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Dehydrated hazelnut husk carbon: a novel sorbent for removal of Ni(II) ions from aqueous solution

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ABSTRACT

The present study has been performed to examine the adsorption ability of novel sorbent dehydrated hazelnut husk carbon (DHHC) towards Ni(II) ions from aqueous solution using the batch adsorption technique. The effective factors such as initial pH of the aqueous solution, contact time, initial Ni(II) concentration, adsorbent dosage, and temperature were investigated. The studies were also conducted to understand the effect of some co-existing ions which may be present in aqueous solutions. DHHC showed good adsorption potential for Ni(II) ions. The optimum initial pH value was selected as 5.0. The experimental data fitted well to the Langmuir adsorption isotherm model. Among the kinetic models tested for the adsorption of Ni(II), the pseudo-second-order model showed a good fit of the kinetic data. The thermodynamic parameters including the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes indicated that the adsorption of Ni(II) ions onto DHHC was feasible, spontaneous, and exothermic in the temperature range of 25–55°C. The results of this study showed the effectiveness and feasibility of DHHC for the removal of Ni(II) ions from aqueous solution.

Keywords: Ni(II); Removal; Adsorption; Activated carbon; Hazelnut husk

1. Introduction

Many heavy metal ions have toxicological properties for ecosystems and human health and also, unlike organic pollutants, heavy metal ions are non-biodegradable in the environment and can accumulate in living organisms [1–3].

Nickel can be found in the effluent of silver refineries, electroplating, zinc base casting, and storage battery industries [4,5]. Nickel and its compounds are hazardous to human health and the environment. Some nickel compounds are carcinogenic and easily absorbed by the skin [6]. High concentration of nickel causes cancer of lungs, nose, and bone [7,8]. Hence, nickel containing wastewater should be treated before discharge.

A number of conventional methods including extraction, chemical precipitation, reverse osmosis, ion exchange, filtration, membrane processes, evaporation, and coagulation have been used for the treatment of heavy metal contaminated wastewaters. Incomplete metal removal, high consumptions of reagent and energy, low selectivity, high capital, operational cost, and generation of secondary wastes are the main drawbacks of the conventional treatment methods [2,9,10].

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Besides the classical wastewater treatment techniques, adsorption may be the favorite in many cases due to its economical advantages and ease of applicability and high efficiency in removing very low levels of heavy metals from dilute solutions [11,12]. In the adsorption technique, several sorbents including silica gel, activated alumina, oxides and hydroxides of metals, zeolites, clay minerals, synthetic polymers, and carbonaceous materials, such as activated carbon (AC) and molecular carbon sieves have been used [13–23].

AC is the most attractive sorbent for the removal of different contaminants from waters and wastewaters due to its excellent properties such as porosity, easy regeneration, large surface area, and high adsorption capacity. Because of the high cost of commercial AC, new, economical and easily available sorbents are required, which comprise a strong adsorbent having high affinity and loading capacity. In recent years, agricultural waste materials which are locally available in large quantities have been focused by the scientists for the preparation of low cost sorbents [13,24]. ACs can be prepared using physical or chemical methods. Various chemicals such as $ZnCl_2$, H_3PO_4, H_2SO_4, KOH, and $CaCl_2$ are used in the production process of AC by chemical activation methods at elevated temperatures [25,26]. Another important method for the preparation of carbonaceous sorbent from lignocellulosic waste materials is dehydration process using sulfuric acid at low temperatures. Some of the reported sorbents prepared by this technique include wheat bran carbon [27], Indian rosewood sawdust carbon [28], sunflower head and sunflower stem carbonaceous adsorbent [29], fruit shell carbon of Indian almond [30], dehydrated peanut hull [31], and parthenium carbon [32].

In the present work, hazelnut husk (HH) was used as a precursor for the preparation of novel carbonaceous sorbent material by treatment with sulfuric acid. Hazelnuts are produced in commercial quantities in Turkey, Italy, and USA [33]. HH is a green and leafy husk, and surrounds the brown shell (hazelnut shell) including the nut. Waste materials of hazelnut cultivation are hazelnut shell and HH. While hazelnut shell has been used as a fuel, HH is waste material of hazelnut production and is not utilized for any purpose and hence, it does not have any economical value. HH production of Turkey was reported as 1.39×10^5 t/y in the literature [34]. Hence, it has a great potential with zero price and huge amounts. While a number of hazelnut shell based sorbents were reported, HH based sorbents was a few in the literature. Imamoglu and Tekir [34] were prepared AC from HH using $ZnCl_2$ activation methods. This study is the first report about the preparation of dehydrated HH carbonaceous sorbent material.

The objective of this study was to investigate the adsorption potential of dehydrated hazelnut husk carbon (DHHC) for the removal of Ni(II) ions from aqueous solutions. The effects of several parameters such as contact time, initial pH of Ni(II) solution, initial Ni (II) concentration, DHHC dosage, etc. were evaluated in detail in the adsorption process. Furthermore, the interferences of alkali metal ions on the Ni(II) uptake were studied. The adsorption mechanisms of Ni(II) ions were evaluated in terms of thermodynamics and kinetics. The adsorption isotherms were described using Langmuir and Freundlich models.

