Eqs. (2)-16) are selected and discussed because they are commonly used in the literature.

The Langmuir isotherm model is based on the assumptions that the adsorption process occurs at particular homogeneous sites on the surface of the adsorbent. This model is valid for monolayer adsorption on a surface with a finite

number of adsorption sites of equal energy [54]. The model is expressed by equation (5) [55].

$$q_e = \frac{K_L C_e}{1 + q_{\max} \cdot C_e}, \quad (5)$$

where  $C_e$  is the concentration of adsorbate at equilibrium (mg/L),  $q_e$  is the amount of adsorbate adsorbed per unit mass of solid (rice husk)(mg/g),  $q_{\max}$  is the maximum monolayer coverage capacity (mg/g), and  $K_L$  is the Langmuir adsorption constant related to the energy of adsorption (L/mg). The essential features of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor  $R_L$  [56, 57], defined in equation (6).

$$R_L = \frac{1}{1 + K_L \cdot C_o}, \quad (6)$$

where  $C_o$  is the initial concentration of adsorbate (mg/L).  $R_L$  value denotes the adsorption nature to be either favorable if  $0 < R_L$  or irreversible if  $R_L = 0$  (this occurs if  $K_L$  is very large, which means that adsorption is too strong), unfavorable if  $R_L > 1$ , linear if  $R_L = 1$ .

The Freundlich isotherm model is applicable to the gas-solid phase nonideal and multilayer adsorption on heterogeneous surfaces with interaction between adsorbed molecules. It is defined in equation (7) [58].

$$q_e = K_F C_e^{1/n}, \quad (7)$$

where  $q_e$  is the amount of adsorbate (pollutant) adsorbed per unit mass of adsorbent at the equilibrium (rice husk, mg/g),  $C_e$  is the equilibrium solution concentration of the adsorbate (mg/L),  $K_f$  is the Freundlich adsorption constant (L/g), and  $n$  (dimensionless) is the empirical constant that indicates whether the adsorption is linear ( $n = 1$ ), chemisorption ( $n < 1$ ), or physisorption ( $n > 1$ ).

The Hill isotherm model is expressed as equation (8) below.

$$q_e = \frac{Q_{\text{Hill}} C_e^{n_{\text{Hill}}}}{K_{\text{Hill}} + C_e^{n_{\text{Hill}}}}, \quad (8)$$

where  $Q_{\text{Hill}}$  is the maximum adsorption capacity (mol/kg),  $K_{\text{Hill}}$  ((mol/L) <sup>$n_{\text{Hill}}$</sup> ) is the Hill constant,  $1/K_{\text{Hill}}$  ((L/mol) <sup>$n_{\text{Hill}}$</sup> ) is the Hill equilibrium constant, and  $n_{\text{Hill}}$  (dimensionless) is the exponent of the Hill model.

The Redlich-Peterson isotherm model is expressed as equation (9).

$$q_e = \frac{K_{\text{RP}} C_e}{1 + a_{\text{RP}} C_e^{n_{\text{RP}}}}, \quad (9)$$

where  $K_{\text{RP}}$  (L/kg) and  $a_{\text{RP}}$  (L/mol) <sup>$n_{\text{RP}}$</sup>  are the Redlich-Peterson constant and the Redlich-Peterson equilibrium constant, and  $n_{\text{RP}}$  (dimensionless) is the exponent of the Redlich-Peterson model (ranging from 0 to 1).

TABLE 1: Main functional groups present in untreated rice husk sample.

Wave number (cm <sup>-1</sup> )	Vibration mode	Intensity	Functional group	Functional group name
3328.26	Tension	Medium	O-H	Hidroxyyl
2929.64	Tension	Low	C-H	Saturated
1716.56	Tension	Low	C=O	Carbonyl
1604.28	Tension	Low	C=C	Unsaturated
1033.74	Tension	Strong	C-O	Carboxilyc/ alcohol
1033.74	Tension	Strong	Si-O	Siloxane

The Temkin isotherm model is expressed as equation (10).

$$q_e = a_T (\ln k_T C_e), \quad (10)$$

where  $q_e$  (mg/g) is the equilibrium cadmium adsorption capacity,  $a_T$  is a constant and is related to the adsorption heat,  $k_T$  is the equilibrium binding constant (L/mg) and corresponds to the binding energy maximum, and  $C_e$  is the equilibrium concentration in the liquid phase (mg/L).

2.9. Error Analysis. The suitability of the adsorption data was analyzed by calculating the sum of squared errors (SSE), according to the following equation (11).

$$\text{SSE} = \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2}, \quad (11)$$

where  $q_{t,e}$  and  $q_{t,m}$  are the experimental biosorption capacities of Cd (II) ions (mg/g) at time  $t$  and the corresponding calculated values that are obtained from the kinetic models.

### 3. Results and Discussion

3.1. FTIR Analysis. The untreated and NaOH-treated rice husk samples were characterized using infrared spectroscopy to identify the main functional groups present in both samples. Table 1 shows the main functional groups identified in the untreated rice husk before the adsorption process. The spectrum range used was between 450 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>. Figure 2 shows the untreated rice husk infrared spectroscopy results before the adsorption process, where several peaks are observed. The peak at 3328.26 cm<sup>-1</sup> is wide and of medium size due to the stretching vibration of the OH group in the fibers of lignocellulosic compounds (cellulose, hemicellulose, lignin, etc.), and the other long peak at 1033.74 cm<sup>-1</sup> indicates the presence of silicon while the third peak at 1604 cm<sup>-1</sup> forms because of the C=C carbon double bonds present in lignin.

Figure 3 shows the infrared spectroscopy results of the analyzed NaOH-treated rice husk sample before the adsorption process. The percent transmittance corresponding to the OH<sup>-</sup> group peak (around 3330 cm<sup>-1</sup>) went down to around 73%, as opposed to the percent transmittance of the untreated rice husk sample that went down to 84%. There is a higher absorption by OH<sup>-</sup> groups in the treated

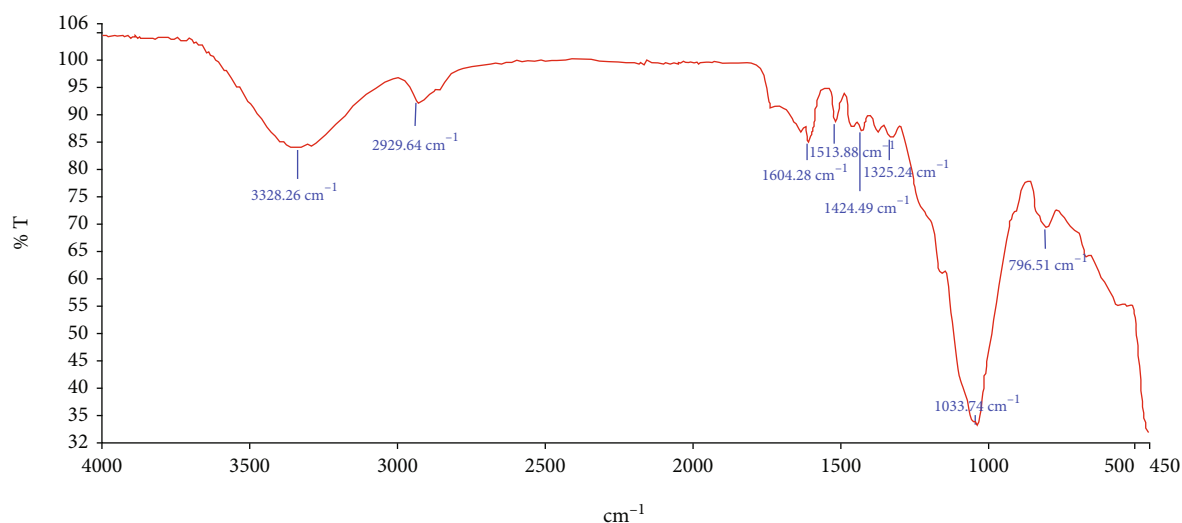


FIGURE 2: Infrared spectroscopy of untreated rice husk sample before adsorption.

