



Biosorption of Cobalt(II) Ions from Aqueous Solution using Rice Straw and its Modification

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Abstract Biosorption of Co(II) ions onto rice straw (RS) and activated rice straw (NaC-RS) is investigated over pH range (1–7) via batch adsorption technique. The chemical activation of rice straw with 0.1M Na₂CO₃ at 301 K enhanced the removal efficiency of RS and NaC-RS (71.7 % and 73.3 %) before and after treatment, respectively at 28 °C. The chemical and morphological structures of adsorbents were investigated by scanning electron microscopy (SEM), energy Dispersive Analysis of X-rays (EDAX), element analyzer and Fourier-Transform Infrared spectroscopy (FTIR). The study also investigated the effects of process parameters such as initial Co (II) concentration, solution pH, dosage and temperature. Langmuir and Freundlich adsorption isotherms were applicable to the adsorption process and defined very well the Langmuir isotherm model. The good correlation coefficient was obtained from pseudo second-order kinetic model, which agreed with conception as the rate-limiting mechanism. The numerical values of thermodynamic parameters indicated the endothermic nature, spontaneity and feasibility of the sorption process.

Keywords Adsorption, Co(II), Rice Straw, Kinetic, Thermodynamic

1. Introduction

Various industries use processes that include a finishing treatment consisting of metal compounds. These heavy metals can cause contamination in the discharged water. For example, the effluents from electroplating industries contain various types of toxic substances, such as cleaning agents, heavy metals and solvents. Among them, metals such as copper, cobalt, nickel and chromium are harmful if they are discharged without treatment [1].

Environmental contamination by toxic heavy metals is becoming a serious dilemma now days due to their incremental accumulation in the soil, plants and water bodies [2–4]. Heavy metals are predictably the elements with atomic number >20 and have metallic properties, such as conductivity, ductility, stability as cations, and ligand specificity, etc. [5]. Toxic metal ions form compounds that can be toxic, carcinogenic or mutagenic even in low quantities [6] and due to their mobility in natural water ecosystems, they are prioritized as major inorganic contaminants of the environment [7].

The methods currently used for removal of heavy metals are focused on a given innovative physico-chemical removal processes such as; solvent extraction [8], electroflotation [9], membrane separation [10], reverse osmosis [11], chemical precipitation [12], photocatalysis [13], electro dialysis [14], ion-exchange [15] and adsorption [16-17], which are expensive and can result in the generation of toxic sludge that is another serious problem.

Millions of tons of rice straws (RS) are burnt annually in Egypt through wildfires, post-harvest burning of cultivation fields, and domestic uses for cooking and heating. However, biomass burning is an important source of aerosol particles which may affect local and regional air quality [18], and also contribute to global climate changes. Many ideas have been suggested for valorising RS as pulp and paper [19]; construction materials [20]



compost [21]; fuel [22]; production of chemicals such as ethanol [23] bio-adsorbents [24]; and precursors for activated carbons [25]. Nevertheless, since other more competitive resources are already available, the use of RS for the aforementioned purposes is still minor. Yet the applications of RS are limited due to its high silica content; its potential use as food for cattle is restricted (< 2 % of bodyweight) by its low digestibility. Activation of rice straw (NaC-RS) is a material of major industrial importance due to its well developed pore structure and excellent related adsorption properties.

2. Materials and Methods

2.1. Preparation of adsorbent

The natural Rice Straw (RS) used in the present experiments was obtained from a market in Menoufia Country, Egypt. The (RS) was thoroughly washed with a stream of distilled water to remove all dirt and then was dried at 110 °C. The dried (RS) were stored in desiccators until used. The Modified Rice Straw (NaC-RS) sample was prepared by alkali treatment. Alkali treatment was carried out by placing the RS sample in contact with Na₂CO₃ (0.1 M), with constant stirring for 24 h. The liquid/solid ratio was 10 ml/g. It was then filtered, washed OH⁻ free with distilled water, and dried at 110 °C for 24 h to constant weight. And it was ground and sieved. The particles 0.63 mm was selected and preserved at room temperature in a sealed bottle.