2. Materials and methods

2.1. Preparation of DHHC

The HH was obtained from the Ardıçbeli village of Sakarya-Turkey. The husks were washed with deionized water, dried at 105°C and crushed in a mortar and coffee grinder machine. Then, they were sieved and 53–106 μm fractions were used for the preparation of DHHC. The precursor were treated in a 1:1 weight ratio with concentrated H_2SO_4 (w/w, 98%) for 24 h. The obtained material was washed with hot deionized water and then soaked in 1% $NaHCO_3$ solution to remove any remaining acid. Then, DHHC was washed with deionized water until the pH of the material reached 6.0 and dried at 105°C for 4 h.

2.2. Adsorption experiments

All chemicals used in this work were of analytical reagent grade and were used without further purification. Deionized water (chemical resistivity:18 $M\Omega\,cm^{-1}$) was used throughout the study. All glassware and plastics used were soaked in 10% (v/v) nitric acid solution for 1 day before being used and then cleaned repeatedly with deionized water. The Ni(II) stock solution was prepared as 1,000 $mg\,L^{-1}$ by dissolving appropriate amounts of $NiSO_4 \cdot 6H_2O$ in deionized water. The required concentrations of working solutions were prepared by dilution of the stock solution. The pH of the working solutions was adjusted using dilute HCl or NaOH solutions. The studies for adsorption of Ni(II) ions onto DHHC were carried out using the batch technique. For that purpose, 50 mL of Ni(II) solution in the concentration range of 25–200 $mg\,L^{-1}$ was transferred into a glass flask. Definite amount (50–150 mg) of DHHC was added to this solution and the mixture was agitated in an incubator orbital shaker (IKA, KS 4000i) at 250 rpm for 24 h (except in effect of contact time studies). The suspension was then filtered through the blue ribbon filter paper (Whatmann or Macherey-Nagel) and the filtrate was analyzed for the Ni(II) concentration by a flame atomic absorption spectrometer, FAAS (Shimadzu AA6701F). All experiments were conducted in triplicate and the averages of the results were presented in this study.

The amount of Ni(II) adsorbed at time t (min) onto DHHC (q_t, $\mathrm{mg\,g^{-1}}$) was calculated by a mass balance relationship,

$$q_t = (C_o - C_t)\frac{V}{m} \tag{1}$$

where C_o ($\mathrm{mg\,L^{-1}}$) is the initial Ni(II) concentration in solution; C_t ($\mathrm{mg\,L^{-1}}$) is the residual Ni(II) concentration in solution at time t; V (L) is the solution volume; m (g) is the DHHC mass.

Adsorption % was calculated by using Eq. (2)

$$\text{Adsorption }(\%) = \frac{C_o - C_t}{C_o} \times 100 \tag{2}$$

3. Results and discussion

3.1. Characterization of DHHC

The surface functional groups of DHHC were investigated using FTIR spectroscopy and the spectrum is shown in Fig. 1. The peaks observed at 2,926 and 2,849 $\mathrm{cm^{-1}}$ were due to C–H strechings. The peaks at 1,703 and 1,598 $\mathrm{cm^{-1}}$ were attributed to C=O and C=C vibrations, respectively. The broad peak at 1,180 $\mathrm{cm^{-1}}$ that could be regarded as C–O bond belongs to $\mathrm{COO^-}$ groups. Furthermore, the deformation of the bands between 3,600 and 2,200 $\mathrm{cm^{-1}}$ could be assumed that the $-\mathrm{CH_2OH}$ groups of the cellulosic structure of HH oxidized to acid groups.

A scanning electron microscope (SEM) analysis was used to investigate the surface texture and morphology of DHHC. According to SEM image depicted in Fig. 2, the surface of DHHC exhibits porous structure.

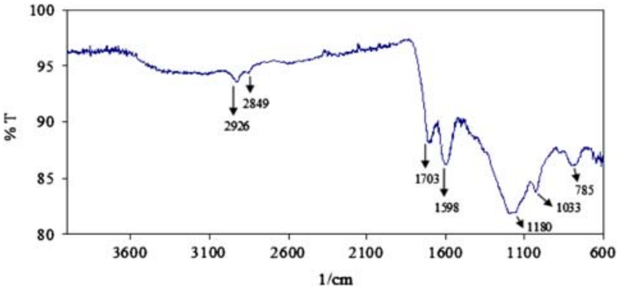

Fig. 1. FTIR spectrum of DHHC.

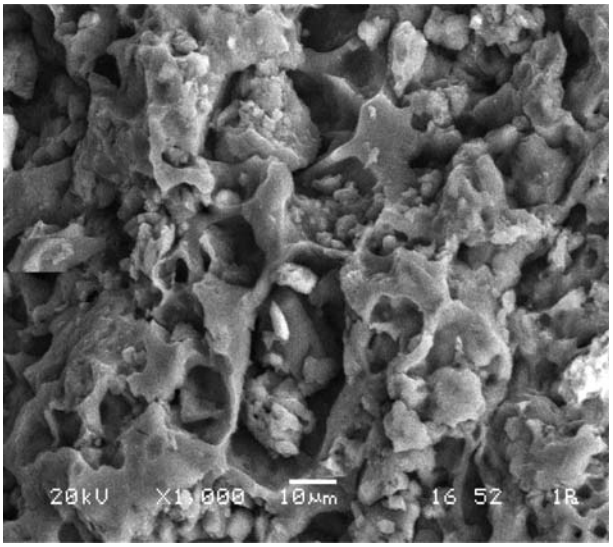

Fig. 2. SEM images of DHHC (magnification: 1,000 folds).