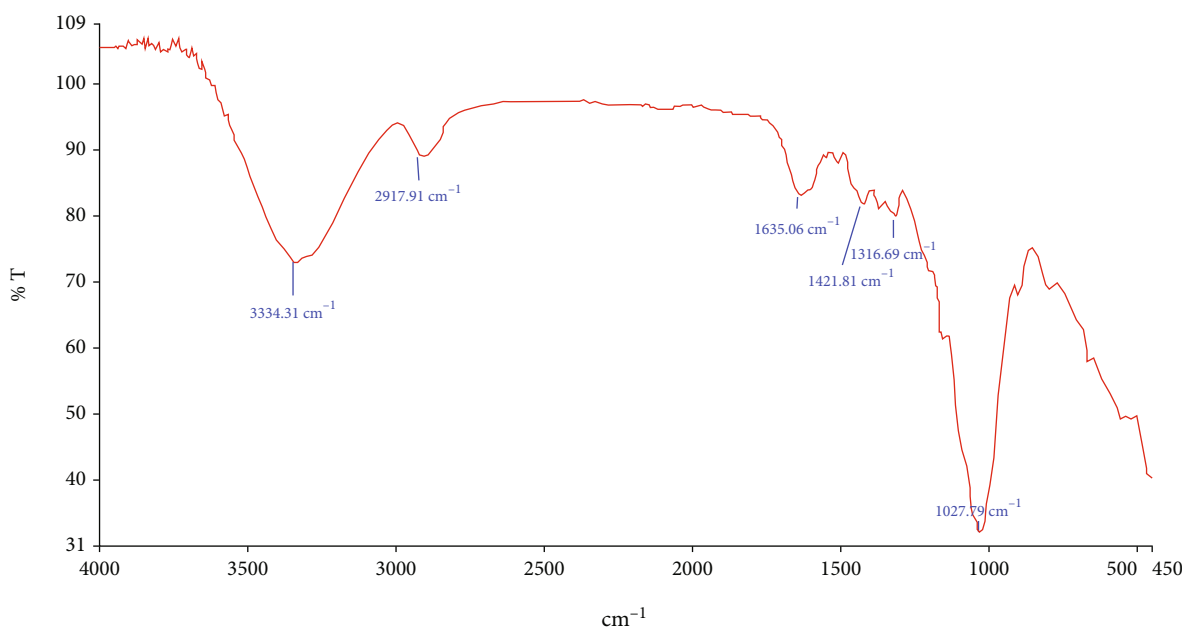


FIGURE 3: Infrared spectroscopy of rice husk sample treated with NaOH before adsorption.

sample because caustic soda removes surface impurities from the rice husk; thus, more OH<sup>-</sup> groups are exposed, or it could be because of some OH groups that remain after washing the sample with distilled water after treating it with NaOH.

Table 2 shows the main functional groups present in the NaOH-treated rice husk sample before adsorption. None of the carbonyl groups were identified even though they could be seen in the untreated rice husk sample. This may be because lignin and hemicellulose are soluble in alkaline media; so, they are more sensitive to caustic soda treatment than cellulose [59, 60]. The lignin content in rice husks can decrease by 96% when rice husks are treated with caustic soda concentrations between 4 and 8% [61].

The existence of silicon in both samples is confirmed by the bands close to 1030 cm<sup>-1</sup> and 796.51 cm<sup>-1</sup> of the spec-

TABLE 2: Main functional groups in rice husk treated with NaOH before adsorption.

Wave number (cm <sup>-1</sup> )	Vibration mode	Intensity	Functional group	Functional group name
3334.31	Tension	High	O-H	Hidroxyl
2917.91	Tension	Low	C-H	Saturated
1635.06	Tension	Low	C=C	Unsaturated
1027.09	Tension	Strong	C-O	Alcohol
1027.09	Tension	Strong	Si-O	Xiloxane

trum, which decrease slightly when the rice husk is treated with NaOH. The lower adsorption of silicon in the treated rice husk is due to leaching of the silicon by NaOH. Pretreatment with 2-4% w/v NaOH could reduce the ash content

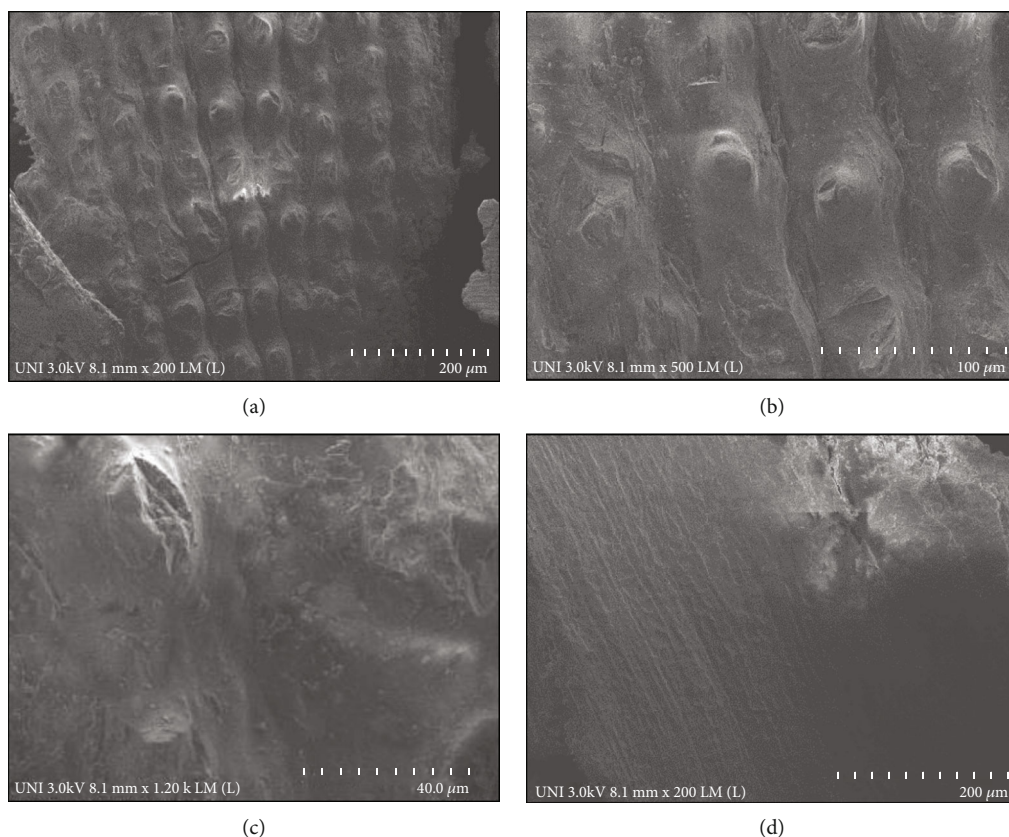
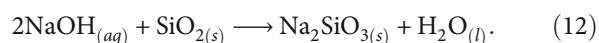


