Biosorption Of Ni (II) And Cd (II) Ions From Aqueous Solutions Onto Rice Straw

[1]*G O El-Sayed, [1]H A Dessouki, [2]S S Ibrahim

[1] Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

[2] National Water Research Center, Central Lab for Environmental Quality Monitoring, Elqanater Elkhayria, Egypt

*Correspondence to: G O El-Sayed, gamaloelsayed@yahoo.com

Abstract

The adsorption of Ni(II) and Cd(II) ions onto rice straw was investigated. The effects of pH, initial adsorbent concentration, initial metal ion concentration, contact time and temperature were studied in batch experiments. The Langmuir and Freundlich models were applied and the adsorption equilibrium followed the two adsorption isotherms. The maximum adsorption capacities for Ni(II) and Cd(II) were 35.08 and 144.19 mg/g, respectively. Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have been calculated on the basis of Langmuir constants. The negative values of $\Delta G°$ were indicative of the spontaneity of the adsorption process. The negative values of $\Delta H°$ revealed the exothermic nature of the adsorption process whereas the positive $\Delta S°$ reflected an irregular increase of the randomness at the adsorbent/solution interface during the sorption of metal ions.

Keywords: Nickel; cadmium; adsorption; isotherms; rice straw.

1. Introduction

The presence of heavy metals in the water environment is a major concern due to their toxic effects since they cause severe health problems to animals and human beings. Many industrial processes produce aqueous effluents containing toxic metal contaminants. According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. In particular, cadmium and cadmium compounds are especially dangerous and highly toxic. Cadmium toxicity contributes to a large number of health conditions, including the major killer diseases such as heart disease, cancer and diabetes. Cadmium concentrates in the kidney, liver and various other organs and is considered more toxic than either lead or mercury. It is toxic at levels one tenth that of lead, mercury, aluminum, or nickel [1]. Cadmium is produced in different industrial activities such as galvanizing, pigments, stabilizers, thermoplastics, batteries and alloys [2]. On the other hand, nickel is a toxic heavy metal and nickel compounds, are suspected to cause cancer [3]. Waste streams from nickel electroplating industries and textile industries are the main sources of nickel environmental pollution. The concentrations of these pollutants must be reduced by means of treatment to meet legislative standards. Several methods have been proposed for the removal of heavy metals as ion exchange [4], filtration [5], coagulation [6], adsorption [7] and electrochemical deposition [8]. Most methods to remove metal ions from solution are expensive [9], so the use of cheap agricultural wastes such as rice straw [10], sawdust [11], carrot residues [12], tobacco dust [13], orange residue [14], apple residue [15], coconut shell powder [16] and powdered leaves of castor tree [17] as adsorbents have been highlighted for metal removal from wastewater. Rice straw is one of the abundant lignocellulosic waste materials in the world. In terms of total production, rice is the third most important grain crop in the world behind wheat and corn [18]. Rice straw has several characteristics that make it a potential adsorbent with binding sites capable to tack up metals from aqueous solutions. In terms of chemical composition, the straw predominantly contains cellulose (32–47%), hemicellulose (19–27%) and lignin (5–24%) [19]. The aim of this work is to study Ni(II) and Cd(II) ions adsorption from aqueous solutions onto rice straw as a cheap agricultural waste material. Different factors affecting the adsorption as the initial solution pH, temperature, contact time, ionic strength and initial metal ion concentration on the adsorption isotherm were examined to optimize the adsorption process. The biosorption equilibrium and kinetic data are fitted using different models and process parameters were evaluated. The loading capacity of the rice straw was optimized.

2. Methods

Rice straw used as the adsorbent in this study was collected from a cultivated area near Benha city. The straw was washed with distilled water several times and dried at room temperature. The straw was dried in a drying furnace at 90 °C for two hrs, ground and sieved between 400 and 600 µm and stored in a plastic bottle prior to use. The rice straw was characterized by applying FTIR analysis (using Jasco FT/IR-300E spectrometer) to predict the functional groups on the surface of the biomass responsible for the

adsorption process. This was done by mixing approximately 1.0 mg dried sample of straw with 100 mg KBr (1%), ground to fine powder and pressed under vacuum to a pellet. The pellet was analyzed in the range 4000–400 cm^{-1}. The FTIR spectra of the free unloaded rice straw were compared with those obtained for straw loaded with nickel and cadmium. Also, SEM (Scanning Electron Microscopy) (Model JEOL JEM-1200EX) was employed for the observation of the surface microporous structure of rice straw before and after loading with cadmium.

