Removal of Nickel (II) from Aqueous Solution Via Carbonized date Pits and Carbonized Rice Husks

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Abstract

The adsorption of nickel from liquid solutions onto carbonized date pits (CDP) and rice husks (CRH) has been investigated in the current study. The process was studied in a batch system with respect to the initial pH, contact time, temperature, adsorbent dose and nickel initial concentration. The results showed that the experimental data was well represented by first order model for CDP and second order model for CRH. Based on the kinetic modeling, the apparent activation energies calculated were 7.84 kJ and 18.502 kJ/mol for CDP and CRH, respectively. The results also indicated that process of nickel uptake by CDP and CRH was physical adsorption process. The equilibrium data for CDP indicated that it fitted both Freundlich and Langmuir models. However, adsorption onto CRH fitted Freundlich model better based upon the higher value of R^2 obtained. The thermodynamic parameters (ΔH^o, ΔS^o and ΔG^o) calculated from the experimental data indicated that the process was endothermic and spontaneous.

Introduction

Heavy metal pollution has become a serious environmental problem since the early 1970s [1, 2]. Wastewater discharged from a number of industrial activities such as mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides production play a major role in the introduction of these toxic metal ions into the aquatic streams [3, 4]. Because of their persistence in the environment and their recalcitrant nature, these metals can accumulate in living tissues and become concentrated throughout the food chain [5]. Subsequently, their removal and remediation from aqueous streams has become a priority for water resource conservation and safe use.

About 40% of the nickel produced globally is used in steel factories, Ni batteries and in the production of some alloys [6]. Essentially, the presence of Ni in wastewater is considered an environmental risk [7]. This is because of the wide range of health effects that can materialize due to nickel poisoning that range from simple headache, dizziness and dermatitis to the damage of the nervous system and cancer [8, 9]. On the other hand and economically, the presence of Ni in wastewaters may be regarded as an important indicator of resource depletion [7].

Generally, conventional methods applied for the removal of toxic metal ions from aqueous medium included chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electro dialysis and ultra filtration [3, 4, 7]. However, these techniques may not be economically viable as well as they have the potential to generate a large volume of toxic sludge. In addition, some of these techniques, such as chemical precipitation and electrochemical treatment, may be ineffective in the case the metal ion concentration in aqueous solution ranged between 1 to 100 mg/L. Consequently and because of the noted technical limitations associated with these methods, investigations for the sorption of toxic metal on low cost renewable organic materials have gained momentum [3].

Generally, agricultural materials containing cellulose show a good potential metal biosorption

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capacity [3]. In this effect, various agricultural products and by-products may provide suitable sorbent materials for the removal of toxic metals from aqueous materials [10]. In Egypt, rice husks are an undesirable agricultural waste that account for 20% of the rice harvested in tons annually [11, 12]. While there may be some local options available for its reuse, it was reported that not all were able to contain the entire bulk of waste generated. As well, with the noted volume of waste generated, the traditional method for disposal of this bulk has been to burn it in the open fields, an event that has incurred serious environmental problems since 1999. Another abundant waste available locally is that which comes from the over eight million date palms planted in the country [13]. These palms generate a considerable amount of low-cost and non-valuable waste material, the main bulk of which originate at the food processing and jam production industries [13]. Both wastes were reported to contain lignin and cellulose which make them amenable for use as inexpensive sorbents for the removal of some organic pollutants [11] and some heavy metals from wastewaters [14].

The objective of present study is to investigate the feasibility of the use of carbonized rice husks and date pits for the removal of Ni (II) from aqueous solution. Batch adsorption experiments were utilized to study the metal removal efficiency using the selected sorbent material. The effect of various parameters such as contact time, initial metal concentration, pH, adsorbent mass, and temperature upon the removal of nickel were studied and the kinetics of the process were elucidated. The experimental data obtained were fitted to Langmuir and Freundlich models to analyze the adsorption equilibrium and the thermodynamic parameters for free energy, enthalpy, and entropy change were calculated.

Materials and Methods

Sorbent materials

Carbonized rice husks (CRH) were obtained from Abu-Qeir Company for Environmental Waste Treatment, Egypt. Date pits (DP) were brought from the local market in Egypt. Before use, DP was washed thoroughly to remove any dirt and then dried. Carbonization of DP was carried out twice in a muffle furnace at 200-250°C for 2 hours, after which it was ground using a mortar, washed and dried. Both CDP and CRH were kept in a desiccator and were used as is. The chemical characteristics of CDP and CRH are provided in Tables 1 and 2, respectively.