FIGURE 4: Scanning electron microscopy of the external and internal part of untreated rice husk: (a) external part ( $\times 200$ ), (b) external part ( $\times 500$ ), (c) external part ( $\times 1200$ ), and (d) internal part ( $\times 200$ ).

between 74 and 93% [1, 62], as (Eq. (12)) demonstrates [1, 63]. Sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) is soluble in water and washing with water removes it.



**3.2. SEM Analysis.** Figures 4(a) and 4(b) show the external part of the untreated rice husk. Convex cells with protrusions in the center are observed. These cells are separated by grooves in the longitudinal direction of the husk. The dimensions of these cells are approximately  $65 \times 50 \mu\text{m}$ . Figures 4(c) and 4(d) show the internal part of the shell, which do not present these convex cells but do present lines in the longitudinal direction.

Figure 5 shows the SEM micrographs results obtained for the NaOH-treated rice husk: Figures 5(a) and 5(b) show the external part. Greater imperfections, perforations, and protrusions are observed when compared to the untreated rice husk, in addition to the convex cells and the furrows that make up its surface. Perforations of the rice husk can also be observed in both figures indicating material leach which could originate or expose active sites in the treated rice husk [64], improving its ability to retain Cd. In Figures 5(c) and 5(d), longitudinal lines are observed, and there is not much variation compared to the internal part of the untreated sample.

**3.3. pH Effect.** The pH of the solution is one of the most important factors with a heavy impact in the adsorption process. It influences the ionization of functional groups of the sorbent and the chemistry of sorbate in the solution [65, 66]. The interactions between sorbent and sorbate depend on the pH of the solution [67].

Figure 6 shows the percentage of Cd removal at different pH values, using untreated rice husk (S1 and S2) and rice husk treated with caustic soda (S1-NaOH, S2-NaOH). In all cases, the increase in pH improves the percentage of removal. The highest removal percentages were obtained at a pH value of 7. The rice husk treated with caustic soda (S1-NaOH) shows a 32.4% better Cd removal compared to the untreated rice husk (S1). This happens because the alkaline treatment causes a greater exposure of the transference area. Rice husk treated with caustic soda (S2-NaOH) showed an improvement in Cd removal of 33.4% in comparison to untreated rice husk (S2).

The surface characteristics of an adsorbent determine the pH at which the net charge is zero. When the pH is less than the point of zero charge, the adsorbent is positively charged facilitating the adsorption of negatively charged species; however, when the pH is greater than the point of zero charge, the adsorbent becomes negatively charged, and adsorption of positively charged contaminants is favored. [65, 66].

The low values of adsorption capacity shown in the experimental results with pH values from 2.5 to 4 may be

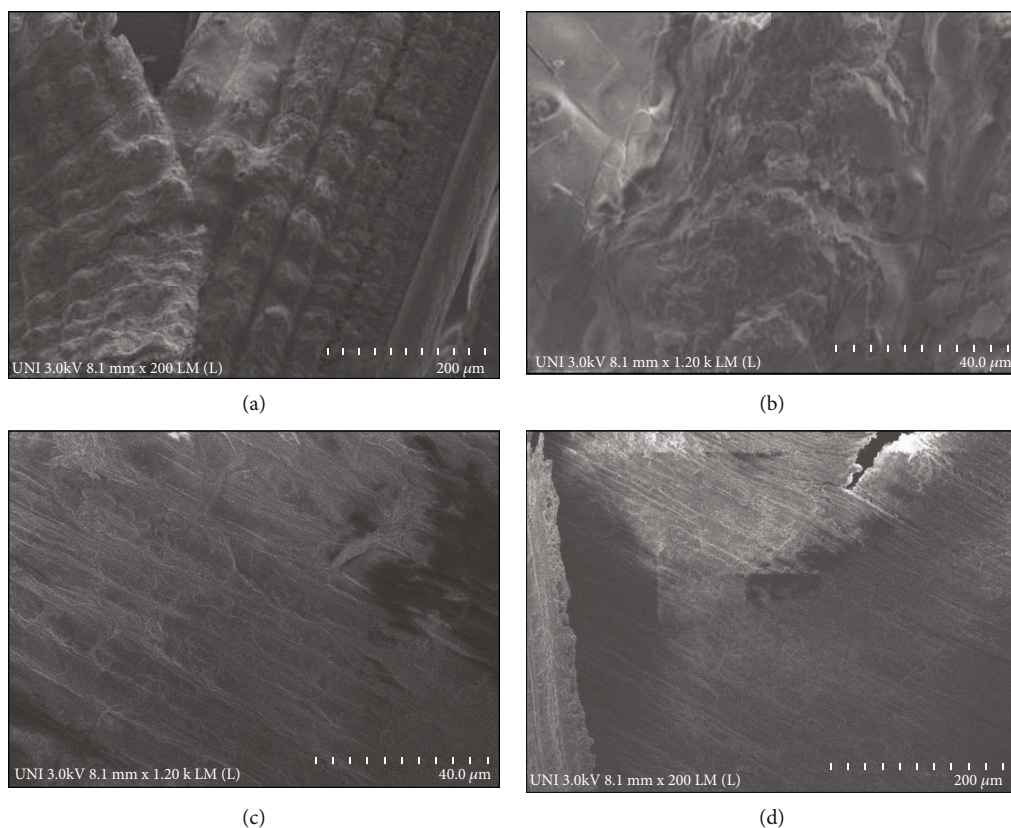


FIGURE 5: Scanning electron microscopy of rice husk treated with NaOH: (a) and (b) external part ( $\times 200$ ), (c) external part ( $\times 1200$ ), and (d) internal part ( $\times 200$ ).