Stock solutions (2000 mg/L) of the nickel and cadmium ions under study were prepared by dissolving an appropriate weight of pure salt (NiSO$_4$ or CdCl$_2$.2$\frac{1}{2}$H$_2$O) in the desired volume of de-ionized water. The stock solution was successively diluted with de-ionized water to obtain the desired test concentration of metal ion. All the chemicals used in the study were of analytical reagent grade and all experiments were performed at room temperature (24±1 °C). In order to optimize the design of a sorption system for the removal of metals from wastewater, it is important to establish the most appropriate correlation for equilibrium curves. Experimental data acquired at different conditions is fitted to different models of sorption isotherms because equilibrium isotherm models are used to describe the experimental data. The batch mode was used to study the adsorption of Ni(II) and Cd(II) on rice straw. Sorption studies were conducted in a number of plugged Pyrex glasses Erlenmeyer containing a definite volume (50 ml in each case) of solutions of the metal ion of desired concentration, pH and temperature were placed in a thermostatic rotary shaker. For the studies, 0.2 g of adsorbent was treated with 50 ml of metal ion solution. The flasks were agitated at a 200-rpm constant shaking rate for 3 hrs to ensure equilibrium was reached. Samples (3 ml) were taken before mixing the sorbent and the metal ion solution and at pre-determined time intervals. The metal solution was separated from the sorbent by centrifugation at 5000 rpm for 5 min. The metal ion content in the test flask was evaluated by ICP-OES 2010 Serial Optical Emission Spectrometer, Optima (PerkinElmer). Uptake values were determined as the difference between the initial metal concentration and that in the supernatant.

All the experiments were carried out in duplicates and the average of the values were used for further calculations. For the calculation of average value, the percent relative standard deviation for samples was calculated and if the value of standard deviation for any sample was greater than 5% the data were not used. The pH of the test solution was monitored by using a pH-meter model HI 8014, Hanna Instruments (Italy). The samples were analyzed three times and the mean values were computed. The amount of metal ion adsorbed per unit mass of the biosorbent was evaluated by using following equation:

$$q_{max} = (C_o - C_e)\frac{V}{W}$$

Where, C_o is the initial metal ion concentration in mg/L, and C_e is the metal ion concentration at equilibrium in mg/L and V is the volume of metal ion solution in milliliters, W is the mass of adsorbent in grams. The percent of metal ion removal was evaluated from the equation:

$$\% \, Removal = \frac{(C_0 - C_e)}{C_0} \times 100$$

3. Results and Discussion

3.0. Biosorbent characterization

FTIR spectroscopy was applied to identify the functional groups of rice straw responsible for metal adsorption. To reveal the systematic changes in the spectral features upon reaction with metal ions, FTIR spectra were obtained for the sample after reacting with Ni(II) and Cd(II) (Figure 1). By comparing the FTIR spectra of rice straw before and after adsorption, there were remarkable shifts in some bands (Table 1). These bands are the function groups of rice straw participate in Ni(II) and Cd(II) biosorption.

Table 1. FTIR spectral characteristics of rice straw before and after biosorption of Ni(II) and Cd(II).