Table 1
Chemical Analysis of carbonized date pits (% wt/wt)

Characteristic	%wt/wt
Ash content	2.0
Carbon Content	68.8
Moisture Content	8.0
SiO_2	1.5

Table 2
Chemical Analysis of carbonized rice husks (% wt/wt)

Characteristic	%wt /wt
Ash content	54.82
Volatile mater	15.62
Carbon Content	30.56
Sulfur content	0.32
Ash content Analysis	
SiO_2	88.06
Fe_2O_3	2.86
CaO	3.69
MgO	1.13
Al_2O_3	1.06
MnO	0.04
K_2O	1.86
TiO_2	0.10
P_2O_5	0.25
ZnO	0.13
Na_2O	0.16

Reagents and chemicals

All reagents and chemicals used were of analytical reagent grade. Stock solution of 1000 ppm Ni (II) was prepared from reagent grade $NiSO_4.7H_2O$ (Imperial Chemicals) by dissolving the required mass in 1 L of double distilled water. This solution was used to obtain diluted metal ion solutions as required. Metal standards and concentration were quantified using Atomic Absorption Spectrophotometer (Varian Spectra AA, Australia) and colorimetrically during the batch treatment process using dimethylglyoxime (Merck, USA).

Adsorption experiments

Batch adsorption experiments were carried out in a thermo stated water bath/shaker at a constant shaking rate. The effect of contact time, concentration, solution pH, adsorbent dose and temperature were studied. 50 mL of Ni solution of known concentration (25-200 mg/L) were shaken with different weights of adsorbent material (0.25-2.50 g) at different temperatures (25-60ºC), for various mixing time (1-120 min) and throughout the pH range of (3-10). Separation of the solid phase from liquid was achieved first by centrifuging for 10-15 min (4000 rpm) followed by filtration. The filtrates were analyzed for the remaining nickel ion concentration spectrophotometrically at 445 nm (Jenway 6350 UV–Visible Spectrophotometer) using dimethylglyoxime method [15].

The % of metal ion removal was calculated as follows:

$$\%\ \text{removal} = [C_0 - C_t / C_0] \times 100 \ldots\ldots \qquad (1)$$

where C_0 and C_t are the initial and final concentration of metal ions in solution (mg/L or ppm), respectively. The amount of metal ion accumulated per unit mass of adsorbent was evaluated using the following equation [14, 16, 17]:

$$q_t = (C_0 - C_t)\ V/\ m \qquad (2)$$

where m is the weight of sorbent used (g) and V is the volume of metal solution (L). At equilibrium contact time t_e, C_t becomes C_e and the amount of metal ion sorbed (q_t) is equivalent to amount at equilibrium (q_e).

Adsorption Kinetics

To a series of 50 mL capacity tubes containing the desired amount of metal ion solution with known concentrations, a predetermined amount of adsorbent was added and the mixture was agitated in a thermostated water bath shaker. At set time intervals, the solutions were filtered and the metal ion concentration was determined.

Thermodynamic parameters (ΔH^o, ΔG^o and ΔS^o) were calculated from the adsorption results. The optimum weight of each adsorbent material/L was added to a solution of 25 mg Ni (II) /L at pH 6 and was shaken for 30 mins at different temperatures.

Results and discussion

Effect of Adsorbent weight

The effect of varying the dose of CRH and CDP upon the metal ion removal % from solution is shown in Figure 1. The results indicated that Ni (II) removal % increased as the weight of both CDP and CRH increased, with the latter achieving higher removals (20-92%) than former (0-54%). Moreover, the observed increase in removal efficiency was rapid under 20 g/L adsorbent dose using CRH relative to CDP. This may be attributed to the fact that increasing the adsorbent dose increased the surface area available for more metal ion adsorption. On the other hand, the high removal efficiency achieved using CRH may be attributed to the fact that it contained 88.06% SiO_2 (Table 2) relative to 1.5% in CDP (Table 1). Such an increase in silica content of CRH was reported to provide it with a good granular structure and a high mechanical strength for better removal of heavy metal from wastewater with or without treatment [18]. As well, CRH was indicated to have a small particle size per unit mass that provided for a higher surface area for metal adsorption [11, 19]. From another perspective, it was reported that using boiled-and-dried RH sorbent material achieved 51.8% removal of the same metal ion from 100 mg/L solution using an adsorbent dose of 20g/L [20].