The BET surface area of DHHC was obtained by applying the BET equation to N_2 adsorption at 77 K and given in Table 1. The elemental analysis of DHHC was determined and the percentage amount of C, H, N, S, and O contents is also given in Table 1. The surface acidic functional groups were determined by Boehm titration according to the literature [35–37]. Treatment of HHs with sulfuric acid created carbonized material bearing a high amount of total acidic groups value and hence, it is expected that DHHC should have a great affinity for Ni(II) ions. Point of zero charge ($\mathrm{pH_{PZC}}$) is another important characteristic of the ACs. $\mathrm{pH_{PZC}}$ of DHHC was determined according to the literature [38] and given in Table 1. At a higher pH of solution than $\mathrm{pH_{PZC}}$, the surface will be negatively charged and otherwise will be positively charged. All other characterization parameters were determined using standard methods [39] and listed in Table 1. Iodine number of the AC is important because it is accepted as model molecules of small (pore diameter <1 nm) adsorbates.

3.2. Effect of initial pH and its optimization

It is well known that pH of the batch adsorption system is one of the main factors which seriously affects the amount of adsorbed metal ions.

The adsorption of Ni(II) ions onto DHHC was studied over the initial pH range of 1.0–6.0 at initial Ni(II) concentrations of 50 and 100 $\mathrm{mg\,L^{-1}}$. The initial

Table 1
Characteristics of DHHC

Elemental analysis (wt.%)	
C	60.07
H	3.61
N	0.85
S	1.39
O[a]	34.08
Surface functional groups (mmol g^{-1})	
Carboxylic	0.80
Phenolic	1.41
Lactonic	0.79
Total acidic value	3.00
Iodine number (mg g^{-1})	88.8
pH_{PZC}	5.30
BET surface area ($m^2 g^{-1}$)	35.7
Moisture (wt, %)	11.30
Volatile matter (wt, %)	66.90
Fixed carbon (wt, %)	31.80
Ashes (wt, %)	1.30

[a] By difference.

pH value of the aqueous solution was adjusted in the range of 1.0–6.0 to avoid especially the chemical precipitation of Ni(II) as $Ni(OH)_2$. Fig. 3 shows the effect of initial pH on the adsorption of Ni(II) by DHHC. A steep increase in adsorption amount of Ni(II) ions was observed by increasing the initial pH from 1.0 to 4.0, indicating that the adsorption was highly pH dependent. The adsorption efficiencies increased from 0 to 26.4 mg g^{-1} (0–52.8%) and from 2 to 32.5 mg g^{-1} (2–32.5%) for initial Ni(II) concentrations of 50 and 100 mg L^{-1}, respectively, by increasing the initial pH from 1.0 to 4.0. Small increases were observed in the adsorbed amount of Ni(II) with increasing the initial pH from 4.0 to 6.0 (Fig. 3).

Both surface charge of the adsorbent and ionization degree of the metal ions were determined by the pH of the adsorption system. At highly acidic pH values the surface of DHHC was associated with H_3O^+ ions and the competition between the metal cations and H_3O^+ ions for the active adsorption sites on the surface of the adsorbent lead to decrease in uptake of metal ions. On the other hand as the pH value was increased, the surface of DHHC became more negatively charged and hence electrostatic repulsion between the metal cations and adsorbent surface sites and competing effect of H_3O^+ ions decreased which in turn increased the adsorption amount of metal ions onto DHHC [40–43].

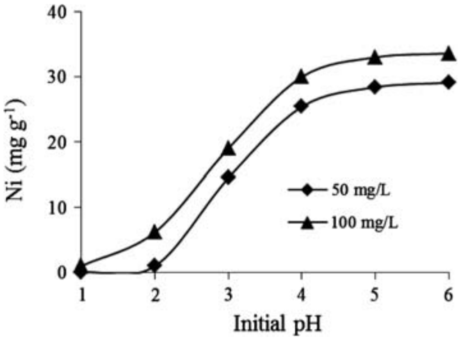

Fig. 3. Effect of initial pH on the adsorption of Ni(II) (initial Ni(II) concentrations: 50 and 100 mg L^{-1}, amount of DHHC: 50 mg, solution volume: 50 mL, contact time: 24 h).

Different cationic and/or anionic species of metal ions are formed by changing the pH of the solution. Most cations such as Cu(II), Pb(II), and Ni(II) are hydrolyzed beyond pH 6. Hydrolysis of divalent metal ions can be written as (Eq. (3)) [44].

$$M^{2+}(aq) + nH_2O \rightleftharpoons M(OH)_n^{2-n} + nH^+ \qquad (3)$$

These metal ion species in aqueous solution should be considered for the selection of optimum pH in adsorption studies [45]. According to the speciation diagram of Ni(II) given in the literature, the percentage of free divalent Ni(II) ions in aqueous solution is almost 100% at $pH \leq 8.0$ [45,46]. Hence, Ni(II) adsorption may occur at the studied pH values by electrostatic attraction between negatively charged surface and metal ions [47]. From the results, pH 5.0 was selected for further adsorption tests of Ni(II) onto DHHC.