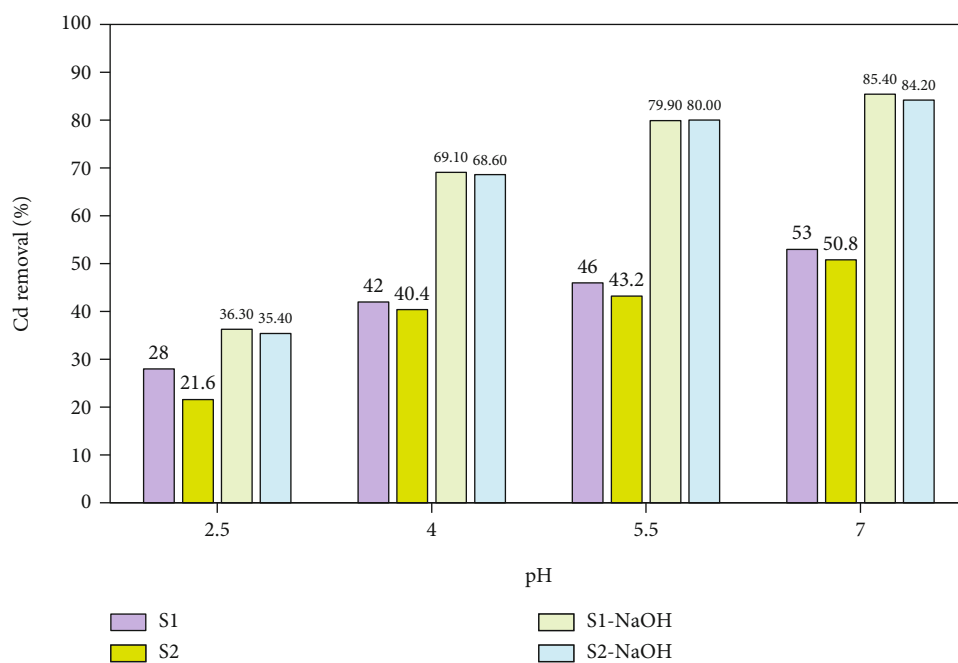


FIGURE 6: Cd removal percentage at different pH values, using 150 mg rice husk size S1:  $<212-425 \mu\text{m}>$  and 150 mg S2:  $<425-600 \mu\text{m}>$ , 20 mg/L of Cd (II).

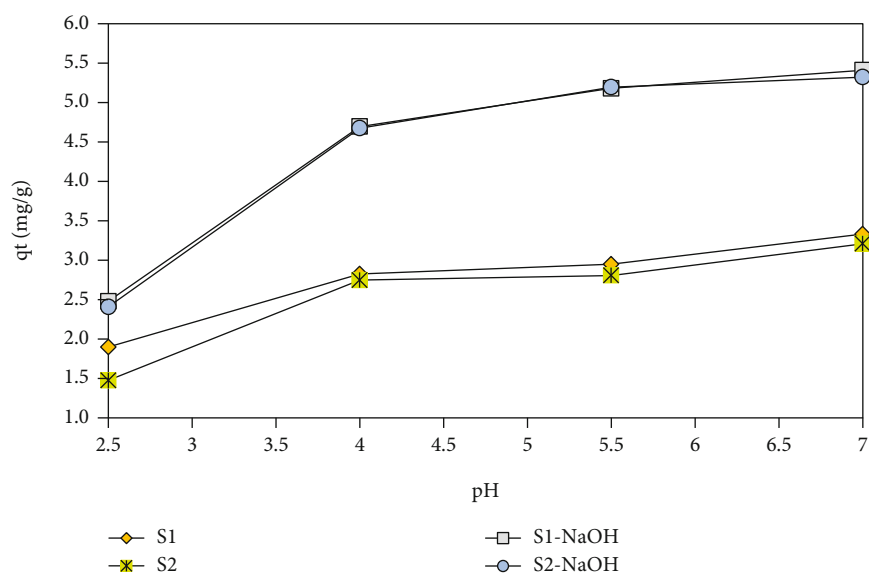


FIGURE 7: Cd adsorption capacity vs. pH using untreated and NaOH-treated samples of rice husk. (rice husk size S1: <212–425  $\mu\text{m}$ > and S2: <425–600  $\mu\text{m}$ >, 20 mg/L of Cd (II) using 150 mg of rice husk).

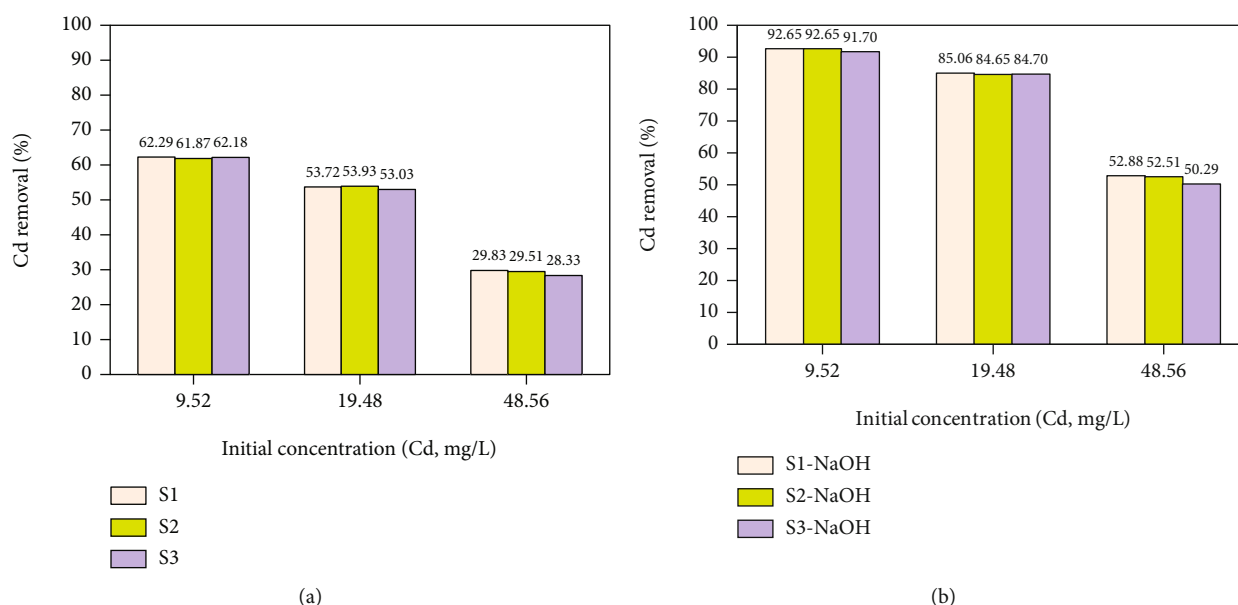


FIGURE 8: Effect of initial Cd concentration on removal percentage: (a) untreated rice husk and (b) NaOH-treated rice husk (pH = 7, adsorbent dosage = 150 mg, and rice husk size S1: <212–425  $\mu\text{m}$ >, S2: <425–600  $\mu\text{m}$ >, and S3: <600–850  $\mu\text{m}$ >).

due to the fact that the adsorbent is positively charged and to the competition that exists between the Cd (II) and the H<sup>+</sup> ions that predominate in the solution [68].

On the other hand, at higher pH values (5.5 to 7), the adsorbent would be negatively charged due to deprotonation of surface functional groups, promoting a better adsorption of positive Cd (II) ions.