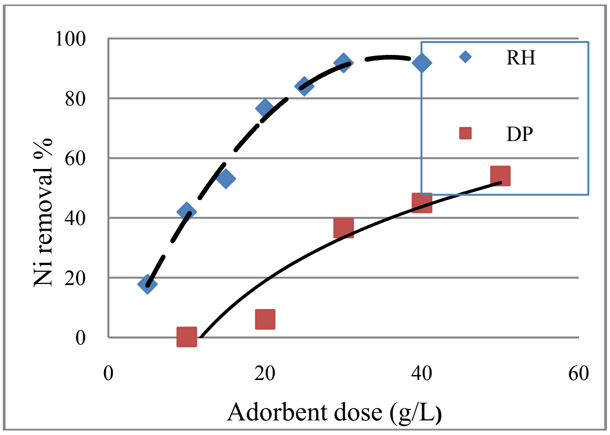

Fig. 1. The effect of adsorbent weight (CDP and CRH) upon Ni (II) removal % at pH 6, t = 120 min, T = 25°C, volume of solution 50 mL, and C_o = 100 mg/L.

The lower adsorption efficiency reported for CDP removal of Ni from solution may be attributed to the fact that CDP material was used as a whole after grinding with no particle size grading/ separation. Similar observations were reported by Gupta et al. [21] using bagasse fly ash, Blázquez et al. [22] using olive stones carbon, and Kandah et al. [23] and Belala et al. [24] using date pits during the removal of divalent metals from solution. As well, it was noted that the use of large particle size DP decreased its sorption capacity [23, 24]. This factor manifested itself more with the increase in weight of DP added to the metal ion solution [24].

Concerning the adsorption capacity of CRH, the maximum capacity obtained in this study was 1.05 mg Ni/g at 10 g/L, which was significantly higher than that reported by Chuah at al. [19] using modified RH for Ni removal. As for CDP, the maximum adsorbent capacity obtained in this study was 1.22 mg Ni/g at 30 g/L, which was higher than that reported for Cu removal with raw DP [24]. In addition, Kandah et al. [23] and Belala et al. [24] reported a similar pattern for metal uptake per weight for non-activated date pits in their study for the removal of other divalent ions. Overall, the current results indicated that the optimum adsorbent dose for Ni (II) removal from solution was 40 g/L (2g/50 mL) for CRH and 50 g/L (2.5g/ 50 mL) for CDP.

Effect of Initial metal concentration

Figure 2 reveals that as the initial Ni (II) concentration increased from 25-200 ppm, the % metal ion removal decreased for both sorbent materials employed. As well, the maximum metal removal % obtained using both CRH and CDP (92% and 46%, respectively) was achieved at 25 ppm Ni. However, the removal efficiency sharply decreased from 92% to 30% applying CRH, while there was a gradual and steady decrease in the case CDP. These results also indicated that the maximum adsorption capacity for CDP attained was 0.700 mg Ni/g at 100 ppm, while that for CRH; it was 0.576 mg Ni/ g at 75-100 ppm. With respect to the adsorption capacities of both CRH and CDP, the data indicated that there was a rapid increase in adsorption capacity going from 25-100 mg Ni/L after which there was a noted decrease. Similar observations were reported during the study for nickel ion removal from solution using activated carbon prepared from almond husks [25].

Bansal et al. [20] reported a similar pattern for RH removal of Ni in solution. In their study, the removal efficiency decreased from 82.5% to 30.5% throughout the concentration range of 5-500 mg/L. This decrease in adsorption efficiency was attributed to the fact that at higher concentrations, most of the excess Ni ion was left un-adsorbed in solution as the adsorption sites' reached the point of saturation [20, 26, 27]. Similarly, El-Sayed et al. [27] indicated that Ni(II) removal efficiency using raw-dried Egyptian rice straw decreased from 91% to 45% as the initial ion concentration increased from 45 mg/L to 1000 mg/L, respectively.

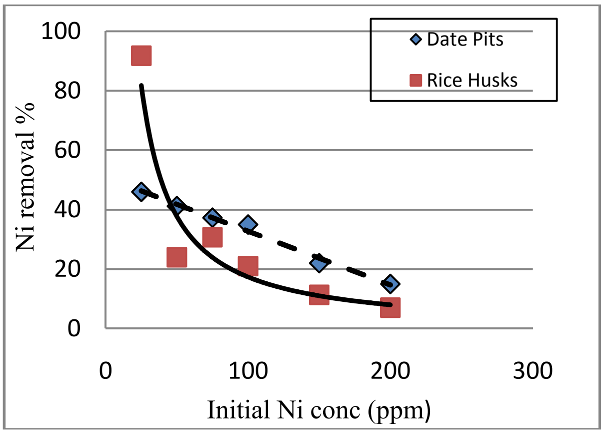

Fig. 2. The effect of the initial Ni(II) concentration (ppm) upon metal % removal using CDP and CRH at pH 6, t = 120 min, T = 25ºC, volume of solution 50 mL, and DP wt = 50 g/L and RH = 40 g/L.