FTIR peak	Transmission band (cm^{-1})			Assignment	Reference
	Before adsorption	After adsorption of Ni(II)	After adsorption of Cd(II)		
1	3340	3326	3427	Stretching vibration of -OH	20
2	2921	2923	2924	Aliphatic C-H group	21
3	2372	2348	2361	phosphine	22
4	1650	1654	1633	double bands of the carboxylate ion	23
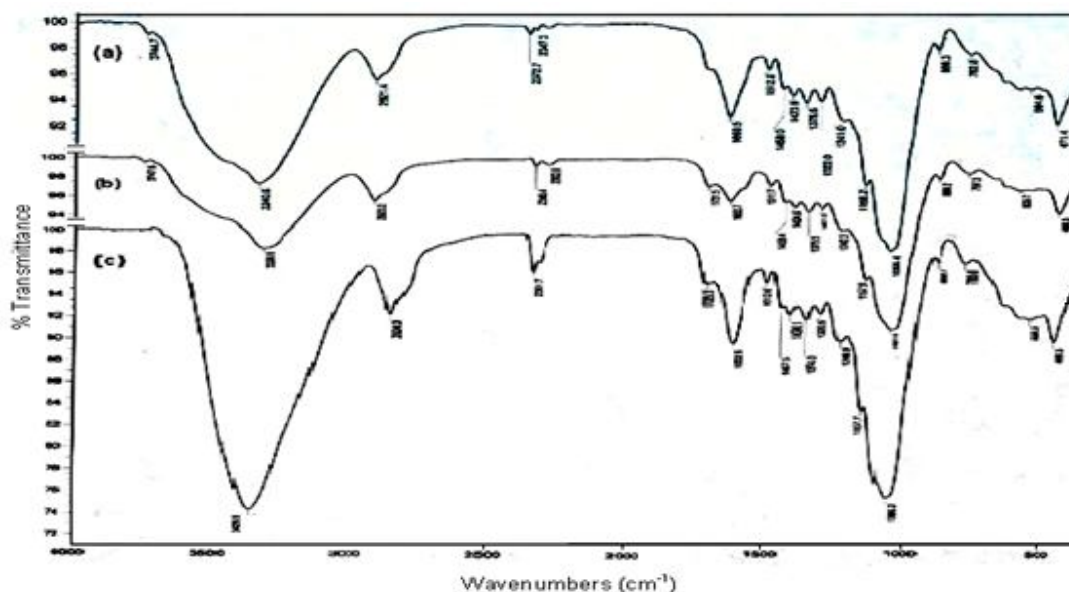
Figure 1. FTIR transmission spectra of rice straw (a) unloaded; (b) loaded with Ni(II) and (c) loaded with Cd(II).

Scanning electron micrographs realized on raw rice straw and cadmium loaded rice straw are shown on Figure 2. The initial structure of the rice straw (Figure 2a) shows the presence of a few macropores of various size at the surface, in contrast, mineral matter can be observed within the macropores of the sample after adsorption of cadmium (Figure 2b).
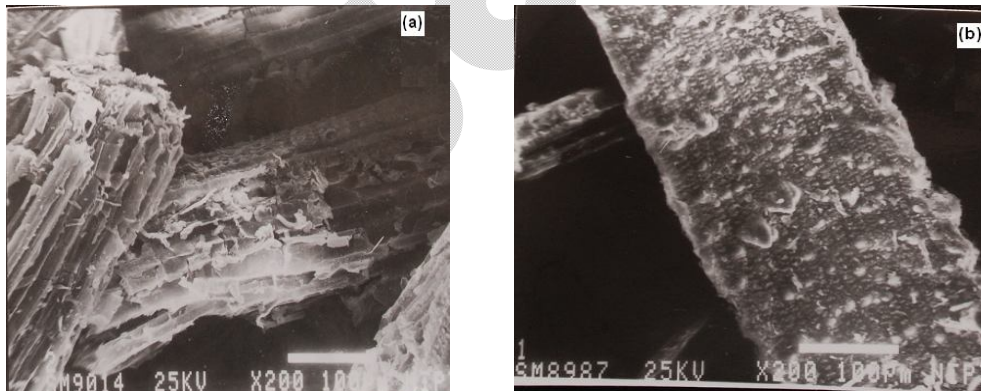
Figure 2. Scanning electron micrographs of (a) raw rice straw (b) cadmium loaded rice straw.

3.1. Effect of initial pH

The pH of the solution is one of the important factors governing the adsorption of metal ions. Figure 3 shows the effect of pH change in the range 1 to 8 on the adsorption of Ni(II) and Cd(II) on rice straw. The initial pH of the solution has a significant influence on the amount of metal ion adsorbed. It was observed from the figure that the removal percent of Ni(II) and Cd(II) ions in the aqueous solution is low at low pH values and increased with increasing the initial pH of the solution. The removal of Ni(II) was about 28% at a pH 1.0 and it reached its maximum value (47%) at about pH 5.0. Further increase of pH leads to slight decrease in Ni(II) removal efficiency. The removal percentage of Cd(II) showed a rapid increase from 25% to 76% when the pH increased from 1.0 to 6.0. This behavior is expected for many metal ions including nickel and cadmium [24-26]. The influence of pH can be related with the fact that in an acid environment competition between metals and H$^+$ ions occurs and the metal retention in such condition is not significant. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption [27].
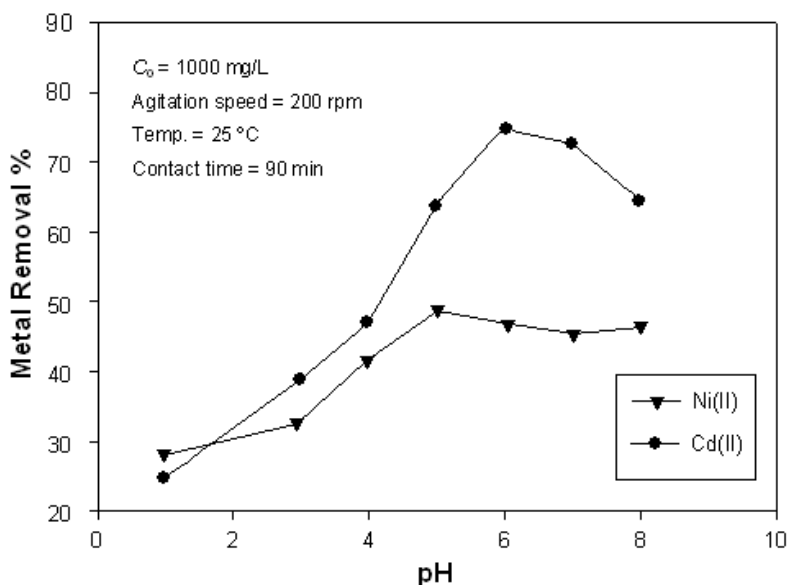
Figure 3. Effect of pH on removal percent of Ni(II) and Cd(II) ions onto rice straw.