2.2. Preparation of metal-solutions

The Co (II) stock solution containing 1000 mg/L was prepared by dissolving cobalt chloride (analytical reagent grade) in distilled water. Cobalt working solutions in different concentrations was prepared by diluting the Co (II) stock solution with distilled water.

2.3. Analytical technique

The concentrations of the Co (II) metal ions were performed using Flame Atomic Absorption Spectrophotometer (FAAS) Vario 6. Elements were determined using an air– acetylene flame.

3. Results and Discussion

3.1. Characterization of Adsorbents

3.1.1. Chemical composition

The chemical composition of the rice straw was determined at each stage of treatment and the data are summarized in Table 1.

Table 1: Chemical Characterization of RS and NaC-RS

No.	Chemical Characterization	Samples	
		RS	NaC-RS
1	Moisture Content %	7	6.50
2	Ash Content %	6	8.2
3	Lignin Content %	12.5	15.1
4	Holocellulose %	75.5	85.6
5	Alpha Cellulose	56	60.4

3.1.2. Spectroscopic analysis (FTIR)

The FT-IR technique is an important tool to identify some characteristic functional groups, which are capable of adsorbing metal ions. The FTIR spectra of RS and NaC-RS are presented in Fig. 1(a,b). As shown in the figure, after alkali modification of RS, a large decrease in the intensity of some absorption bands were occurred, which indicates a change in the functionality of the raw material. The band at ≈ 3425 cm⁻¹ is common to both spectra and is assigned to O–H stretching vibration. The bands at ≈ 2993 and 2894 cm⁻¹ are attributed to C–H stretching vibration. The decreased intensity of these bands in NaC-RS spectrum indicates that hydrogen was broadly removed during the modification process.

The bands at ≈ 1640 cm⁻¹ are assigned to C=O axial deformation of aldehyde, lactone, ketone, and carboxyl groups [26]. The remained absorption peak at these bands for NaC-RS is an indication of the presence of a carboxylic acid group. This means that there are still carboxylic groups or C=O groups which are not reacted by



NaOH solution. The peaks associated with the stretching in aromatic rings were verified at $\approx 1519\text{ cm}^{-1}$ while deformations related to C–H and C–O bonds were observed from $\approx 1050\text{ cm}^{-1}$.

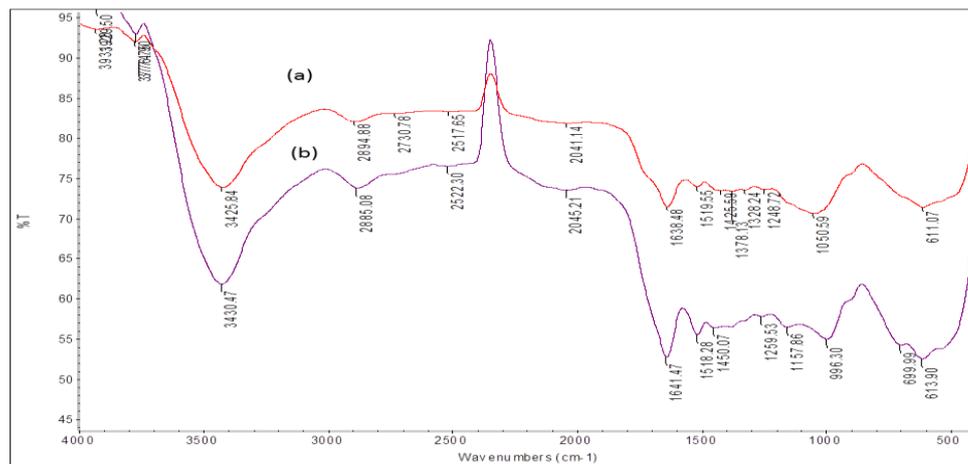


Figure 1: (a,b) FTIR spectra for RS (a) and (b) NaC-RS.