Effect of agitation time

The effect of agitation time upon the amount of Ni (II) adsorbed using fixed CRH and CDP weights is shown in Figure 3. Overall, the initial Ni (II) uptake (50%-90%) from solution using CRH was rapid and the equilibrium was attained after the first 100 mins. However, for the application of CDP to metal ion solution, the initial metal uptake was rather sluggish (5%-44%) and equilibrium was reached after 120 min after which it remained unchanged. The maximum amount of metal adsorbed obtained in this study was 0.223 mg Ni/g and 0.574 mg Ni/g for the applied weights of CDP and CRH, respectively. Thus, 120 min was applied as the optimal experimental equilibrium time.

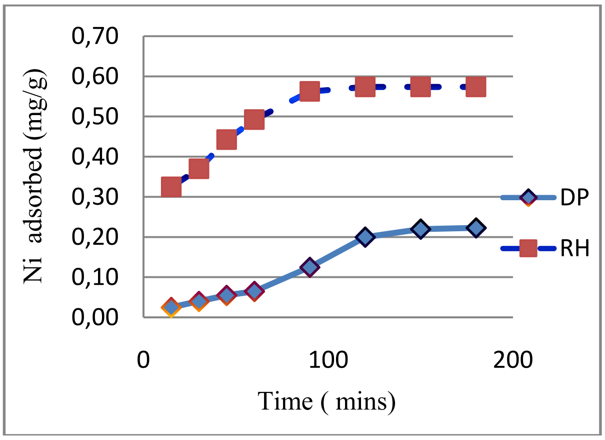

Fig. 3. The effect of varying the agitation/contact time (min) upon the amount of Ni (II) adsorbed (mg/g) at pH 6, T = 25ºC, volume of solution 50 mL, and CDP wt = 50 g/L and CRH = 40 g/L

Concerning the range of equilibrium times reported for the removal of Ni (II) from solution, previous studies indicated that it was 80 min for the application of bagasse fly ash [21], 90 min using peanut hull carbon [28] and Egyptian rice straw [27], 120 min using waste tea [29,30] and boiled RH [20]. Furthermore, El-Sayed et al. [27] reported that the equilibrium time of 90 min was sufficient to achieve 46% removal of Ni(II) from solution, which is comparable to the removal % obtained using CRH in the current study. On the other hand, previous studies conducted on the sorption of Cd ions from solution concluded that 120 mins was the optimal equilibrium time when inactivated date pits were employed [11].

Moreover, other researchers reported that as the initial nickel concentration increased, the equilibrium time increased to 90 min using peat [31] and to 120 min using waste tea [30]. This was attributed to the availability of more adsorption sites at low metal ion concentrations. However, at higher concentrations, the interparticle diffusion was predominant in order to create more adsorption sites. Ho et al. [31] postulated that the decrease in removal rates was indicative of the formation of a monolayer of Ni (II) ions on the outer surface of the sorbent material and further increase may be due to pore (inter particle) diffusion of adsorbent particles onto the inner surface through the formed film as a result of the continuous agitation maintained during the experiments. Bansal et al. [20] also reported that at the equilibrium time of 120 min was the time at which most of the surface sites were exhausted and that, after which, repulsive forces between solute molecules and bulk phase were becoming more dominant. Aikpokpodion et al. [30] considered that agitation between the adsorbate and adsorbent might increase the reactants energy which in turn increases the binding of Ni (II) ions onto functional groups present in the biomass. Blázques et al. [22] and Belala et al. [24] concluded that such low % of metal removal and equilibrium time were indicative of the bonding of the metal ion onto the active sites on the solid surface with no significant ion diffusion towards the inside of the particles.

Effect of pH

The pH of the solution was reported to be one of the important controlling parameters for metal sorption on biomass [8, 36, 31, 32]. As well, variation in pH was reported to change not only the characteristics and availability of metal ions in solution but also the chemical status of the functional groups responsible for biosorption [22, 32]. More explicitly, at higher pH, these groups may begin to change their activity and binding properties, thus more metal adsorption may be achieved. Figure 4 shows the influence of pH on the adsorption of nickel onto CRH and CDP. The results indicated that overall CRH achieved higher % removals from pH 3-8 which decreased sharply between pH 9 and 10, a pH where the formation of $Ni(OH)_2$ was favored over $Ni(OH)^+$ [32]. As well, it was reported that adsorption of metal ion on rice hush ash was favored at pH 6 and higher, as the number of positively charged sites on the adsorbent decreases and the negatively charged sites increased [32]. As for DP, a sharp decrease in metal ion removal was observed at pH 5, which was followed by a gradual increase thereafter till pH 9. This may be attributed to the fact that date pits were reported to be acidic in nature (pH solution = 4.6) with carboxylic and other functional groups that become protonated at low pH values and, thus, become repulsive towards metal ions [33, 34]. In both cases, previous studies indicated that the optimal pH for the removal of Ni(II) ion from solution was pH 6 [8, 23, 32, 33]. In addition, metal removal above pH 8.5-9 should be avoided as it may lead to the precipitation of its hydroxide [8, 23, 32, 33].