3.2. Effect of contact time

The plot of percent of metal removal against contact time for Ni(II) and Cd(II) ions at optimum pH values is shown in Figure 4. It was observed that the adsorption of Ni(II) and Cd(II) by rice straw was highly influenced by contact time. The kinetics of metal removal by rice straw was relatively fast within 5 min and during the first hour was remarkably changed with time. At the equilibrium time the metal ion uptake of 46% for Ni(II) and 76% for Cd(II) were achieved. The equilibrium time was taken as 90 min for further experimental measurements. Equilibrium time is a crucial parameter for an optimal removal of metal ions in the waste water. The increased uptake of both metal ions with contact time can be due to the decreased mass transfer coefficient of the diffusion controlled reaction between the adsorbent and the metal ion.
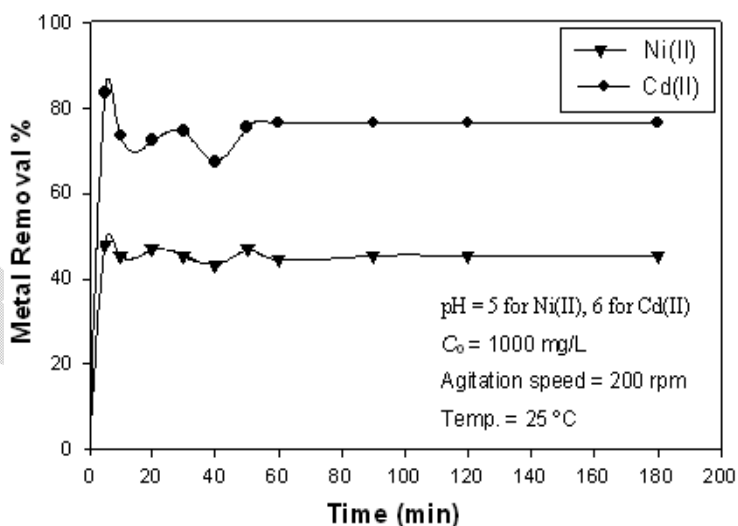

Figure 4. Effect of contact time on removal percent of Ni(II) and Cd(II) ions onto rice straw.

3.3. Effect of ionic strength of metal ion solution

Ionic strength of the solution may be an important factor influencing aqueous phase equilibrium between adsorbed species and adsorbent. Generally, adsorption decreases with increasing ionic strength of the aqueous solution which can be attributed to the presence of sorption sites of different affinities [28]. The effect of addition of NaCl on the removal capacity of Ni(II) and Cd(II) ions is