3.1.3. The SEM micrographs and EDX analysis

The surface morphology of Egyptian raw rice straw is shown in Fig. 2(a,b). The SEM image shows the physical features of the fiber structure. It can be seen in the SEM image that the raw rice straw has cracks in its surface, mostly irregular in shape and roughly with hollow cavities of porous structure, which can be used for entrapping ions of heavy metals. This crack and porosity come from the oven heating effect after washing [27]. EDX analysis was done to determine elemental composition of the raw rice straw. Fig. 2(c,d), indicates the presence of major constituents – carbon and oxygen in the two samples adsorbents.

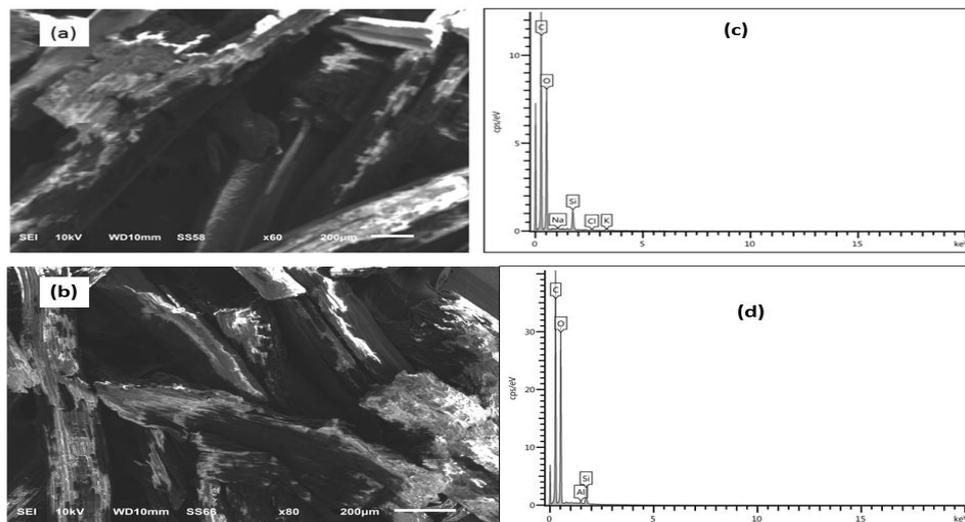


Figure 2: SEM image for (a) RS and (b) NaC-RS - EDX for (c) RS and (d) NaC-RS

3.1.4. X-ray diffraction (XRD)

Crystallinity of the raw rice straw is shown in Fig. 3 (a). The XRD pattern shows a typical spectrum of cellulosic crystalline material, having main and secondary peaks at $2\theta = 16$ and 21.6 respectively. The main peak is taken as indicative of highly organized crystalline cellulose, while the secondary rather weak peak is a measure of a less organized polysaccharide structure and assigned to broad peak with low angle. This low angle indicated that presence of mesoporous structure. This refers to that the particles are ordered in the preferred orientation to give very thin peaks beside each other because of instrumental resolution the peak as seemed with this shape [28].

Diffraction peaks corresponding to fine crystallinity were observed as a result of carboxylic groups in NaC-RS, whereas, amorphous form may be slightly is identified in the biosorbent as in Fig. 3 (b). The fine crystalline



nature of the biosorbents suggested that the metal ion could more easily penetrate into the surface of the biosorbent. Optimization of Co (II) biosorption by chemically modified rice straw [29].