3.3. The effect of contact time and kinetics of adsorption

The effect of contact time on Ni(II) adsorption onto DHHC at different initial Ni(II) concentrations is shown in Fig. 4. From Fig. 4, the Ni(II) adsorption amount onto DHHC increased quickly within the first hour of adsorption for all initial Ni(II) concentrations. After 1 h contact time, adsorbed amount of Ni(II) was increased slowly. The increase in the contact time allowed greater amounts of Ni(II) ions to be removed from the aqueous solution and the adsorption equilibrium was almost established within the 10 h of contact for 30, 50, and 70 mg L^{-1} of initial concentrations of Ni (II). But, for practical reasons, the subsequent experiments were run for 24 h.

The adsorption mechanism of Ni(II) ions onto DHHC was explained by utilizing three different kinetic models, namely pseudo-first order, pseudo-second-order, and intraparticle diffusion models.

The pseudo-first-order kinetic model of Lagergren is widely used for adsorption [48] and given in the linear form (4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of the metal ion adsorbed on the sorbent at equilibrium and at any time t, respectively; and k_1 (min^{-1}) is the rate constant of the first-order model. The value of k_1 and q_e can be calculated from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ vs. t, respectively.

The pseudo-second-order kinetic model can be given in the following linear form [49,50]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the second-order equation; q_e (mg g^{-1}) is the maximum adsorption capacity; q_t (mg g^{-1}) is the amount of adsorption at time t (min). The values of q_e and k_2 can be determined from the slope and intercept of the plot of t/q_t against t, respectively.

The linear graphs of $\ln(q_e - q_t)$ vs. t for the pseudo-first order kinetic model were plotted in order to determine the suitability of pseudo-first order kinetic model (Fig. 5(b)), and the rate constant k_1 and q_e values were calculated from the slope and intercept of the graphs, respectively (Table 2). The obtained correlation coefficient (r^2) values are not high and the experimental q_e values are not compatible with the calculated q_e values. Therefore the pseudo-first-order model is not suitable for modeling the adsorption of Ni(II) onto DHHC. Many examples of this situation have been reported in the literature [51].

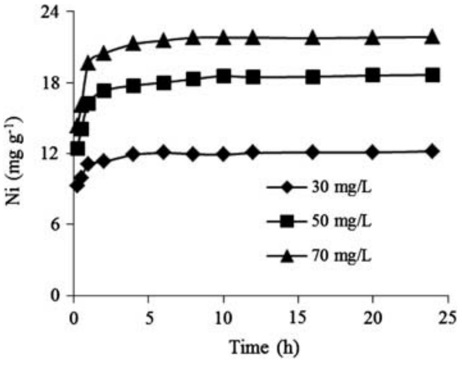

Fig. 4. Effect of contact time on the adsorption of Ni(II) (initial Ni(II) concentrations: 30, 50, and 70 mg L^{-1}, amount of DHHC: 100 mg, solution volume: 50 mL, pH of solution: 5.0).

The linear plots of t/q_t vs. t for the pseudo-second-order kinetic model are shown in Fig. 5(a). The pseudo-second-order rate constant k_2 and the value of q_e were determined from the model and given in Table 2. It can be seen that the calculated r^2 is very close or equal to unity and that the calculated q_e values agree well with experimental ones. These results suggested that the pseudo-second order model describes the adsorption kinetics of the studied system more appropriately than the pseudo-first order model.

In order to analyze the mechanism of the adsorption of Ni(II) ions onto DHHC, an intraparticle diffusion model was also investigated in which the governing equation reads as [52]:

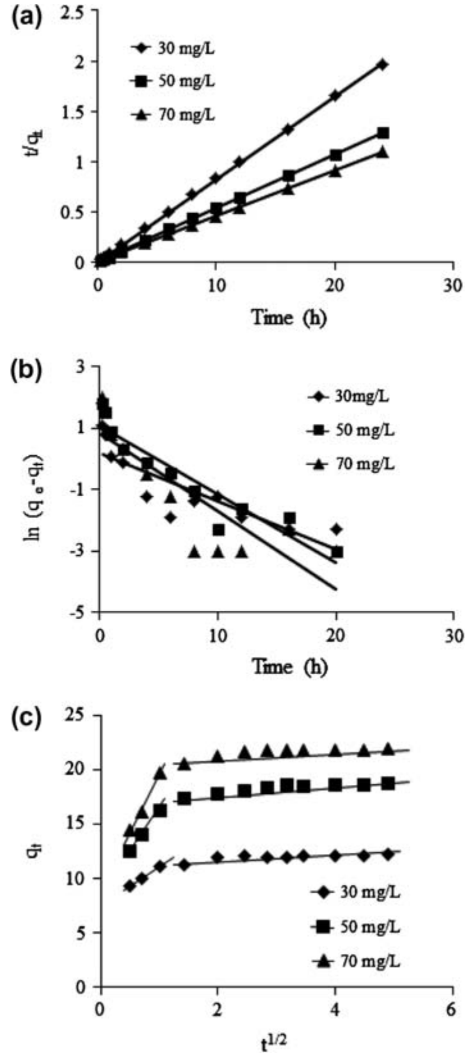

Fig. 5. Kinetic models for Ni(II) adsorption onto DHHC; (a) pseudo-second order, (b) pseudo-first order, and (c) intraparticle diffusion models.