shown in Figure 3. The results indicate that there was a little significant decrease in the removal of Ni(II) and Cd(II) ions for the interval of (1-10 g/L) NaCl ionic concentration.
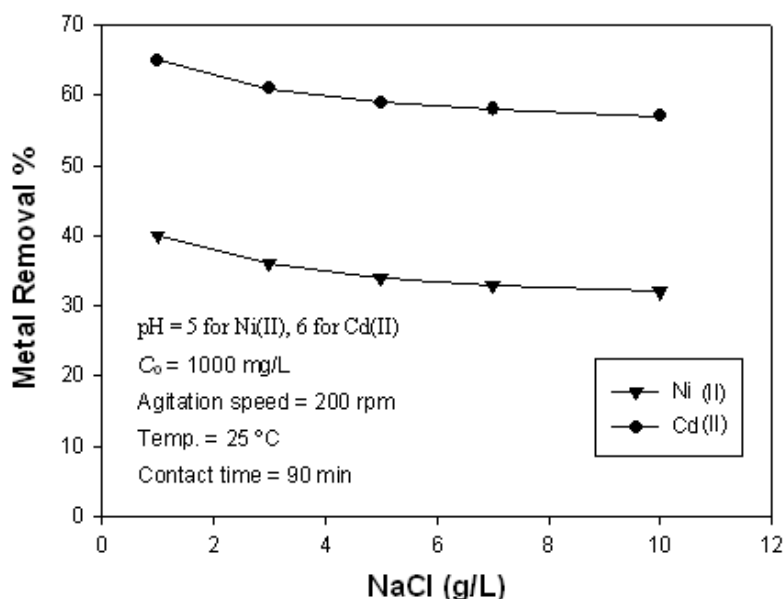

Figure 5. Effect of NaCl concentration on Ni(II) and Cd(II) removal onto rice straw.

3.4. Effect of temperature

The effect of the solution temperature on the adsorption capacity was investigated for Ni(II) an Cd(II) ions solutions at initial metal concentration 1000 mg/L and adsorbent dose 20 g/L. Four different temperatures of 25, 30, 35 and 40 °C were considered. From Figure 6, it can be observed the removal percent was slightly decreased for the two metal ions. It decreased from 47% to 44% for Ni(II) and from 75.5% to 70% for Cd(II) when temperature was increased from 20 to 40 °C. These results indicate that the adsorption of Ni(II) and Cd(II) ions is exothermic in nature [29].
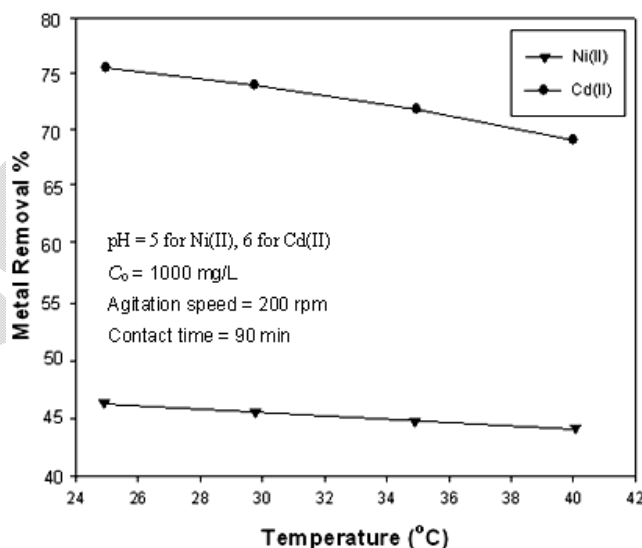

Figure 6. Effect of temperature on Ni(II) and Cd(II) removal by rice straw.

3.5. Effect of initial metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are adsorbed by specific active sites, while at higher concentrations; lower adsorption yield is due to the saturation of adsorption sites.

Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. This appears to be due to the increase in the number of ions competing for the available active sites on the surface. In addition, typical mass-transport controlled kinetics of pollutants removal by the rice straw is another factor which control removal rate of zinc and at higher concentrations, more metal ions are left in solution [30]. The influence of the initial concentration on the adsorption capacity of Ni(II) and Cd(II) ions is presented in Figure 7. For Ni(II) removal, a decrease in removal percent from 91% (for C_o = 40 mg/L) to 45% (for C_o = 1000 mg/L) could be observed. The same behavior was observed with Cd(II), where a decrease in removal percent from 98% (for C_0 = 40 mg/L) to 76% (for C_0 = 1000 mg/L) occurred.
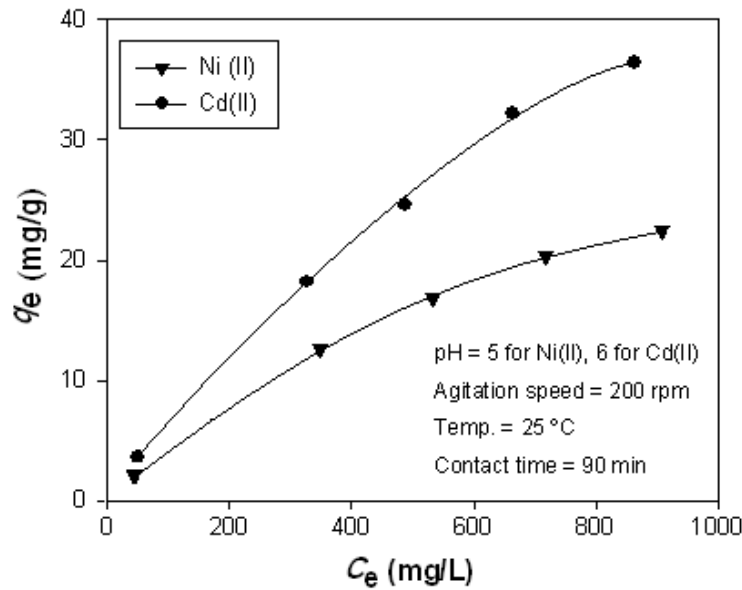