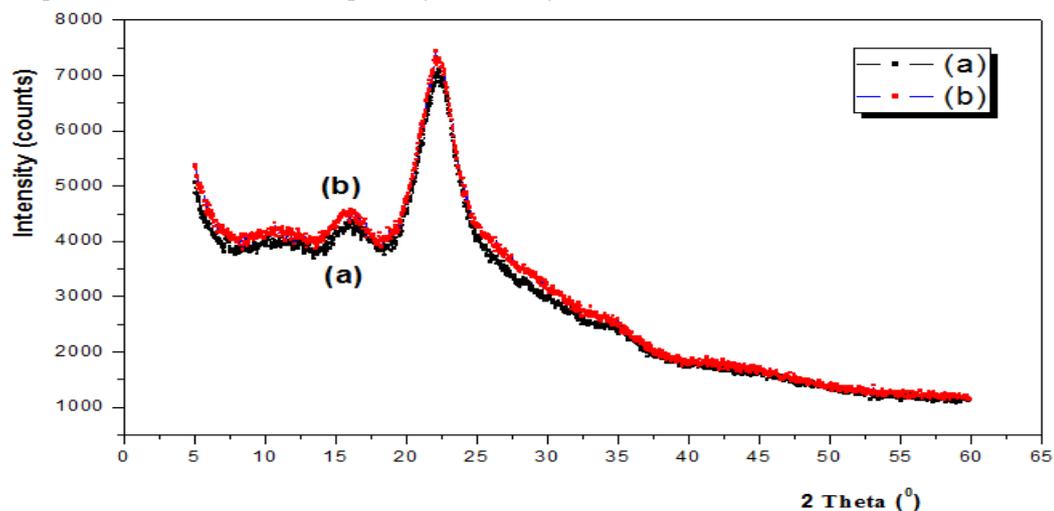


Figure 3: XRD for (a) RS and (b) NaC-RS

3.2. Effect of the adsorbent dose on the adsorption of the metal ion

The removal of cobalt as a function of the adsorbent dosage using RS in aqueous solution shows in Fig 4. The adsorbent dosage varied from 0.1 to 1.0 g and equilibrated for ≈ 5.5 h. Fig. 4 also shows that increasing the NaC-RS dose increases the percent removal (R%) but decreases the adsorption capacity of cobalt, i.e., increasing the adsorbent dosage increases the percent removal (R%) from 50 ml solution containing 353.58 mg/l of Co (II) and attained maximum removal at a particular NaC-RS dose (0.8g) and after which (1g) there is a decrease in the removal cobalt percent. Based on the results obtained, a minimum adsorbent dosage of 0.8 g/50ml) was required for Co (II).

As There are many factors, which can contribute to this adsorbent dose effect: (i) as the dosage of the adsorbent is increased, the adsorption sites were increased, but at a higher dose the adsorption sites remained unsaturated during the adsorption reaction leading to drop in adsorption capacity (q_e) [30]; (ii) One plausible reason could be due to overlap of active sites at higher adsorbent doses resulting in a reduced effective surface area required for adsorption [31].

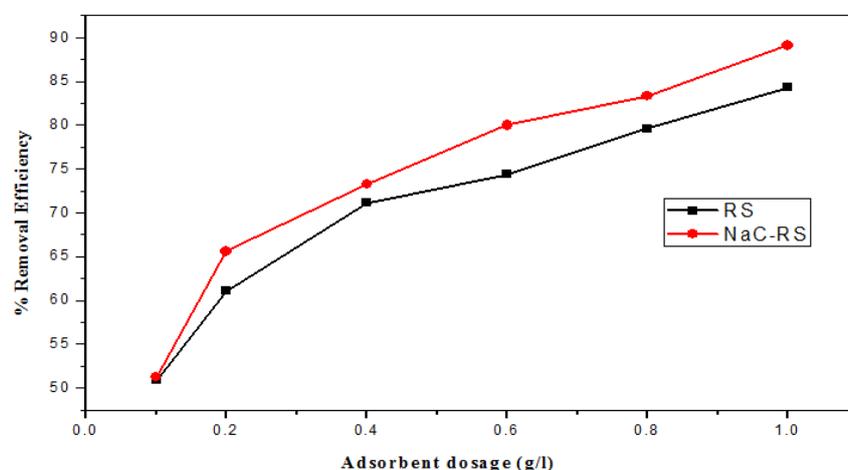


Figure 4: The Effect of adsorbent dosage on biosorption of Co(II) by RS and NaC-RS



3.3. Effect of the initial concentration of the metal ion

The Co (II) adsorption by RS capacity increased with the Co (II) equilibrium concentration increasing from 235.72 to 825.05 mg/L. This capacity of the RS was 23.1, 31.7, 34.7, 40.05, 43.5 and 46.1 mg/g, respectively. On the other hand, we can observe that, with an increase of the Co (II) equilibrium concentration, the removal percentage of cobalt, show an opposite trend. The results of the Co (II) adsorption isotherm experiments are shown in Fig. 5 (a).

