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Sorption of nickel ions from aqueous solutions using activated carbon derived from walnut shell waste

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ABSTRACT

Studies on a batch sorption process using activated carbon derived from walnut shell were investigated to remove Ni(II) ions from aqueous solutions. The influence of operational conditions such as contact time (0–150 min), solution initial pH (2–8), Ni(II) initial concentration (10–80 mg/L), sorbent mass (0.05–1.0 g/100 mL) and temperature (293–313 K) on the sorption was studied. Sorption data of Ni(II) ions onto walnut shell carbon (WSC) obeys the Langmuir isotherm model. Maximum sorption capacity of sorbent was 15.34 mg/g at 303 K. The kinetic data was fitted to pseudo-first-order model and pseudo-second-order model for different initial concentration to evaluate the model parameters. Pseudo-second-order model is better to represent the sorption process. Values of ΔG^0 ranging from –1.58 to –3.47 kJ/mol suggest that the sorption process is spontaneous and mainly governed by specific surface interaction mechanism. The values of ΔH^0 and ΔS^0 were 26.35 kJ/mol and 0.095 kJ/mol K, respectively. Results of this study will be useful for future scale up for using this waste material as a low-cost sorbent for the removal of Ni(II) ions from wastewater.

Keywords: Sorption; Nickel; Activated carbon; Kinetic model; Langmuir isotherm

1. Introduction

Removal of heavy metals from wastewaters and industrial wastes has become an environmental problem of global concern, because of their accumulation in liver organisms [1]. Nickel is a toxic heavy metal that is commonly used in silver refineries, electroplating, storage battery industries, and in the production of some alloys. The chronic toxicity of Ni(II) to humans and the environment is well known and high Ni(II) concentration causes higher incidence of lung ,nasal cancers [2]. Hence, it is essential to remove Ni(II) from industrial wastewaters before discharge into natural water resources.

The conventional methods for heavy Ni(II) metal removal from water and wastewater include chemical precipitation, electrochemical reduction, co-precipitation, membrane filtration, ion exchange and sorption [3]. However, these techniques have certain disadvantages (cost and suitability) and, activated carbon sorption is the most attractive process among these methods, due to its excellent sorption capability.

Though the use of commercial activated carbon is a well-known sorbent for the removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an sorbent in developing countries. Thus, great effort has been made to find cheaper and locally available waste materials to prepare activated carbon. Recently, different kinds of sorbents have been employed for Ni(II) ion removal such as waste apricot [4], peanut hulls [5], granular biomass [6], crab shell [7], clay [8], almond hulls [3], sheep manure waste [9]. In spite of several researchers adopted various low-cost

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sorbents there is still a need to develop suitable sorbents for the removal of Ni(II) from aqueous solutions. Walnut shell is readily available in great abundance in China. It is generally discarded as a waste. The cell walls of walnut shell consist of cellulose, lignin, carbohydrates which have hydroxyl groups in their structures.

The study of sorption equilibrium, isotherms and kinetics is essential in supplying the basic information required for the design and operation of sorption equipments for wastewater treatment. Langmuir isotherm and kinetics model such as pseudo-first-order and pseudo-second-order model, have been put forward to describe or predict the sorption isotherms and kinetics, respectively.

This work concerns the sorption of Ni(II) in aqueous solutions by activated carbon from walnut shell waste. The influence of experimental parameters such as pH, contact time, sorbent dosage and Ni(II) concentration on Ni(II) uptake were studied. The sorption isotherm and kinetics parameters were deduced from the adsorption measurements.

2. Experimental details

2.1. Procedure of WSC preparation and activation

Activated carbon was prepared in an isothermal reactor heated by a furnace. At the beginning of each run, the walnut shell waste was screened and a particle size of 2–3 mm (100 g) was chosen to place in the reactor. High purging nitrogen was used as the purging gas flowing through the sample bed at 400 mL/min. The reactor was then heated to the desired temperature (850 °C) at a heating rate of 8 °C/min and a holding time of 1 h. After the pyrolysis process, the product was activated at the same temperature for 1 h by using steam as an oxidizing agent. During the experiments, the steam flow rate was kept as 3 g/min. After activation, the sample was cooled to ambient temperature under N_2 flow rate. The activated carbon was ground and stored (< 100 mesh) for further experimental studies.

2.2. Sorbates

Analytical grade Ni(II) sulphate was employed to prepare a stock solution containing 1 g/L of Ni(II). The stock solution solution was further diluted with deionized water to the desired Ni(II) concentrations.