Figure 7 shows the adsorption capacity of the untreated and NaOH-treated rice husk dependent on the pH. Increasing the pH has a positive effect on the adsorption capacity. The smaller untreated particles (S1) have slightly better

adsorption capacity than the coarser untreated particles (S2), due to the larger area of exposure by S1. The values at pH 7 were 3.33 and 3.21 mg/g, respectively. The particles (S1-NaOH and S2-NaOH) have practically the same adsorption capacity but higher than those without treatment. The greatest differences with respect to S1 and S2 were 2.08 mg/g and 2.11 mg/g at pH 7, respectively.

A similar behavior was observed in the investigation of [68] that used CaCO<sub>3</sub>/chitin hydrogel for Cd (II) adsorption, where the removal efficiency increased from 57% to 95%, when the pH increased from 3 to 7, respectively.



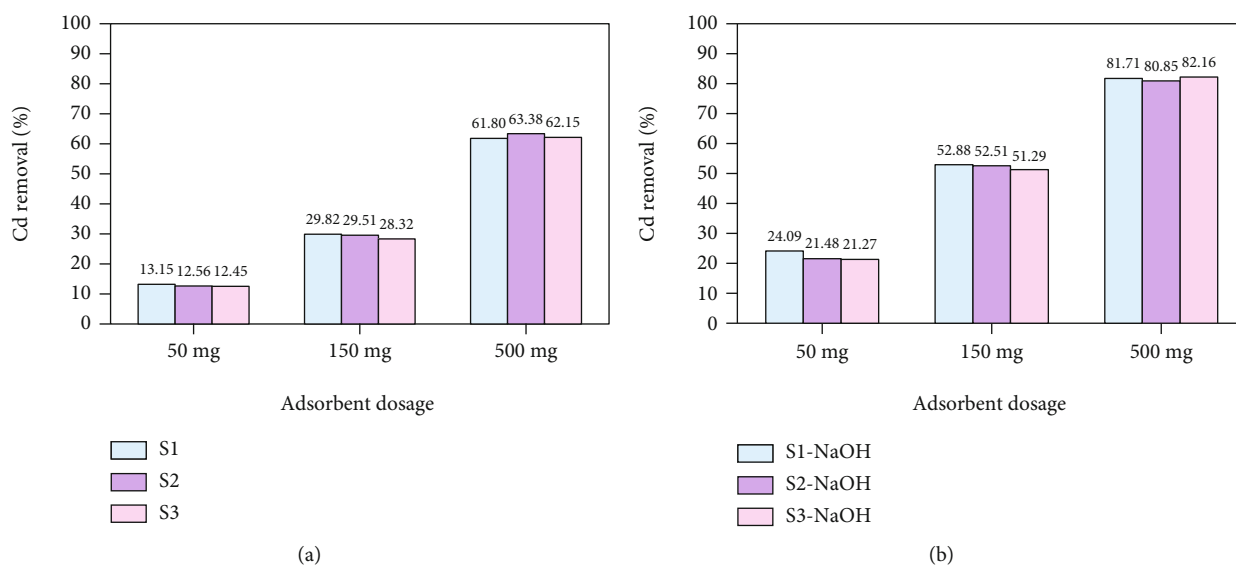


FIGURE 9: Adsorbent dosage effect on Cd removal with rice husk (a) untreated and (b) treated (pH = 7, cadmium initial concentration = 50 mg/L, and rice husk size S1: <212-425 μm >, S2: <425-600 μm >, and S3: <600-850 μm >).

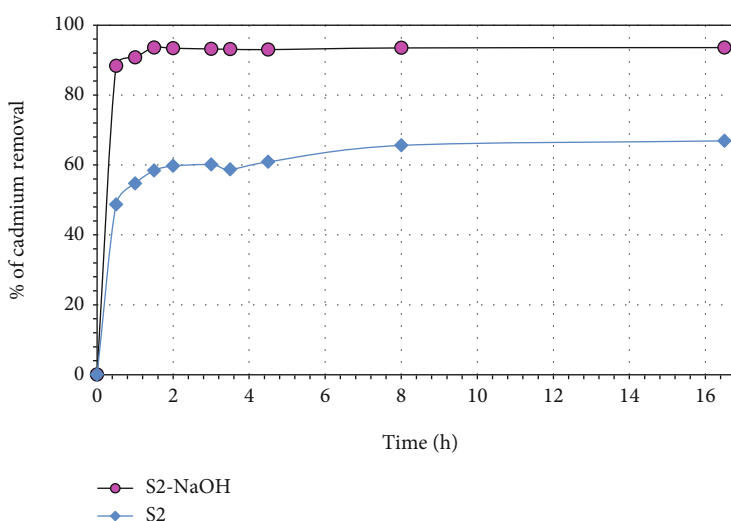


FIGURE 10: Percentage of cadmium removal by S2 and S2-NaOH (pH = 7, 10 mg/L of Cd (II), and 150 mg of biosorbent).

TABLE 3: Values of the pseudofirst and second order kinetic parameters.

Rice husk sample	Model						$q_e$ (mg/g)	
	$k_1$ (h <sup>-1</sup> )	KPFO $R^2$	SSE	$k_2$ (g/mg.h)	KPSO $R^2$	SSE	KPFO	KPSO
S2	2.85	0.97	0.41	2.356	0.992	0.38	2.22	2.357
S2-NaOH	1.45	0.72	0.53	10.007	0.999	1.43	3.21	3.22

3.4. Effect of Cadmium Initial Concentration. The initial concentration of the contaminant determines the amount of molecules present in the aqueous solution that are available to be adsorbed by the active sites of the adsorbent [66].

Figure 8 shows the effect of the initial concentration of Cd (9.52, 19.48, and 48.56 mg/L) at pH 7 on the removal percentage with the untreated (a) and treated (b) rice husk. For

S1, S2, and S3, the removal percentage decreases with increasing Cd concentration. For each concentration tested, the rice husk without treatment removes almost the same percentage regardless of the grain size, the average removal values are (62.11% ± 0.22), (53.56% ± 0.47), and (29.22% ± 0.79), respectively. For S1-NaOH, S2-NaOH, and S3-NaOH, the same behaviors occur, but with better