Figure 7. Effect of initial metal ion concentration on adsorption capacity.

3.6. Adsorption isotherms

The study of adsorption isotherms is fundamental in supplying the essential information required for the design of the sorption process. The adsorption of a substance from one phase to another leads to a thermodynamically defined distribution of that substance between the phases as the system reaches equilibrium state [31]. This distribution can be expressed in terms of adsorption isotherms. In this investigation, Langmuir and Freundlich isotherm models were used to analyze the equilibrium data.

3.6.1. Langmuir adsorption isotherm

Langmuir adsorption isotherm [32] applied to equilibrium adsorption assuming a mono-layer adsorption onto the surface of the adsorbent with a finite number of identical sites. This isotherm can be represented by the following relationship:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}}$$

where, q_e is the metal uptake at equilibrium per unit mass of adsorbent (mg/g), q_{max} is the maximum adsorption capacity of metal per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the metal in solution (mg/L). The plot of C_e versus C_e/q_e should give a straight line its slope equals to $1/q_{max}$ ant the intercept has the value of $1/q_{max}b$, where b is the adsorption coefficient (L/mg). From the plot (Figure 8), q_{max} and b values of the Ni(II) and Cd(II) were obtained (Table 1). The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L, defined by [33]:

$$R_L = \frac{1}{1 + bC_o}$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). As shown in Table 1, The maximum adsorption capacities of rice straw towards Ni(II) and Cd(II) are 35.08 and 144.19 mg/g, respectively. The values of R_L ranged from 0.941 to 0.390 and from 0.982 to 0.694 for Ni(II) and Cd(II) ions, respectively in the initial metal ion concentrations 40-1000 mg/L. The values of R_L indicated that the adsorption process is favorable.

Table 2. Langmuir and Freundlich adsorption isotherm parameters for Ni(II) and Cd(II).

Metal Ion	Langmuir Isotherm				Freundlish Isotherm		
	q_{max}	b	R_L	R^2	K_F	n	R^2
Ni(II)	35.08	0.00156	0.941-0.390	0.9866	0.1388	1.314	0.9930
Cd(II)	144.19	0.00044	0.982-0.694	0.9600	0.0839	1.086	0.9972
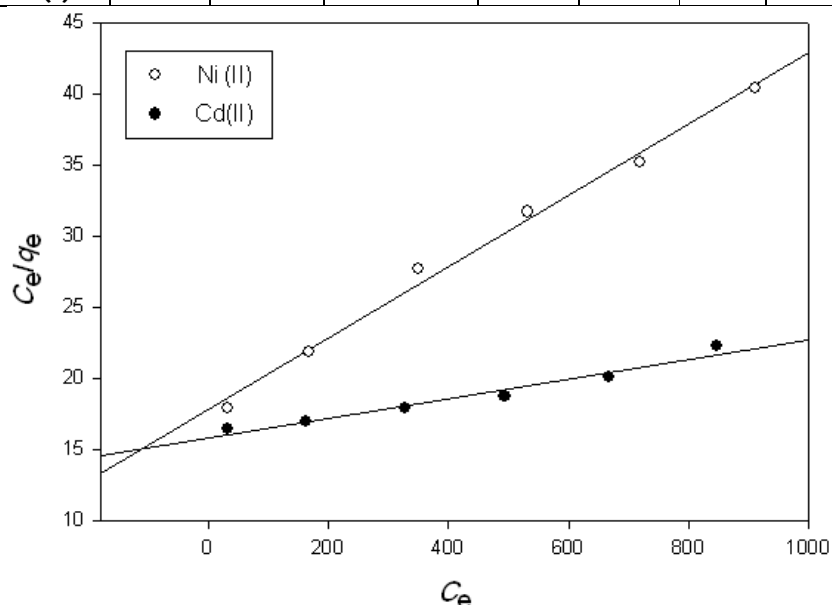
Figure 8. Langmuir isotherm for adsorption of Ni(II) and Cd(II) on rice straw.