However, the increase in cobalt concentration beyond about 707.16 mg/l causes little increase in the amount of cobalt adsorbed indicating that the adsorption sites are almost saturated Fig. 5 (b). Also, the percentage adsorption of Co (II) decreases with increasing initial concentration of Co (II). The percentage is high (> 90.3), but the adsorbed amount is an appreciable value (26.6 mg/g). This suggests that NaC-RS can remove $\approx 90.3\%$ Co (II) from water if its concentration below 235.72 mg/l.

Actually, as the initial concentrations of Co (II) increased, the driving force became higher as well, the accessibility of the heavy metal ions to the binding sites of the RS is relatively high with increased initial concentration, the ion exchange frequently and the uptake of heavy metals becomes more and more [32].

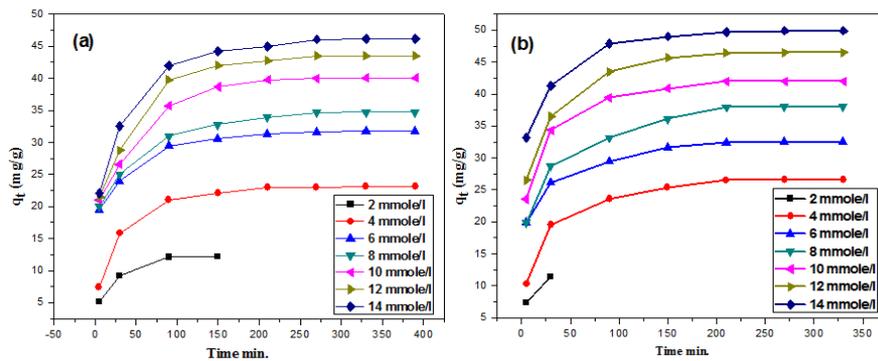


Figure 5: Effect of initial metal ion concentration on the adsorption uptake of Co(II) by (a) RS and (b) NaC-RS

3.4. Effect of the solution pH on the adsorption of the metal ion

Particle size of 0.63 mm, 0.4 g of sorbent dose and pH6.3 showed maximum performance for both RS and NaC-RS, so these were selected as optimized conditions for sorption process. The study of pH has pronounced effects on sorption, so it was studied over the range 1.8–7.1 at prior mentioned conditions. The removal efficiency of sorbent increased with the increase in pH up to 6.3, further increase of pH decreased the sorption as depicted in fig. 6 (a,b).

Less sorption at low pH may be attributed to the presence of H^+ and H_3O^+ ions in the solution, which compete with the metal ions and thus hinders their approach to protonated binding sites of the sorbent surface. The increase in sorption with an increase of pH (up to pH 6.3) may result owing to more electrostatic interactions between the negatively charged binding sites available on the NaC-RS surface more than RS and the metal cationic species, which thus decrease the stability of metal ions in the solution [33, 34].

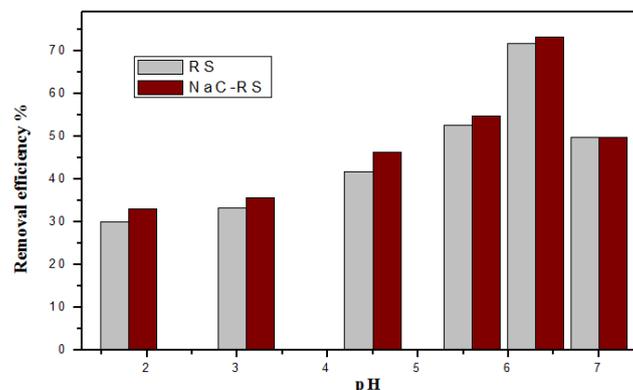


Figure 6: The effect of pH on biosorption of Co(II) by (a) RS and (b) NaC-RS at 28 °C



3.5. Adsorption isotherm models

In addition to the experimental data, the linearized forms of Langmuir[35] and Freundlich[36] using Eqs. (1) and (2) are compared.

Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \ln C_e \dots\dots\dots 1$$

where K_F (mg g^{-1}) and n are isotherm constants indicate the capacity and intensity of the adsorption, respectively.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \dots\dots\dots 2$$

Where C_e is the equilibrium concentration of adsorbate (mg L^{-1}), q_e is the amount of soluted sorbate at equilibrium (mmol g^{-1}), K_L is the Langmuir adsorption constant (L mmol^{-1}) and Q_{max} is the theoretical maximum adsorption capacity (mg g^{-1}). For the Langmuir isotherm model, a dimensionless constant (R_L), commonly known as separation factor or equilibrium parameter can be used to describe the favorability of adsorption on the polymer surface by:

$$R_L = \frac{1}{1 + K_L C_0} \dots\dots\dots 3$$

Where C_0 is the initial metal ions concentration and K_L is the Langmuir equilibrium constant. The isotherm constants and corresponding correlation coefficients for the biosorption of Co^{+2} is presented in Table 1. The correlation coefficients demonstrate that Langmuir and Freundlich models adequately fitted the data for three metal ions adsorption. However, the coefficient of determination (R^2) values is higher in the Langmuir model for cobalt adsorption when compared to Freundlich in both RS and NaC-RS.

Table 1: Adsorption isotherm parameters for (6 mmol/L) of Co(II) on RS and NaC-RS in aqueous solution

Rice Straw	Langmuir parameters				Freundlich parameters		
	Q_0 (mg/g)	B (L/mg)	R_L	R^2	n	K_f (mg/g)	R^2
RS	28.5	0.009	0.24	0.99240	4.7	86.1	0.92857
NaC-RS	29.4	0.109	0.025	0.99592	4.96	81.6	0.91343

3.6. Kinetic Modeling

The experimental data obtained were used to set up adsorption kinetic models. The kinetic parameters for RS and NaC-RS were calculated by pseudo-first-order [37] and pseudo-second-order kinetic equations [38]. The equations were expressed as following:

The pseudo-first-order kinetic equation

$$\log(q_e - q_t) = \log q_{e,1,cal} - k_1 t \dots\dots\dots 4$$

where q_e and q_t are the amount of metal sorbed per unit weight of sorbent at equilibrium and at any time t , respectively (mg g^{-1}) and k_1 is the rate constant of pseudo-first order sorption (min^{-1}).

The pseudo-second order equation

$$\frac{t}{q} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_{e,2}} t \dots\dots\dots 5$$

Where k_2 is the rate constant of pseudo-second order sorption ($\text{gm mmol}^{-1} \text{min}^{-1}$), q_e is the amount of soluted sorbate at equilibrium (mmol/g) and q_t is the amount of soluted sorbate on the surface of the resin at any time t (mmol/g).

$$h = k_2 q_{e,2}^2 \dots\dots\dots 6$$

where h ($\text{mmol g}^{-1} \text{min}^{-1}$) means the initial adsorption rate, and the constants can be determined experimentally by plotting of t/q against t .

Intra-particle diffusion model

The initial rate of the intraparticle diffusion is the following:



$$q_t = K_i t^{0.5} + C \dots\dots\dots 7$$

Where K_i is the intraparticle diffusion rate coefficient ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C (mmol g^{-1}) provides an idea about the thickness of the boundary layer. The K_i and C can be obtained from the slope and intercept of a straight line plot of q_t versus $t^{0.5}$.

For Fickian diffusion law, all the correlation coefficients were relatively low and the intercept of plots revealed obvious boundary layer effect [39].