2.3. Batch sorption experiments

Batch sorption experiments were conducted in a series of stoppered reagent bottles. A weighed amount of sorbent was introduced into reagent bottles (150 mL) containing 100 mL aqueous solutions of Ni(II) solution of initial concentrations (C_0) from 10 to 80 mg/L. The concentration ranges were chosen to be representative of Ni(II) concentration in raw water and wastewater. The solution pH was adjusted to the desired value by adding HNO_3 or NaOH. Then, the bottles were shaken at room temperature (30 ± 1 °C) using a mechanical shaker for a prescribed time to attain the equilibrium. The solutions were filtered in a Hirsch funnel ceramic filter with the aid of a vacuum pump which assures a very rapid and efficient separation of the granular material. The concentrations of Ni(II) of the filtered solutions were determined by dimethylglyoxime spectrophotometric method according to the Chinese standard procedure (GB 11910-89). The effects of concentration (10–80 mg/L), contact time (1–150 min), initial solution pH (2–8) and sorption dose (5–1000 mg) were studied. Blank solutions were treated similarly (without sorbent) and the recorded concentration by the end of each operation was taken as the initial one. All the experiments were carried out in duplicate and mean values are presented. Maximum deviation was 5.0%.

The amount of adsorbed Ni(II) was calculated as follows:

$$q_e = (C_0 - C_t) \times V/W \tag{1}$$

where q_e is the amount of Ni(II) adsorbed onto sorbents (mg/g); C_0 is the initial Ni(II) concentration (mg/L); C_t is the Ni(II) concentration after a certain period of time (mg/L); V is the initial solution volume (L); and W is the sorbent mass (g).

3. Results and discussion

3.1. Characteristic of WSC

The main chemical and physical characteristics of WSC is listed in Table 1. The FT-IR spectrum of WSC in the range of 400–4000 cm^{-1} was recorded to obtain information regarding vibrational frequency changes in the functional groups present in the sorbent using a FT-IR spectrometer (IRPrestige-21). The FT-IR spectrum of WSC is presented in Fig. 1. The sorption at 3427 cm^{-1} can be assigned to –OH stretching the surface hydroxyl groups [10, 11]. The bands appearing at 1421 and 1570 cm^{-1} are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties, respectively [11]. The additional peaks at 1490 and 1174 cm^{-1} indicate the presence of C-H and S=O groups, respectively. The C=O and S=O functional groups show very high coordination with heavy metals. Hence, the good sorption properties of the sorbent towards Ni(II) can be attributed to the presence of these functional groups on the sorbent.

Table 1
The main chemical and physical characteristics of the sorbent.

Parameters	Value
BET surface area (m^2/g)	740.6
Iodine number (mg/g)	800.4
Methylene Blue number (mg/g)	250.5
Bulk density (g/cm^3)	0.5
Moisture (%,w/w)	8.9
Ash (%)	1.8
Ultimate analysis (%, w/w) on dry basis	
Carbon (%)	86.2
Hydrogen (%)	1.4
Oxygen (%)	12.1
Nitrogen (%)	0.3

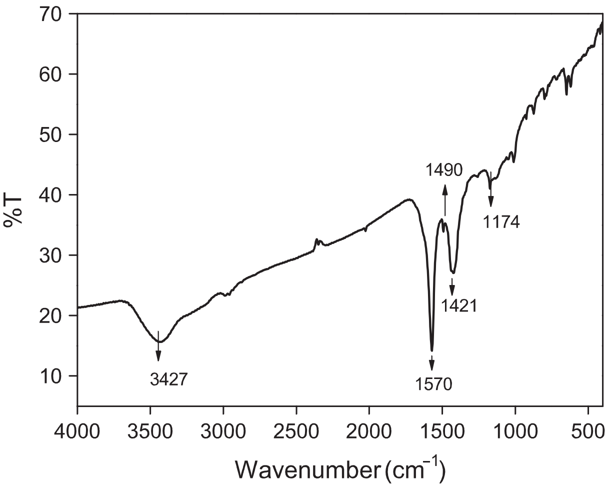

Fig. 1. FT-IR Spectrum of WSC.