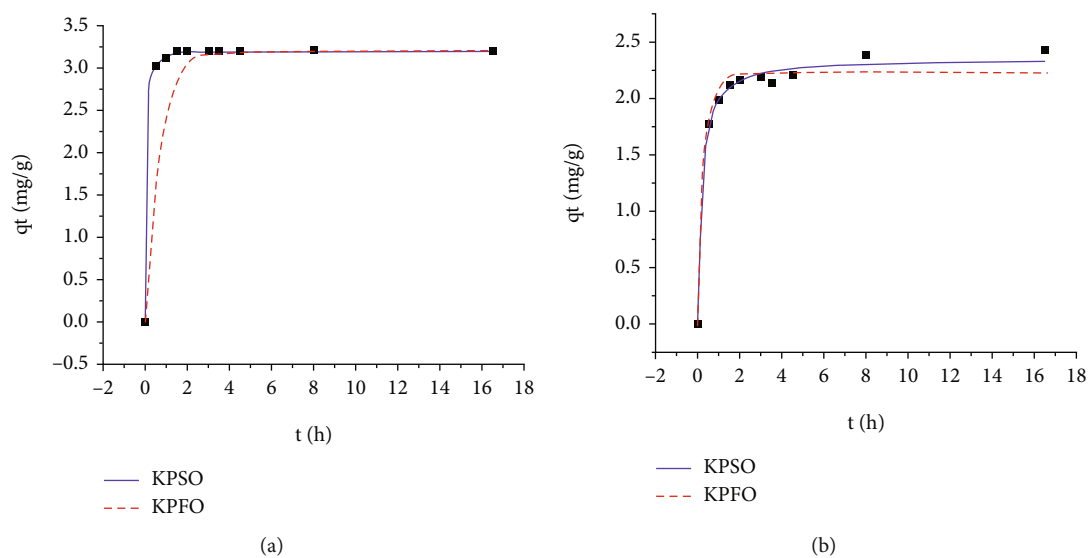


FIGURE 11: Adjustment of adsorption data to the kinetics models: (a) S2-NaOH and (b) S2 (pH = 7, 10 mg/L of Cd (II), and 150 mg of rice husk size S2: <425-600  $\mu\text{m}$  >).

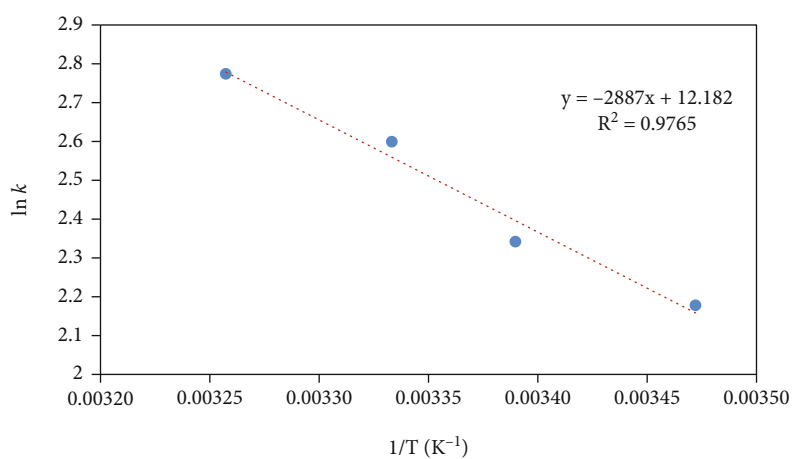


FIGURE 12: Variation of  $\ln(k)$  versus  $1/T$ .

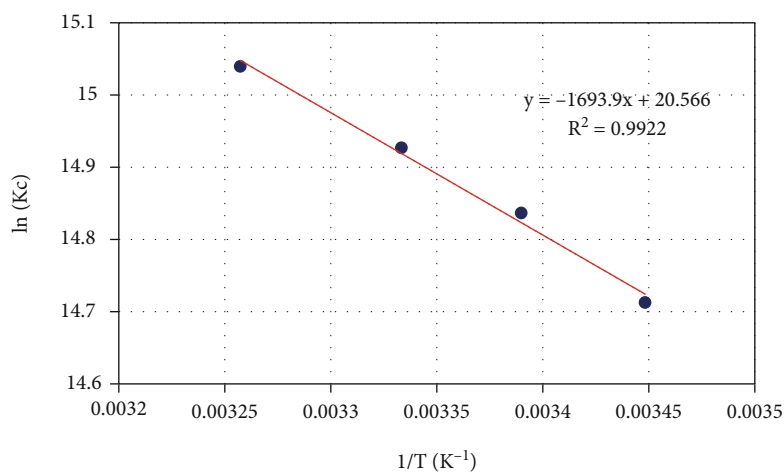


FIGURE 13: Thermodynamic plot for biosorption of Cd (II) on chemically modified rice husk.

TABLE 4: Thermodynamic parameters of adsorption process.

T (K)	ln Kc	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol.K)
290	14.71	-35.47	14.08	170.98
295	14.83	-36.39		
300	14.92	-37.23		
307	15.03	-38.37		

TABLE 5: Parameters of Langmuir and Freundlich adsorption isotherms.

Rise husk	Type of adsorbent	
	S2	S2-NaOH
Langmuir model		
$q_{\max}$ (mg/g)	5.13	11.06
$K_L$ (L/mg)	0.237	0.393
$R^2$	0.995	0.987
Freundlich model		
$K_F$	2.11	4.31
$n$	4.96	4.23
$R^2$	0.976	0.976
Hill model		
$Q_{\text{Hill}}$	5.09	12.72
$K_{\text{Hill}}$	4.58	2.54
$n_{\text{Hill}}$	1.06	0.66
$R^2$	0.982	0.988
Redlich-Peterson model		
$K_{\text{RP}}$	1.29	6.75
$a_{\text{RP}}$	0.27	0.91
$n_{\text{RP}}$	0.98	0.90
$R^2$	0.98	0.99
Temkin model		
$a_T$	0.81	1.80
$K_T$	6.73	7.93
$R^2$	0.94	0.98

removal responses, and the average values in this case were (92.33%  $\pm$  0.55), (84.80%  $\pm$  0.22), and (451.89%  $\pm$  1.40), respectively.

Figure 8 shows higher removal rates at lower initial concentrations; however, this rate decreases with increasing initial concentration because the saturation point has already been reached [68].

An increase in the initial concentration of the contaminant causes the active sites to be gradually occupied by Cd (II) ions until equilibrium is reached. Once equilibrium is reached, removal decreases due to the lack of available active sites.

A similar behavior was observed in the investigation of [69] that used cane bagasse as adsorbent, where the removal efficiency decreased from 40.11% to 30.96% when the concentration increased from 5 mg/L to 130.68 mg/L.

3.5. *Effect of Sorbent Dosage.* The increase in the amount of adsorbent has a significant contribution to the efficiency of contaminant removal, since it increases the availability of active sites for the adsorption of sorbate [67]. However, at a higher amount of adsorbent, the adsorption equilibrium is reached, and an excess of adsorbent would no longer affect the removal efficiency or would decrease it due to the interaction between the active sites of adsorbent [66].

Figure 9 shows the effect of the dosage of rice husk (a) untreated and (b) treated on the removal percentage of Cd. For S1, S2, and S3 in each dosage of the adsorbent, the removal percentages are very similar with each particle size. Cd removal increases with increasing dosage, and the mean values were (50 mg, 12.72%  $\pm$  0.38), (150 mg, 29.22%  $\pm$  0.79), and (500 mg, 62.44%  $\pm$  0.83), respectively. For S1-NaOH, S2-NaOH, and S3-NaOH, with the same dosages, there are better responses of the Cd removal percentages, with the same previous behavior, and the average values were (50 mg, 22.28%  $\pm$  1.57), (150 mg, 52.23%  $\pm$  0.83), and (500 mg, 81.57%  $\pm$  0.67).

Similar results were observed in the studies conducted by [46, 70], and the removal of heavy metals also improved with increasing adsorbent dosage.