3.6.2. Freundlich adsorption isotherm

The Freundlich adsorption isotherm is an empirical equation based on the adsorption on a heterogeneous surface [34]. The linear form of Freundlich adsorption isotherm can be defined by the following equation:

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

The constant n is an empirical parameter that varies with the degree of heterogeneity and K_F is a constant related to adsorption capacity. The constants n and K_F were calculated from the previous equation by plotting $ln C_e$ against $ln q_e$ (the slope = $1/n$ and the intercept = $ln K_F$) (Figure 9). The values of n (which reflect the intensity of adsorption) are between 1 and 10 represent a favorable adsorption. From the results are presented in Table 2. It can be seen that the adsorption of Ni(II) on rice straw follows the two adsorption models, whereas Freundlich model is more fitted in for Cd(II) adsorption (depending of the values of R^2).

3.7. Adsorption thermodynamics

The thermodynamic parameters such as Gibbs free energy change ΔG^0, standard enthalpy change ΔH^0, and standard entropy change ΔS^0 were also studied to understand better the effect of temperature on the adsorption. The values of standard Gibbs free energy change were evaluated by using b values obtained from the Langmuir model presented in Table 2 by applying the following equation [35].

$$\Delta G^0 = -RT ln b = -ln K$$

where R is universal gas constant (8.314 J/mol K) and T is absolute temperature.

The values of ΔG^0 for the biosorption process of Ni(II) and Cd(II) were evaluated at different temperatures and are presented in Table 2.
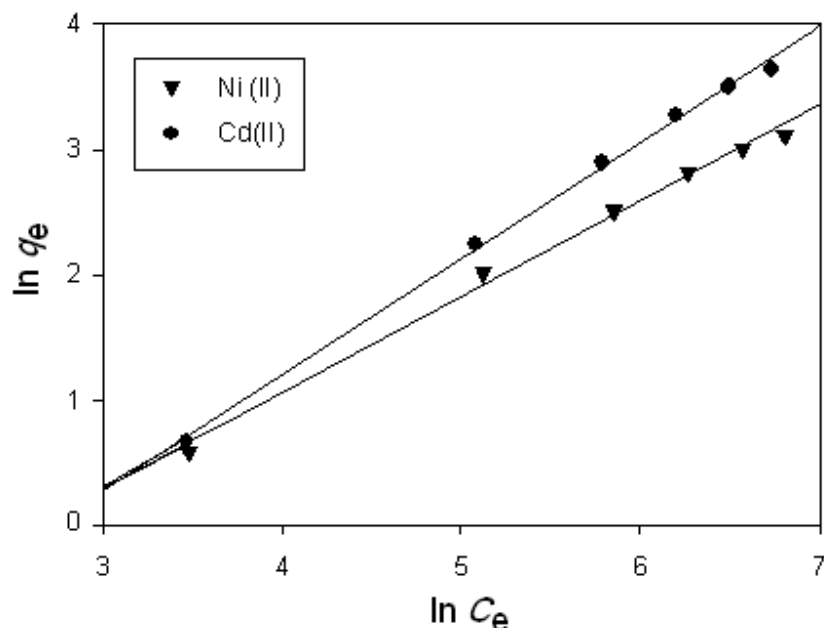
Figure 9. Freundlich isotherm for adsorption of Ni(II) and Cd(II) on rice straw.

Table 3. Thermodynamic parameters of Ni(II) and Cd(II) adsorption on rice straw at different temperatures.

T (K)	ΔG° (kJ/mol)		ΔH° (kJ/mol)		ΔS° (kJ/mol K)	
	Ni(II)	Cd(II)	Ni(II)	Cd(II)	Ni(II)	Cd(II)
298	-3.865	-1.090				
303	-3.930	-1.108	-5.723	-5.821	0.0199	0.0062
308	-3.994	-1.126				
313	-4.060	-1.145				

The equilibrium constant K may be related to $\Delta H°$ and $\Delta S°$ at different temperatures by the following relationship:

$$lnK = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

The plot of $ln K$ against $1/T$ (Vant's Hoff plot) of the metal ion solution was carried out as indicated in Figure 8, in which the slope equals to $-\Delta H°/R$ and the intercept equals to $\Delta S°/R$. These thermodynamic parameters are presented in Table 2. The negative values of $\Delta G°$ at all temperatures examined indicate the feasibility of the process and the spontaneous nature of the adsorption. The negative values of $\Delta H°$ reveal the adsorption is exothermic and physical in nature. Generally, the change in adsorption enthalpy for physicorption is in the range of −20 to 40 kJ mol^{-1}, but chemisorption is between −400 and −80 kJ mol^{-1} [36]. Furthermore, slightly positive $\Delta S°$ of Ni(II) and Cd(II) adsorption processes indicate an irregular increase of the randomness at the adsorbent/solution interface during adsorption.