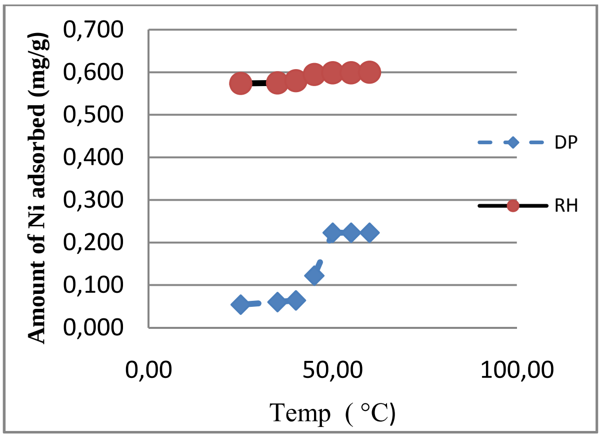

Fig. 4. The effect of varying the pH upon the amount of Ni (II) adsorbed (mg/g) at t = 120 min, T = 25ºC, volume of solution 50 mL, and CDP wt = 50 g/L and CRH = 40g/L.

Effect of temperature and adsorption kinetics

The relationship between the Ni uptake% by rice husks and dates pits at different temperatures (25-60°C) was investigated and the results are illustrated in Figure 5. It was clear from the plots that CRH achieved higher adsorption rates (over 90%) and remained almost constant throughout the studied temperature range (q_e = 0.574-0.600 mg/g). On the other hand, metal adsorption onto CDP was noted to increase sharply from 40ºC to 50ºC (q_e = 0.064-0.223 mg/g). This increase in adsorption indicated that the rise in temperature favored the adsorbate transport within the pores of the adsorbent, i.e. the process was endothermic.

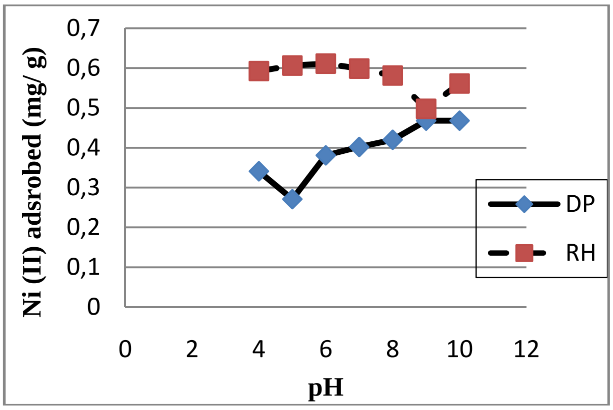

Fig.5. The effect of varying the temperature (25-60ºC) upon the amount of Ni (II) adsorbed (mg/g) at pH 6, t = 120 min, volume of solution 50 mL, and CDP wt = 50 g/L and CRH = 40g/L.

On the other hand, temperature is one of parameters that significantly influence the rate of reaction [22]. Four temperatures were used for the investigation of the process kinetics (25, 30, 40 and 50ºC) and the contact time was varied between 1-60 min (pH = 6, and C_o = 25 mg/L). Numerous kinetic models have been used to describe the reaction order of adsorption systems based on solution concentration [3, 35, 36]. To test the experimental data obtained, two different kinetic models were used, namely: the pseudo-first-order and pseudo-second-order Lagergren equations presented by Ho [35]. For the pseudo-first order rate, the equation used was:

$$\log (q_e - q_t) = \log (q_e) - k_1 t/2.303 \qquad (3)$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t, respectively. The rate constant k_1 (min^{-1}) and the process activation energy were obtained from the slope of the plot of log (q_e–q_t) vs. t for each adsorbent [3, 36]. The equation used for pseudo second-order rate was:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \;\ldots\ldots \qquad \ldots.(4)$$