Other studies report the opposite; that is, increasing the adsorbent dosage decreases the removal of heavy metals [71, 72]. Bozbas et al., [73] reported a drop in Pb (II) adsorption capacity from 70 mg/g to 20 mg/g when the amount of *Anadara inaequalis* shell adsorbent was increased from 2.5 mg to 10 mg.

The optimal experimental conditions achieved the maximum adsorption efficiency was 92.65%, which are pH = 7, (Cd (II))<sub>i</sub> = 10 mg/L, and 150 mg of adsorbent S2.

Efficiency could be improved if the adsorbent could adopt selective cadmium properties after additional chemical treatment. [74] modified a zeolite with 2 M NaCl, KCl, and CaCl<sub>2</sub> for 24 h, improving the adsorption efficiency of Cd (II). It is also important to highlight that chemically treated bioadsorbents like the one presented in this work are easier to produce than, for example, activated carbon which requires more complex processes to be created. The significant lower cost makes the present treatment a more promising alternative among economically effective adsorbent materials.

3.6. *Effect of Contact Time.* The rate at which cadmium is removed by adsorption by both raw rice husk and treated rice husk is an important parameter to design a continuous or batch system; therefore, it is important to determine the way adsorption depends on time as a variable.

Figure 10 shows that the equilibrium time of adsorption is reached in 8 h and 2 h for the untreated rice husk and treated rice husk, respectively. Cadmium adsorption by S2-NaOH occurs in two stages, a rapid initial stage where 88% cadmium adsorption occurs in the first 0.5 h followed by a second stage with slow adsorption up to 93.59% up to the end time of the experiment of 16 h. Therefore, the time of 0.5 h was considered as the optimal adsorption time, and these results are consistent with the removal of other divalent cations that use plant residues as adsorbents [75].

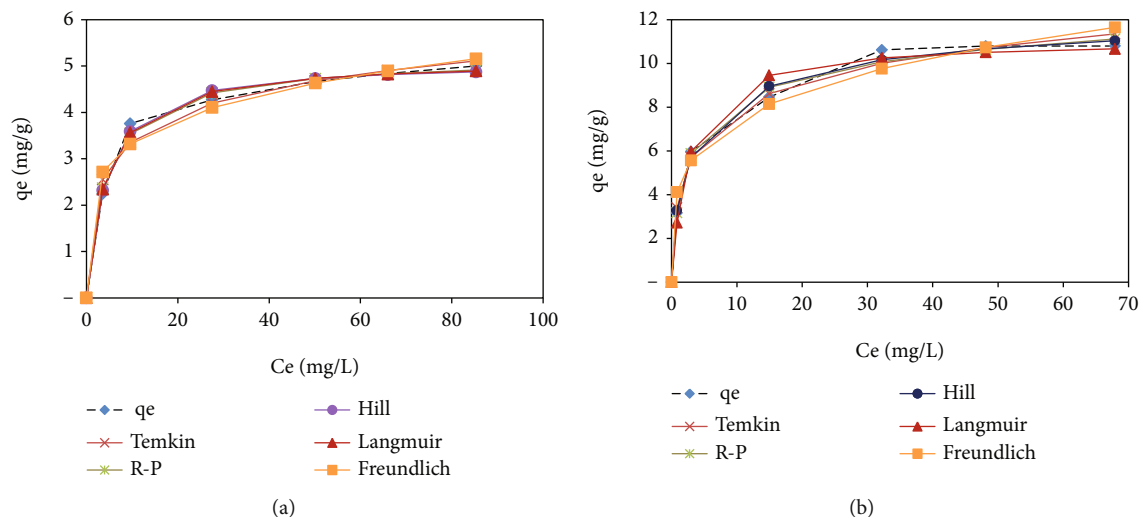


FIGURE 14: Behavior of the Langmuir, Freundlich, Hill, Rendlich-Peterson and Temkin adsorption isotherm models with respect to the experimental data: (a) untreated rice husk and (b) treated rice husk. (pH =7, rice husk size S2: <math> <425 - 600 \mu\text{m}> </math> and 150 mg of biosorbent).

TABLE 6: Comparison of maximum adsorption capacity of other adsorbents with chemically modified rice husk.

Adsorbent	$q_{\max}$ (mg/g)	References
Treated rice husk	11.06	Present work
Rice husk	5.13	Present work
Lignin/chitin film	0.28	[68])
Olive cake	10.5	[83])
Hazelnut shell	5.42	[84])
Almond shell	3.18	[84])
Crab shell	3.43	[85])
<i>Corbicula fluminea</i> shell	4.03	[85])
Oyster shell	3.42	[86])
Chemically modified wheat straw	3.83	[65])
Black gram husk	38.76	[65])
Lentil husk	107.31	[65])
Areca waste	1.32	[66])
<i>L. Cylindrica</i>	6.71	[66])
Deoiled palm kernel waste	1.09	[87])

The kinetics of metal adsorption generally consists of a fast step where the largest amount of metal is adsorbed, followed by a slow step until equilibrium is reached. In this first stage, the metal could be removed by physical adsorption or exchange of metal ions with the counter ions present on biosorbent and occurs very quickly due to the availability of active sites, however, subsequently, the low availability of active sites results in a slower adsorption, till it reaches equilibrium where degradation stays constant with time [65].

Figure 10 shows treating rice husk with caustic soda improves Cd removal by 26.69%. The effect of contact time on the remaining cadmium concentration and its removal efficiency for the raw and treated rice husk after 16.5 hours was 3.61 mg/L and 0.66 mg/L with a removal efficiency of 66.90% and 93.59%, respectively.

3.7. Kinetic Analysis. The data obtained from the Cd adsorption experiments with the biosorbents S2 and S2-NaOH were analyzed with Eq. (3) and Eq. (4). for the pseudofirst order and pseudosecond order kinetic rates, respectively. Table 3 shows the parameter values of the pseudofirst order (KPFO) and pseudosecond order (KSFO) kinetic models. The second order kinetic model has the best coefficients of determination for S2 ( $R^2 = 0.992$ ) and S2-NaOH ( $R^2 = 0.999$ ).

The behavior of adsorption capacity follows a pseudo-second order kinetic model, when using untreated rice husk (Figure 11(a)), as well as when using treated rice husk (Figure 11(b)). It supports the assumption that the rate-limiting step of cadmium adsorption on rice husk may be chemical sorption or chemisorption. In chemisorption, the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface [76]. The pseudosecond order kinetic analysis reveals that initial adsorption rate values of ( $h$ ) increase with an increase of initial cadmium concentration, but rate constant ( $k$ ) decreases with an increase in initial cadmium concentration. The reason for this behavior can be attributed to the lower competition for sorption surface sites at lower pollutant concentration. At higher concentrations, the competition for active surface sites is high and; consequently, lower sorption rates are obtained [77].

This means that the taxa of occupation of the active sites is proportional to the square of the unoccupied sites; therefore, it can be assumed that a 1:2 binding stoichiometry is applicable to the adsorption process, where a divalent metal binds to two monovalent active sites [52, 75].