A JEOL JSM-5600LV was employed for SEM observation of the prepared WSC. The samples of each powder were mounted onto double-side sticky tape over aluminum stubs and coated with gold under vacuum prior to the studies. SEM micrographs obtained before and after 25 mg/L Ni(II) solutions sorption onto WSC are presented in Fig. 2a and b. The scanning electron micrographs clearly reveal the surface texture and porosity of the sample. In Fig. 2a, the surface of the sorbent is a continuous structure with feature around 50 μm, while in Fig. 2b, new shiny and bulky particles appear over the surface of Ni(II) loaded the sorbent.

3.2. Effect of pH

The pH of the sorption solutions has been identified as the most important parameter governing sorption of metal ions on different sorbents. This is partly due to the fact that hydrogen ions themselves are strong competing sorbates and partly that the solution pH influences the chemical speciation of metal ions. The percentage of Ni(II) hydrolytic products was calculated from the following stability constants, and is presented in Fig. 3. It is evident that the Ni(II) ion is the only ionic species present in the solution for pH <6.0. It is obvious that in the alkaline range, precipitation plays the main role in the removal of the Ni(II) ion attributed to the formation of precipitate of $Ni(OH)_{2(s)}$:

$$Ni^{2+} + H_2O \rightleftharpoons Ni(OH)^+ + H^+ \quad pK_1 = 9.86 \tag{2}$$

$$Ni(OH)^+ + H_2O \rightleftharpoons Ni(OH)_2 + H^+ \quad pK_2 = 10.14 \tag{3}$$

$$Ni(OH)_2 + H_2O \rightleftharpoons Ni(OH)_3^- + H^+ \quad pK_3 = 11 \tag{4}$$

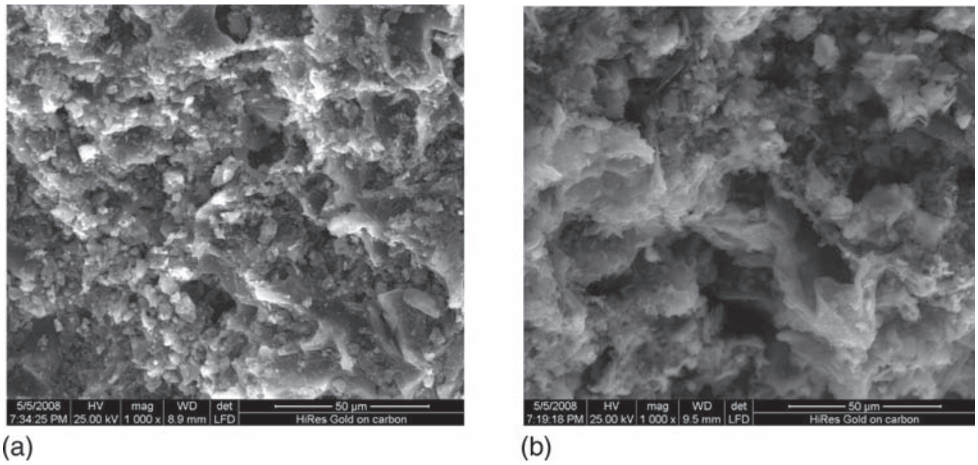

Fig. 2. (a) SEM photograph of native WSC and (b) SEM photograph of Ni(II) loaded WSC.

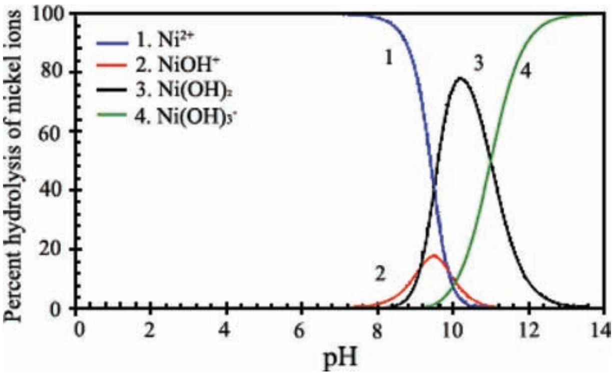

Fig. 3. Distribution of various Ni^{2+} species as a function of pH.

The effect of pH variation on sorption of Ni(II) on WSC was studied at a temperature of 303 K by varying the equilibrium pH of 25 mg/L of Ni(II) solution for fixed sorbent dosage of 0.15 g and the results are shown in Fig. 4. As could be seen, metal removal increased with increasing solution equilibrium pH and a plateau was reached at around pH 6.0. Similar observations were previously reported by several authors that investigated metal sorption by different biomaterials [12–14]. At lower pH, the absence of sorption can be explained by the fact that at these pH values the H^+ concentration is high, which can compete with nickel cations for the sorption sites of carbon. At pH > 6.0 the Ni(II) ions get precipitated due to hydroxide anions forming a nickel hydroxide precipitate. For this reason, the optimal pH value was selected to be 6.0.