4. Conclusion

The potential use of rice straw as an adsorbent for nickel and cadmium was studied. It was found that rice straw is an effective adsorbent for the two metal ions, specially for cadmium, the maximum adsorption capacities for Ni(II) and Cd(II) were 35.08 and 144.19 mg/g, respectively. The sorption capacity was strongly dependent on the adsorbent dosage; initial metal ions concentration and initial pH. The experimental data well fitted to the Langmuir and Freundlich equations, with good correlation coefficients. The study of the thermodynamic parameters indicated that the adsorption process was thermodynamically spontaneous under natural conditions and the adsorption is exothermic in nature.
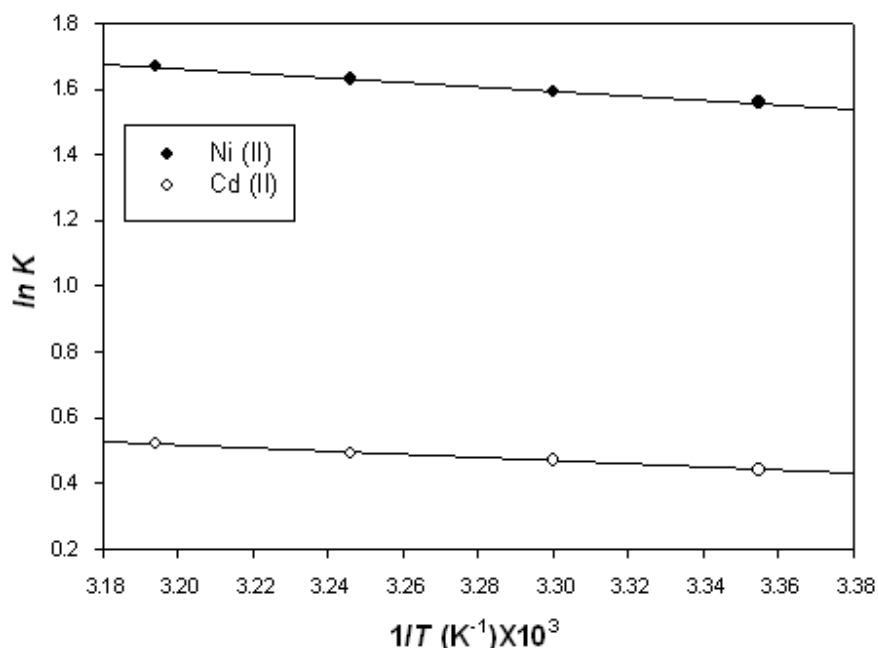
Figure 10. Vant's Hoff plot for the determination of H^o, S^o and G^o.

5. Competing Interests

The authors declare that they have no competing interests.

6. Authors' Contributions

GOE developed the project and assisted with preparation of the manuscript and data analysis; HAD supervised preparation of the manuscript; SSI assisted with sample collection and carried out the project.

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List of Abbreviations

b Langmuir's constant related to energy of adsorption (Lmg^{-1})
C_o initial concentration of metal ($mg\,L^{-1}$)
C_e equilibrium concentration of metal ($mg\,L^{-1}$)
K equilibrium constant at temperature T
K_F Freundlich constant
n Freundlich constanta
q_e amount of metal adsorbed ($mg\,g^{-1}$) at equilibrium
q_{max} Langmuir's constant related to capacity of adsorption ($mg\,g^{-1}$)
R gas constant ($kcal\,mol^{-1}\,K$)
R_L equilibrium parameter, dimensionless
T absolute temperature (K)
V volume of metal solution (L)
W mass of adsorbent (g)
ΔG° standard free energy change ($kJ\,mol^{-1}$)
ΔH° standard enthalpy change ($kJ\,mol^{-1}$)
ΔS° standard entropy change ($kJ\,K^{-1}\,mol^{-1}$)