Table 2
Parameters of pseudo-first-order and pseudo-second-order kinetic models

		Pseudo-first-order			Pseudo-second-order		
C_o (mg L^{-1})	$q_{\text{e exp}}$ (mg g^{-1})	k_1 (h^{-1})	$q_{\text{e cal}}$ (mg g^{-1})	r^2	k_2 ($\text{g mg}^{-1}\,\text{h}^{-1}$)	$q_{\text{e cal}}$ (mg g^{-1})	r^2
30	12.20	0.157	1.22	0.7408	0.6269	12.21	0.9999
50	18.65	0.223	2.95	0.8758	0.2991	18.76	1
70	21.85	0.254	2.30	0.7222	0.3569	21.98	1

$$q_t = k_{\text{id}} t^{1/2} + c \tag{6}$$

where q_t (mg g^{-1}) is the amount of adsorption at time t (min), k_{id} ($\text{mg g}^{-1}\,\text{min}^{-1/2}$) is the rate constant of intraparticle diffusion. The values of k_{id} and c can be obtained from the slope and intercept of the plot of straight line of q_t vs. $t^{1/2}$, respectively.

According to intraparticle diffusion model, in batch adsorption processes, the adsorbates diffuse into the interior of the porous adsorbent and the process rate usually depends upon $t^{1/2}$ rather than t. Fig. 5(c) shows the extent of adsorption of Ni(II) as a function of square-root of time at three different initial Ni(II) concentrations. Multilinearities were observed in Fig. 5(c) for all initial Ni(II) concentrations, indicating that two steps took place, that is, more than one process affected the adsorption of Ni (II). The first step was referred to the diffusion of Ni(II) through the solution to the external surface of DHHC. The second step could be expressed as the gradual adsorption stage, where intraparticle diffusion was rate limiting [53]. The intraparticle diffusion constants k_{id} and c were determined from the slope and intercept of the second linear portion of the plots, respectively (Table 3). Also, from Fig. 5(c), it might be observed that the straight line for intraparticle diffusion did not pass through the origin for all initial Ni(II) concentration, and this further indicated that the intraparticle diffusion was not only the rate controlling step. It can be said that the removal of Ni(II) from aqueous solution is a complex process involving both boundary layer diffusion and intraparticle diffusion.

3.4. Effect of AC dosage

To investigate the effect of DHHC dosage on the adsorption of Ni(II), the process was carried out with initial Ni(II) concentrations of 100 and 200 mg L^{-1} and various DHHC quantities (0.05–0.4 g). At equilibrium, the Ni(II) uptake (mg g^{-1}) in each system was determined and plotted as a function of DHHC quantity, as displayed in Fig. 6. As can be seen from Fig. 6, as the quantity of DHHC was increased, the percentage amount of Ni(II) adsorption increased non-linearly. The increase in the percentage of Ni(II) removal with the adsorbent quantity could be attributed to increase in the number of available adsorption sites for adsorption [54,55]. On the contrary, the quantity of Ni(II) uptake per gram of DHHC (mg Ni(II)/g DHHC) increased with decreasing DHHC quantity. Namely, the lowest DHHC quantity (0.05 g) has the highest Ni (II) adsorption capacity (Fig. 6). This decrease in the adsorbed amount of Ni(II) by increasing the DHHC dosage was attributed to unsaturation of adsorption sites through the adsorption of Ni(II) [55,56]. This kind of behavior was also observed for the removal of Cd(II) by Nordmann fir leaves [57].

Table 3
Parameters of intraparticle diffusion model

	Intraparticle diffusion		
C_o (mg L^{-1})	k_{id} ($\text{mg g}^{-1}\,\text{min}^{-1/2}$)	c (mg g^{-1})	r^2
30	0.181	11.373	0.6231
50	0.363	17.076	0.8231
70	0.309	20.584	0.5867

3.5. Effect of initial Ni(II) concentration and adsorption isotherms

The effect of initial Ni(II) concentrations on the uptake of Ni(II) ions by DHHC was investigated by employing the Ni(II) solutions with initial concentrations in the range of 25–200 mg L^{-1} at different DHHC dosage between 50 and 150 mg per 50 mL solution at 25°C. The equilibrium concentration of Ni(II) increased whereas adsorption percentage decreased with the increase of the initial Ni(II) concentration. The results (for 50 mg of DHHC) are given in Table 4.

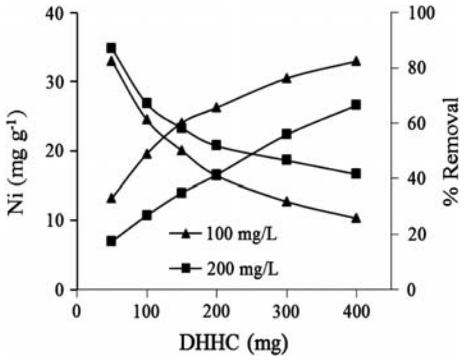

Fig. 6. Effect of DHHC dosage on the adsorption of Ni(II) (initial Ni(II) concentrations: 100 and 200 mg L^{-1}, solution volume: 50 mL, pH of solution: 5.0, contact time: 24 h).