It can be seen from data in (Table 2) that the pseudo-second-order kinetic model provides a good correlation for the adsorption of Co (II) on the RS and NaC-RS at 313 and 323K. The high applicability of the pseudo-second-order equation for the present kinetic data at all temperatures (301, 313 and 323k) is generally in agreement with other researchers' results that the pseudo-second-order equation was able to describe properly the kinetics of Co (II) adsorption [40]

Table 2: Kinetic parameters for (6 mmol/L) of Co(II) on RS and NaC-RS in aqueous solution at different temperature.

Rice Straw	Temp. K	Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion model		
		$q_{e,1,cal}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,2,cal}$ (mg/g)	K_2 (g/mg min)	h (mg/g min)	R^2	K_{int} mg/g $\text{min}^{-0.5}$	C (mg/g)	R^2
RS	301	13.14	0.018	0.99145	32.41	4.0×10^{-3}	4.2	0.99959	0.759	19.779	0.85229
	313	19.83	0.023	0.94626	37.20	3.3×10^{-3}	4.6	0.99916	1.092	20.432	0.88023
	323	20.94	0.024	0.98666	41.05	3.1×10^{-3}	5.2	0.99947	1.261	21.951	0.84888
NaC-RS	301	13.02	0.019	0.9773	33.16	4.4×10^{-3}	4.8	0.99829	0.992	19.202	0.9114
	313	18.03	0.023	0.99432	39.73	3.6×10^{-3}	5.7	0.99939	1.424	20.250	0.84663
	323	20.53	0.025	0.99728	41.96	3.2×10^{-3}	5.6	0.99928	1.495	21.409	0.86581

3.7. Effect of Temperature and Thermodynamic of Biosorption

The equilibrium removal of Co (II) ions as a function of temperature, for experiments conducted at constant concentrations of Co (II) equal to 353.58 mg/L. The adsorption of Co (II) onto the surface of the RS and NaC-RS, was quickly regarded the temperature (301–323 K). On the other hand, enhancement of the adsorption capacity of the RS at higher temperatures may be attributed to the activation of the adsorbing surface, the accelerated diffusivity of metal ions from the external layer into the micro pores of the rice straw with the increasing temperature and increase in the mobility of metal ions. Also, this fact demonstrated an endothermic biosorption process [41]. Removal percentage at (301, 313 and 323 K) for RS are 71.7%, 81.9% and 90.3% respectively and for NaC-RS are 73.3%, 87.9% and 91.9% respectively.

Thermodynamic parameters can be calculated using equation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots 8$$

$$\Delta G = -RT \ln K_d \dots\dots\dots 9$$

$$S^* = (1 - \theta) \exp\left(\frac{E_a}{RT}\right) \dots\dots\dots 10$$

Thermodynamic parameters for the process of Co^{+2} uptake by RS and NaC-RS are presented in Table 3. Values found for ΔG , ΔH and ΔS are indicative of the spontaneous nature of the uptake process. The increase of the equilibrium constant with increasing temperature and positive values obtained for ΔH show the endothermic nature of Co^{+2} uptake. Results obtained in our experiments generally agree with the results previously found for the uptake of heavy metal ions by natural materials [42].

In order to further support the assertion that the adsorption is the predominant mechanism, the values of the activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data.

The effect of temperature on the sticking probability was evaluated throughout the temperature range from 301 to 323 K by calculating the surface coverage at the various temperatures. Table 3 also indicated that the values

of $S^* \leq 1$ (7.19×10^{-9}) for the RS and 7.81×10^{-10} for NaC-RS hence the sticking probability of the Co (II) ion onto the two the adsorbent systems are very high [43].

Table 3: Thermodynamic parameters for (6 mmol/L) of Co(II) on RS and NaC-RS in aqueous solution at different temperature

Rice Straw	Temp.K	ΔG (kJ/mol)	ΔS (J/mol k)	ΔH (KJ/mol)	S^*	Ea (KJ/mol)
RS	301	-50.2	167.0	53.61	7.19×10^{-9}	44.13
	313	-52.2	-	-	-	-
	323	-53.9	-	-	-	-
NaC-RS	301	-55.3	184.0	58.40	7.81×10^{-10}	49.40
	313	-57.5	-	-	-	-
	323	-59.4	-	-	-	-

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