3.7.1. Apparent Activation Energy. The apparent activation energy of the adsorption process was calculated using the Arrhenius equation as observed in Figure 12.

TABLE 7: Comparison of maximum adsorption capacity of several treated rice husks from different geographical regions and variable experimental conditions.

NaOH concentration	Time of treatment (h)	Drying time (h)	Drying temperature (°C)	$q_{\max}$ (mg/g)	Rice husk origin	References
0.5 M	4		40°C	20	India (Asia)	[39]
0.1 M	24	24	80°C	1.58	China (Asia)	[40]
0.013 M	4		45°C	8.5	Malaysia (Asia)	[37]
2%	4	24	60°C		Malaysia (Asia)	[41]
0.1 M	1	48	80°C	2.8	China (Asia)	[38]
(1:1)			50°C	16	Malaysia (Asia)	[42]
0.3 M	17	6	70°C	11.06	Perú (South America)	Present work

Figure 12 shows the correlated experimental data in the linearized Arrhenius equation. From Figure 12, the activation energy  $E_a$  calculated was 24 kJ/mol, and this value is regarding to physical adsorption, where the cadmium molecules are adsorbed by weak bonds similar to Van der Waals forces. A normal range for typical physical adsorption is between 8 and 40 kJ/mol [78].

**3.8. Thermodynamic of the Process.** In order to understand the thermodynamic of the process of cadmium removal by adsorption with treated rice husk, some thermodynamic parameters were determined. The temperatures studied were 17°C, 22°C, 27°C, and 34°C, and the parameters calculated were standard Gibbs free energy variation ( $\Delta G^\circ$ ), standard enthalpy variation ( $\Delta H^\circ$ ), and standard entropy variation ( $\Delta S^\circ$ ). The standard free energy variation in the adsorption process is related to the equilibrium constant.

The variations in standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) were calculated according to the van't Hoff equation, plotting  $\ln K_c$  versus  $1/T$  (Figure 13), to obtain the parameters presented in Table 4.

It is a common mistake to use the isotherm adsorption constant in van't Hoff equation, but this constant is not dimensionless. For the present work, Langmuir isotherm represents the best fit, and the Langmuir constant  $K_L$  is given in L/mg, and the  $K_C$  could be easily obtained as a dimensionless parameter according to equation (13) [79].

$$K_C = 55.51 * K_L * 1000 * \text{molecular weight of adsorbate} \quad (13)$$

From Table 4, it can be observed that when the temperature of the adsorption process increases from 290 K, 295 K, 300 K, to 307 K, the  $\Delta G^\circ$  values become increasingly negative varying from -35.47 kJ/mol, -36.39 kJ/mol, -37.23 kJ/mol, to -38.37 kJ/mol, respectively. That means the process is spontaneous at all temperatures due to the negative value of  $\Delta G^\circ$ . Likewise, as the temperature increases, the Cd (II) ion has higher affinity to be adsorbed by treated rice husk. The  $\Delta G^\circ$  for physical sorption is between -20 kJ/mol and 0 kJ/mol and is ranged from -80 kJ/mol to -400 kJ/mol for chemical sorption [80]. The values of  $\Delta G^\circ$  presented in Table 4 indicate that the sorption process is controlled by physical adsorption for all temperatures. The adsorption

enthalpy is also a parameter used to indicate the intensity of the interaction between the adsorbate and the adsorbent. In the phenomenon of physisorption, this parameter has low values (lower 40 kJ/mol) since it is characterized by a low degree of interaction, being the forces involved of the order of magnitude of van der Waals forces [81].

The  $\Delta H^\circ$  calculated in this work was 14.08 kJ/mol, indicating that the sorption process is controlled by physical adsorption. For other site, positive value of  $\Delta S^\circ$  (170.98 J/mol.K) indicates that the degrees of freedom increase at the solid-liquid interface during the adsorption of cadmium onto treated rice husk.

**3.9. Equilibrium Adsorption.** Adsorption isotherms are important because they help to understand the interactions between the adsorbate and the active sites present on the surface of the adsorbent. Table 5 shows the parameter values of the Langmuir, Freundlich, Hill, Redlich-Peterson, and Temkin adsorption isotherms. The coefficient of determination  $R^2$  of the Langmuir model for both untreated (S2) and treated (S2-NaOH) rice husk samples are higher than those of the Freundlich model. This indicates that the Langmuir model better represents the adsorption mechanism in both cases.

Figure 14 shows the behavior of the Langmuir, Freundlich, Hill, Redlich-Peterson, and Temkin adsorption isotherms: (a) with untreated rice husk and (b) with treated rice husk. The Langmuir model has a better fit in both cases to the experimental data than the Freundlich model. The  $R_L$  separation factors were 0.31 and 0.19 for S2 and S2-NaOH, respectively.

Langmuir's model assumes that the adsorbent has a limited number of adsorption sites, and that the adsorption energies are the same and there are no interactions between molecules [82].

Table 6 presents the adsorption capacities of several biosorbents compared with chemically treated rice husk. The comparison shows the potential of treated rice husk to be used as efficient sorbent to remove Cd<sup>2+</sup> from aqueous medium.

Table 7 shows a comparison of biosorbents obtained from the treatment of rice husk with NaOH solutions at different concentrations. The biosorbent synthesized with rice husk from South America and with relatively low addition of NaOH reached an interesting  $q_{\max}$  (11.06 mg/g) in relation to the other biosorbents. [39, 42] obtained higher values

of  $q_{\max}$ ; however, they used a higher concentration of NaOH during the treatment of their biosorbents, which could have increased the number of active sites on the biosorbent.

#### 4. Conclusions

This work studied the improvements in the adsorption characteristics, when the raw material rice husk from South America is treated by a simple chemical modification process with NaOH; in addition, it compares the adsorption capacity of biosorbent with other treated rice husks from other world regions that cultivate different species of rice husk in other geographical conditions.

The results of SEM and FTIR analysis showed that the rice husk treated with NaOH has a good surface area and greater exposure of its functional groups; therefore, its removal percentages and capacities of sorption of Cd (II) are higher than the untreated rice husk. For the three particle sizes, increasing the initial cadmium concentration from 10 to 50 mg/L reduces the percentage of cadmium removal for both untreated (62 to 29%) and treated (92 to 52%). Similarly, increasing the dosage from 50 to 500 mg increases the percentage of cadmium removal for both untreated (13 to 62%) and treated (22 to 82%) rice husks. The increase in pH improves the adsorption capacity of the untreated and treated rice husk, and the best response was given at pH 7 with the treated rice husk. The experimental adsorption capacities of the untreated and treated rice husks are well adjusted with the Langmuir adsorption isotherm, as well as by the pseudosecond order kinetic model. The nature of the adsorption process is endothermic and occurs in spontaneous form, being de maximum adsorption capacity of 11.06 mg/g for chemically modified rice husk.

The results mentioned above confirm the rice husk chemically modified as a good alternative to removal of metals in an aqueous medium with good efficiency and low cost.

#### Data Availability

The experimental data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare no conflict of interest, financial, or otherwise.

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