The initial Ni(II) concentration acts as a driving force to overcome mass transfer resistance for Ni(II) transport between the solution and the surface of DHHC. On the other hand, at higher concentrations, the excess amount of Ni(II) ions present in the solution cannot interact with the active binding sites on the DHHC surface because of the saturation of these sites [58].

The relationship between the equilibrium Ni(II) concentration and its uptake by DHHC can be explained by various equilibrium isotherm models such as Langmuir and Freundlich.

Langmuir isotherm model assumes monolayer adsorption on the uniform sorbent surface, which is shown in non-linear form by the following equation [59];

$$q_e = \frac{Kq_{\max}C_e}{1 + KC_e} \tag{7}$$

where q_e (mg g^{-1}) is the amount of the metal adsorbed per unit mass of adsorbent, C_e (mg L^{-1}) is the equilibrium metal concentration in the solution, $q_{\max}$ (mg g^{-1}) is the Langmuir constant related the maximum monolayer adsorption capacity and K (L mg^{-1}) is the constant related to the equilibrium constant or bonding energy.

Table 4
Effect of initial Ni(II) concentration (T: 25℃)

C_o (mg L^{-1})	Equilibrium concentration, C_e (mg L^{-1})	Uptake, q_e (mg g^{-1})	Uptake (%)
25.0	7.9	17.1	68.4
50.0	21.6	28.4	56.8
75.0	42.9	32.1	42.8
100.0	67.0	33.0	33.0
150.0	115.6	34.2	22.8
200.0	165.2	34.8	17.4

The linear form of Langmuir equation is expressed to be;

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{Kq_{\max}} \tag{8}$$

The linear plot of C_e/q_e vs. C_e shows that the adsorption obeys the Langmuir model and the constants $q_{\max}$ and K are determined from the slope and intercept of the linear plot, respectively.

The Freundlich isotherm model is based on the multilayer adsorption on a heterogeneous adsorbent surface and given by the following Eq. (9) in non-linear form [60];

$$q_e = K_f C_e^{1/n} \tag{9}$$

where K_f (mg g^{-1}) and n are the Freundlich constants related to adsorption capacity and intensity (or surface heterogeneity), respectively. The Freundlich isotherm in linear form can be written as follows;

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{10}$$

The values of Freundlich constants K_f and $1/n$ are determined from the intercept and slope of linear plot of $\ln q_e$ vs. $\ln C_e$, respectively [46,61].

The non-linear Langmuir and Freundlich isotherms are shown graphically in Fig. 7 for various DHHC dosages. Fig. 7 depicts the comparison of the experimental and the predicted amount of Ni(II) adsorbed onto DHHC for two studied isotherm models. Clearly, the Langmuir isotherm model was better fitted with the experimental equilibrium data than the Freundlich model. The calculated constants and the correlation coefficients for two isotherm models are given in Table 5. It can be said that the Langmuir model was more applicable than the Freundlich model, since the correlation coefficients were higher for all the dosages. The Langmuir adsorption capacity ($q_{\max}$) of DHHC was compared with the adsorption capacities of other adsorbents in the literature, and the comparative data are given in Table 6. The monolayer adsorption capacity of DHHC for Ni (II) at various dosages was found to be in the range of 24.88–36.36 mg g^{-1}. The adsorption capacity of DHHC was found to be also comparable and in some cases better than the other adsorbents reported in the literature.

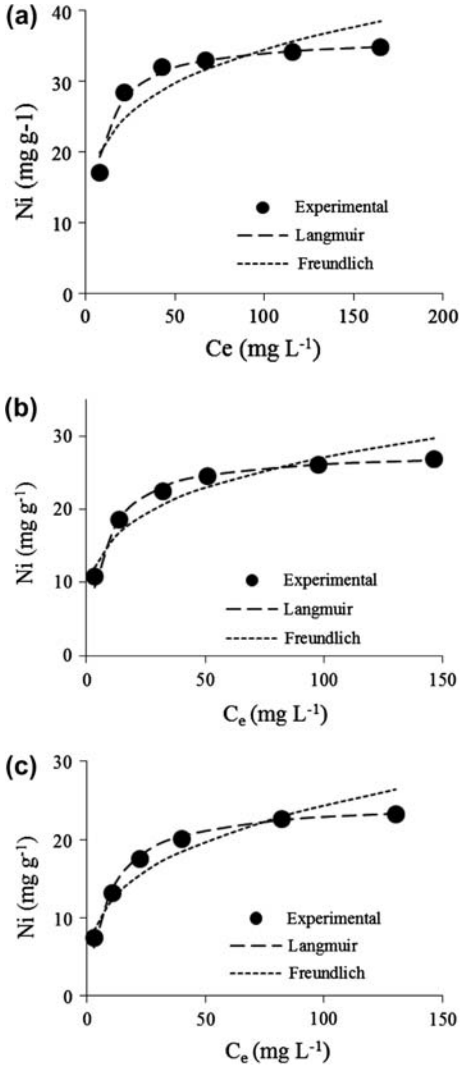

Fig. 7. Relationship between equilibrium Ni(II) concentration and its uptake by DHHC at various DHHC dosage using Langmuir and Freundlich isotherm models: (a) 50 mg, (b) 100 mg, and (c) 150 mg (pH of solution: 5.0, solution volume: 50 mL, contact time: 24 h).