where k_2 is the rate constant of second-order adsorption and the slopes of the plots of t/q_t versus t were used to determine the second order rate constant k_2 as well as the process activation energy [3, 36]. The values for the kinetic parameters calculated for the pseudo first and pseudo second rate of reaction for the adsorption of Ni (II) onto CRH and CDP are provided in Table 3. The correlation coefficients obtained from these calculations indicated that the adsorption of Ni (II) onto DP was best fitted by first order kinetics. Previous investigations of the use of raw DP as sorbent for divalent Cd ion removal solution indicated that the process was a second order endothermic process [24]. As well, previous studies conducted using raw and activated date pits indicated that the using sorbent material with particle size <1.0 mm followed 2nd order kinetics [14, 23, 24]. Nevertheless, it was reported that the adsorption of Ni (II) onto carbonized peanut hulls (particle size 0.575 mm) [28] as well as the use *Calotrpis procera* biomass without particle size grading [8] followed 1st order kinetics. However, some researchers indicated that the q_e values obtained during these removal studies were not affected with the increase in solution temperature [24]. In contrast, in the current study, q_e for the adsorption of Ni(II) onto CDP did increase significantly goingfrom 40ºC to 50ºC (0.064 mg/g to 0.223 mg/g, respectively).

On the other hand, the results obtained herewith indicated that the adsorption of nickel onto CRH was pseudo second order. This is in agreement with previous findings of Bansal et al. [20] and Srivastava et al. [32] which indicated that adsorption of Ni onto raw RH and RH ash followed the second order rate kinetics. Furthermore, the applicability of pseudo-second order rate in these cases may imply that the rate limiting step involved two species namely: the metal ion and biomass [30].

The increase in the reaction rate constant for both CDP and CRH may be described using the Arrhenius equation:

$$\ln k = \ln A_0 - E_a / RT \;\ldots\ldots\ldots \qquad (5)$$

where A_0 is the Arrhenius constant, regardless of temperature, E_a the activation energy (kJ mol^{-1}) and R is the gas constant (8.314 J mol^{-1} K^{-1}). From the plot of ln k and 1/T, the activation energy for the adsorption of Ni onto CDP was found to be E_a = 7.84 kJ/mole and for CRH, it was E_a = 18.502 kJ/mole. The range for activation energy where physisorption predominates was given as 5-20 kJ/ mol [22; 24] or the extended range of 5-40 kJ/mol^{-1} [37]. Moreover, the low speed (time) of reaction reflected that the fact it was physical adsorption process [22, 24]. Nonetheless, obtaining activation energies within the range of 40-800 kJ/mol was considered to reflect a chemisorption process [37]. This may be because chemical adsorption was a specific process that involved much stronger forces equal in magnitude to that in chemical reactions (20 -420 kJ/mol) [38].

Table 3
Kinetic parameters calculated for the sorption of Ni(II) onto CDP and CRH at different temperatures (K), where R^2 is the correlation coefficient

Adsorbent	Temp (K)	q_e (mg/g) calculated	Pseudo-first-order		Pseudo-second-order	
			K_1(min^{-1})x 10^{-2}	R^2	K_2(g mg^{-1} min^{-1}) x10^{-1}	R^2
Carbonized dates pits	298	0.22	1.27	0.9930	4.12	0.8471
	308	0.24	1.31	0.9945	4.70	0.8809
	318	0.26	1.43	0.9986	5.64	0.9195
	328	0.89	1.70	0.9865	5.44	0.9084
Carbonized rice husks	298	2.30	1.41	0.9784	19.45	0.9989
	308	2.30	1.50	0.9027	24.20	0.9997
	318	2.32	0.99	0.9165	45.01	0.9998
	328	2.40	2.33	0.9228	33.40	0.9998

The thermodynamic parameters for the adsorption process of nickel onto dates pit and rice husks were calculated using

$$\ln K_D = \Delta S^o/R - \Delta H^o/RT……… \quad (6)$$

where K_D is the distribution coefficient (ml/g), ΔS^o is standard entropy (J/mol. K), ΔH^o is standard enthalpy (kJ/mol), T is the absolute temperature (K), and R is the gas constant (8.314 J/mol. K). The standard Gibbs free energy ΔG^o values (kJ/mol) were calculated using the following equation:

$$\Delta G^o= \Delta H^o- T\Delta S^o ……. \quad (7)$$

The values of ΔH^o, ΔS^o and ΔG^o were calculated from the slopes and intercepts from linear plot of ln K_D versus 1/T and the results are provided in Table 4. Essentially, obtaining positive values obtained for enthalpy change ΔH^o were indicative of the endothermic nature of the biosorption of Ni(II) onto CDP and CRH [38, 39]. On the other hand, negative values for Gibbs' free energy were reported to reflect the spontaneity of the process which did increase with the rise in temperature. The noted change in entropy for the adsorption system may be attributed to the increase in randomness at the solid/ solution interface during the biosorption process [39]. This may be explained on the basis of the increase in dehydration steps of the adsorbate ions, which possess relatively high energies of salvation and, thus, were stabilized by water sheaths in the absences of the adsorbent [39]. Generally, the change in adsorption enthalpy for physicorption was reported to range from -20 to 40 kJ/ mol and that for chemisorption was between -400 and -80 [27], which is in agreement with the current reported values. Furthermore, obtaining a slightly positive entropy was indicative of an irregular increase of randomness at the adsorbent/ solution interface during adsorption, an observation concluded from this study results.