Table 6
Comparison of maximum monolayer adsorption capacity (q_{max}) for Ni(II) on different adsorbents in the literature

Adsorbent	q_{max} (mg g^{-1})	Ref.
Almond husk AC	37.2	[4]
Coirpith AC	62.5	[5]
Punica granatum peel waste	52	[7]
Walnut sawdust	3.3	[26]
Moringa oleifera wood AC	19.8	[28]
AC from Partherium	54.4	[51]
Commercial AC	5.4	[56]
DHHC	36.36	This study

3.6. Effect of temperature and thermodynamics of adsorption

In order to determine the influence of temperature on the adsorption of Ni(II) onto DHHC, the adsorption studies were conducted at 25, 35, 45, and 55°C for initial Ni(II) concentrations of 50 mg L^{-1}. The effect of temperature variations on the adsorption of Ni(II) from aqueous solution is presented in Fig. 8. From the figure, it is seen that the extent of adsorption decreased along with an increase of temperature.

The obtained results showed that the adsorption capacity of DHHC decreased slightly with rising the temperature (Fig.8), indicating the exothermic nature of the Ni(II) adsorption process.

The thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes were used to decide whether the Ni(II) adsorption on DHHC is spontaneous or not. ΔG values were calculated from the following Eq. (11);

$$\Delta G = -RT \ln K_d \tag{11}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and K_d is the distribution coefficient. The K_d value was calculated using the following Eq. (12);

Table 5
Parameters of Langmuir and Freundlich isotherms at different amounts of DHHC (T: 25°C)

	Langmuir constants			Freundlich constants		
Amount of DHHC (mg)	q_{max} (mg g^{-1})	K (L mg^{-1})	r^2	K_f (mg g^{-1})	n	r^2
50	36.36	0.1435	0.9996	12.67	4.59	0.8151
100	27.93	0.1461	0.9998	8.93	4.15	0.9260
150	24.88	0.1151	0.9984	6.01	3.29	0.9420

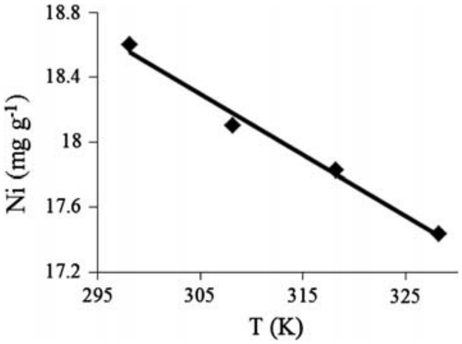

Fig. 8. Effect of temperature on the Ni(II) adsorption by DHHC, (Amount of DHHC: 100 mg, solution volume: 50 mL, initial Ni(II) concentrations: 50 mg L^{-1}, contact time: 24 h, pH of solution: 5.0).

$$K_d = \frac{Q_e}{C_e} \tag{12}$$

where Q_e and C_e are the equilibrium concentration of Ni(II) on DHHC (mg L^{-1}) and in the solution (mg L^{-1}), respectively.

The relation between ΔG, ΔH, and ΔS can be expressed by the following Eqs. (13) and (14);

$$\Delta G = \Delta H - T\Delta S \tag{13}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{14}$$

The values of thermodynamic parameters, ΔH and ΔS, were calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$, respectively [62,63], and the graph is shown in Fig. 9. The values of thermodynamic parameters for the adsorption of Ni(II) ions onto DHHC are given in Table 7. The negative value of ΔH confirmed the exothermic nature of the overall adsorption process. The negative values of ΔG indicated the spontaneous nature of the adsorption process. The magnitude of ΔG also decreased with increasing the temperature indicating that the adsorption of Ni(II) was more favorable at lower temperatures. The negative value of ΔS exhibited the decreased randomness at the solid/solution interface during the adsorption of Ni(II) ions onto DHHC [64–67].

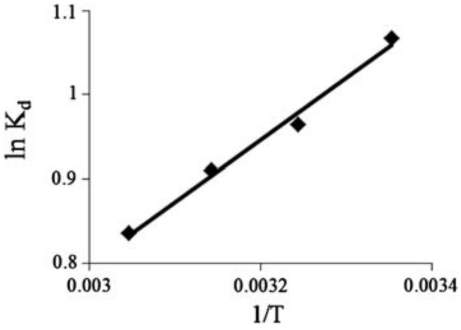

Fig. 9. $\ln K_d$ vs. $1/T$ graph for determination of thermodynamic parameters.

Table 7
Thermodynamic parameters for Ni(II) adsorption on DHHC

T (℃)	ΔG (kJ mol^{-1})	ΔS (J $mol^{-1}K$)[a]	ΔH (kJ mol^{-1})[a]
25	−2.64	−11.70	−6.11
35	−2.47		
45	−2.41		
55	−2.28		

[a]Measured between 298 and 328 K.

3.7. Effect of interfering ions on the adsorption of Ni(II)

In wastewaters and natural waters, the Ni(II) ions are usually present with a number of other metal ions such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, which may interfere with the adsorption of Ni(II) ions onto DHHC. Hence, the effects of these metal ions on the Ni(II) uptake by DHHC were examined. The results showed that the presence of 100 mg L^{-1} of Na^+, K^+, Ca^{2+}, and Mg^{2+}, individually, in 100 mg L^{-1} of Ni(II) solution with a volume of 50 mL containing 100 mg DHHC (2.0 g L^{-1} suspension), partially depressed the adsorption of Ni (II) ions onto DHHC (Fig. 10). Increasing the interfering cationic species can increase the competition with Ni(II) for the DHHC's sorption sites, thus reducing the adsorption yield. In addition, from Fig. 10, the effects of Ca^{2+} and Mg^{2+} are more apparent compared with Na^+ and K^+ ions, because Ca^{2+} and Mg^{2+} can screen more negative charges on DHHC surface, thus exhibiting a higher inhibition of Ni(II) adsorption than Na^+ and K^+ [68]. Similar results were reported in the literature [57,69,70].

3.8. Desorption of Ni(II) ions

Desorption is also a very important concern to allow for reusing the adsorbent and reduce process costs. It is desired that the adsorbent should be close to its original form, and should not lose its adsorption ability after desorption. For the desorption of heavy metals, an appropriate eluent should be selected, which strongly depends on the type of adsorbent and the mechanism

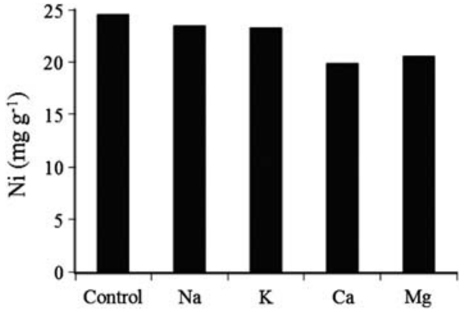

Fig. 10. Effect of alkali metal ions on Ni(II) uptake by DHHC (initial Ni(II) concentration: 100 mg L^{-1}, amount of DHHC: 100 mg, solution volume: 50 mL, pH of solution: 5.0, contact time: 24 h).

of adsorption [71,72]. The dilute solutions of several mineral acids such as sulfuric, nitric, and hydrochloric acids can be successfully used for desorbing the metal ions because they are effective for desorption, nondestructive for the structure of adsorbent, non-polluting to environment and cheap [57,70,71].

Desorption of adsorbed Ni(II) ions from DHHC was studied in a batch system. First, 25 mg L^{-1} initial Ni(II) solution (100 mL) was agitated with 1.0 g L^{-1} DHHC according to the process described in Section 2.2. After the filtration procedure, Ni(II)-loaded DHHC was dried in air. Then, the dried DHHC containing adsorbed Ni(II) ions was treated with 25 mL of various concentrations of HCl (in the range of 0–0.5 mol L^{-1}) to desorb the metal for one hour. As the concentration of HCl was increased, its efficiency in the release of Ni(II) ions increased (Fig. 11). A complete desorption of Ni(II) ions could be achieved using HCl solution at higher concentration than 0.10 mol L^{-1}.

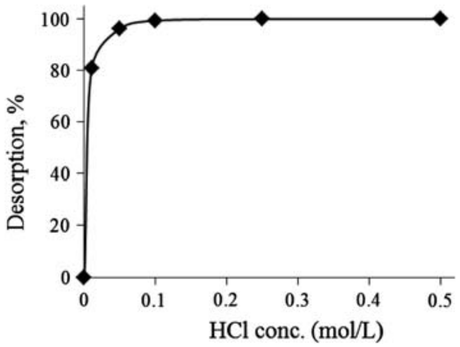

Fig. 11. Effect of HCl concentration on desorption of Ni(II) from DHHC (amount of DHHC: 100 mg, initial Ni(II) concentrations: 25 mg L^{-1}, solution volume: 100 mL, contact time: 24 h, pH of solution: 5.0, volume of HCl solution:25 mL).

4. Conclusions

In this study, DHHC as a novel sorbent was prepared from HH, an agricultural waste product using sulfuric acid. The removal ability of DHHC for Ni(II) ions by adsorption from aqueous solution was tested in terms of equilibrium, kinetics and thermodynamics. Adsorption of Ni(II) on DHHC is highly pH dependent and maximum adsorption was obtained at the pH values of 5.0–6.0. The kinetic studies indicated that the equilibrium in the adsorption of Ni(II) onto DHHC was reached in about 10 h of contact time, and the adsorption kinetics of Ni(II) onto DHHC follows the pseudo-second-order rate expression. The adsorption dynamic studies indicated that the intraparticle diffusion is not only the rate controlling step. The Ni(II) adsorption onto DHHC is rather complex process involving both boundary layer diffusion and intraparticle diffusion. The Langmuir isotherm model better fitted the experimental data than the Freundlich model, and the maximum adsorption capacity of DHHC for Ni(II) was 36.36 mg g^{-1}, indicating that the capacity was comparable with the results reported in the literature. The presence of Na^+, K^+, Ca^{2+}, and Mg^{2+} partially depressed the adsorption of Ni(II) ions onto DHHC. The desorption of Ni(II) ions adsorbed on DHHC was achieved quantitatively with dilute HCl solutions.

The results obtained in this study clearly demonstrated that DHHC can be successfully used in removing Ni(II) ions from aqueous solution. Hence, HH may be one of the most promising agricultural waste materials with high carbon content for the production of AC.

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