Table 4
Thermodynamic parameters for the adsorption of Ni(II) on CDP and CRH.

Adsorbent	ΔH^o (kJ/mol)	ΔS^o (kJ/mol. K)	ΔG^o (kJ/mol)			
			298	308	318	328
Carbonized Date Pits	55.46	0.192	-1.610	-3.525	-5.440	-7.356
Carbonized Rice Husks	21.62	0.119	-13.756	-14.944	-16.131	-17.319

Adsorption Isotherms

Sorption isotherms represent the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium [3, 36]. Both Langmuir and Freundlich isotherm models have been shown to be suitable for describing short-term and mono component adsorption of metal ions by different biosorbent materials. In the current study, the Langmuir and Freundlich isotherms were used to interpret the sorption equilibrium data. The linear equation for Freundlich isotherm applied was [16, 21]:

$$\log q_e = \log K_f + 1/n \log C_e \ldots\ldots \qquad \ldots(8)$$

where K_f is correlated with the quantity of sorbate associated with the sorbent, and n is the Freundlich isotherm constant related to the strength of the sorption. Freundlich isotherm model is based upon the assumption that sorption occurs on heterogeneous surfaces and K_f may be useful for the evaluation of the adsorption capacity of metal ions in dilute solutions [23]. Overall, the Freundlich constants (K_f and n) relate to sorption capacity and sorption intensity of the sorbent, respectively. The values obtained for K_f and (n) were noted to affect the adsorption isotherm, as the larger the values obtained indicate the higher the adsorption capacity [20]. As well, the magnitude of n gives an indication of the favorability of adsorption. In other words, if the value obtained are within the range of 2-10 it indicates a good adsorption characteristics while values between 1-2 reflect moderately difficult and less than 1 have poor adsorption characteristics. As well, $1/n$ values obtained between ($0<1/n<1$) may signify that the surface of the biosorbent was heterogeneous in nature [30].

A plot of log q_e vs. log C_e for CRH and CDP is provided in Figure 6 and the results are presented in Table 5. Based upon the correlation coefficient and the value of n for CDP and CRH, it may be concluded that the experimental data better fitted the Freundlich model. However, the magnitude of n for CRH was within the range 1-2 which indicates that the process was moderately difficult than that applying CDP [20]. In addition, the obtained R^2 values were greater than 0.9 for the Freundlich isotherm, which may be indicative of a multilayer adsorption with physio-sorption type [8].

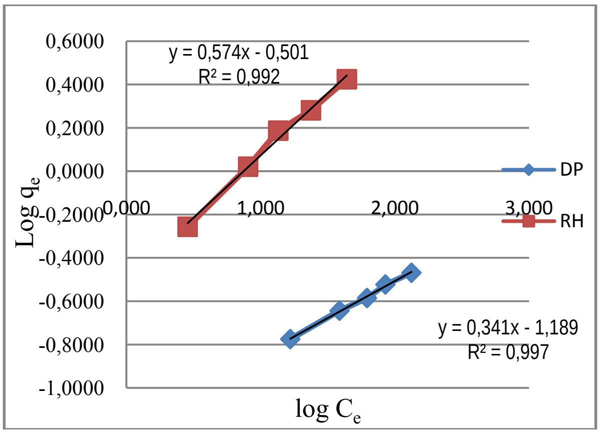

Fig. 6. Freundlich isotherm for Nickel adsorption onto CDP and CRH

The Langmuir isotherm utilized for the sorption equilibrium of CDP and CRH [21] was:

$$C_e/q_e = 1/b\ Q_0 + C_e/Q_0 \ldots\ldots \qquad (9)$$

where Q_0 and b are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively. A plot of C_e/q_e vs. C_e resulted in a straight line with a slope of ($1/Q_0$) and intercept of $1/b\ Q_0$ is depicted in Figure 7 and the values for the slope and intercept of this plot are in provided in Table 5. Essentially, the Langmuir treatment is based upon the assumption that maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface where the energy of adsorption is constant and no transmigration of adsorbate into the plane of the surface may occur [28]. The Langmuir constant b reflects quantitatively the affinity between the adsorbent and adsorbate and the lower the value obtained the more affinity of metal to adsorbent material [26]. In addition, the adsorption capacity may indicate the correlation between the variation of surface area and porosity of the adsorbent, i.e. the higher the surface area and pore volume provide for a higher capacity of metal ion adsorption [23].

The essential characteristics of Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter R_L, which is defined as [28]:

$$R_L = 1/\,(1+bC_o) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad .(10)$$

where b is the Langmuir constant (L/ mg) and C_o (mg/L) is the initial concentration of nickel. There are 4 probabilities for the value of R_L: for favorable adsorption $0<R_L<1$; for unfavorable adsorption $R_L >1$; for linear adsorption $R_L=1$ and for irreversible adsorption $R_L=0$ [20]. In this study, the values for R_L obtained for the studied system indicated the favorability of Ni(II) adsorption onto both CDP and CRH.

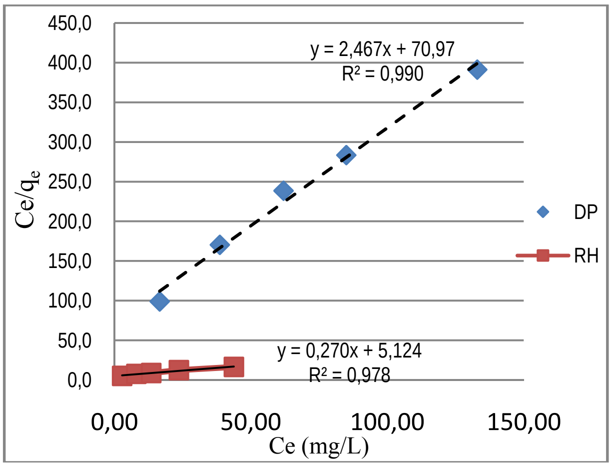

Fig. 7. Langmuir isotherm for nickel sorption onto dates pit and rice husks

Previous studies concerning the adsorption of Ni ions from solution onto the different biosorbent materials revealed that the process followed both the Freundlich and Langmuir models for carbonized peanut hulls [28]; raw RH [20] and rice straw [27]. On the other hand, the application of raw DP for the removal of divalent ions from solution was reported to follow the Freundlich model [23] while the application of activated DP followed the Langmuir model [14, 23]. From Table 5, it can be seen that adsorption of Ni on CDP follows the two adsorption models whereas the Freundlich model better fitted to the Ni adsorption to CRH. Furthermore, the values for R^2 obtained for Freundlich isotherm were greater than 0.9 which may reflect the fact that the adsorption was multilayered and physio-sorption type [8]. On the other hand, the Langmuir constant Q_o obtained showed that RH had a higher adsorption capacity or a higher estimated monolayer surface coverage towards Ni (II) than DP. This is in agreement with the findings of Al-Muhtaseb et al. [14]. This maximum sorption capacity may be attributed to having a complete monolayer coverage [40]. As well, the affinity constant (*b*) values obtained herewith, which is related to adsorption energy, was comparable for both materials indicating that probably not all binding sites on the surface of CDP were available for Ni binding due to its relative hydration energy.

Table 5

Isotherm constants and values of R^2 for carbonized date pits and carbonized rice husks

Adsorbent	Freundlich Isotherm				Langmuir Isotherm			
	1/n (mg/L)	n (L/mg)	Log K (K mg/g)	R^2	Q_o (mg/g)	b (L/mg)	R_L	R^2
CDP	0.3411	2.932	1.1893 (15.46)	0.9973	0.405	0.0348	0.5348	0.9905
CRH	0.5746	1.740	0.5017 (3.175)	0.9922	3.694	0.0528	0.4310	0.9785

Conclusion

The adsorption of nickel from liquid solutions onto carbonized date pits and rice husks has been investigated in the current study. The process was studied in a batch system with respect to the initial pH, contact time, temperature, adsorbent dose and nickel initial concentration. The results showed that the experimental data was well represented by first order model for CDP and second order model for CRH. Based on the kinetic modeling, the apparent activation energies calculated were 7.84 kJ and 18.502 kJ/mol for CDP and CRH, respectively. The results also indicated that process of nickel uptake by CDP and CRH was physical adsorption process. The equilibrium data for CDP indicated that it fitted both Freundlich and Langmuir models. However, adsorption onto CRH fitted Freundlich model better based upon the higher value of R^2 obtained. The thermodynamic parameters (ΔH^o, ΔS^o and ΔG^o) calculated from the experimental data indicated that the process was endothermic and spontaneous.

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