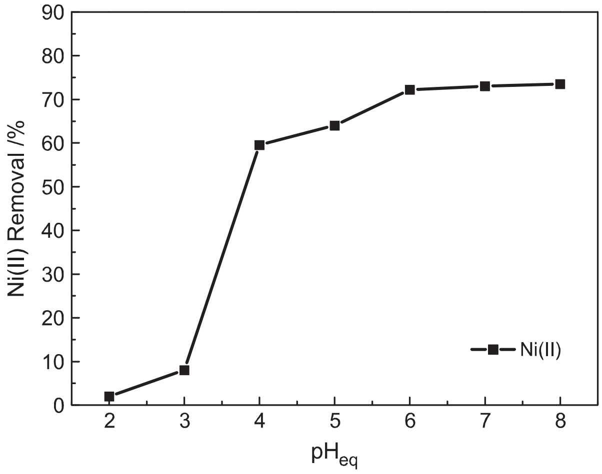

Fig. 4. Effect of equilibrium pH variation on nickel removal (initial concentration 25 mg/L; sorbent dose: 0.15 g/100 mL; contact time 120 min; temperature: 303 K).

3.3. Effect of carbon dosage

Fig. 5 shows the effect of carbon dosage on Ni(II) sorption at pH 6.0. As seen from Fig. 4, the removal percentage increases with increasing sorbent dosage and then becomes constant, indicating that 0.3 g/100 mL of sorbent is sufficient for the optimum removal of Ni^{2+}. This is due to the availability of more surface area with more function groups at higher carbon concentration. Hence, optimal sorbent dosage was selected to be 0.3g/100 mL.

3.4. Effect of contact time and initial concentration

Effect of initial concentration were investigated for different times. The solid–liquid ratio and pH was selected to be constant (0.2 g/100 mL and 6.0). The results obtained from experiments are given in Fig. 6. As seen from this figure, the removal increases with

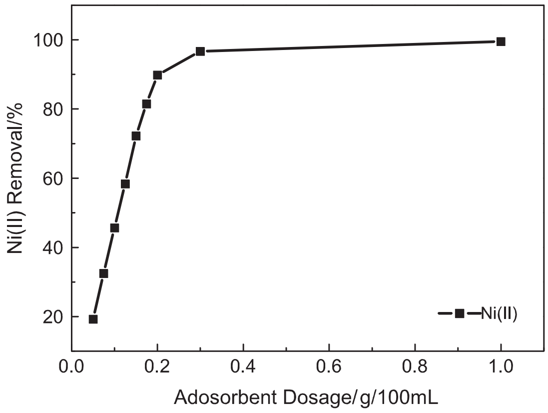

Fig. 5. Effect of sorbent dose on removal of Ni(II) (initial concentration: 25 mg/L; contact time: 120 min; temperature: 303 K).

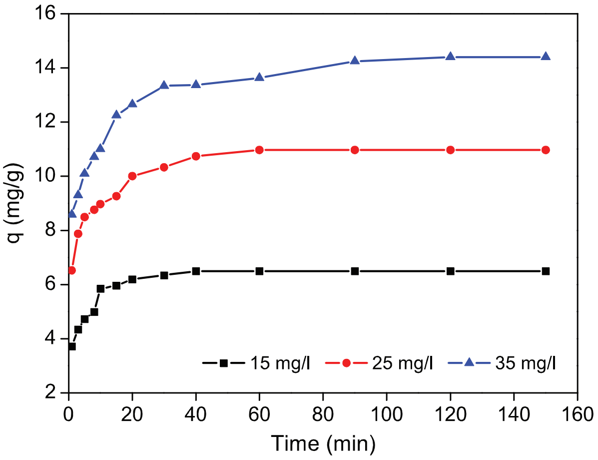

Fig. 6. The effect of initial concentration on the sorption of Ni(II) (sorbent dose: 0.2 g/100 mL; temperature: 303 K).

time and attains equilibrium in 40, 60 and 90 min for the initial concentration of 15, 25, 35 mg/L, respectively. This result is interesting because equilibrium time is one of the important parameters for economical wastewater treatment applications. According to this result, the contact time was fixed at 120 min for the rest of the batch experiments to make sure that equilibrium was reached in all cases.

3.5. *Effect of temperature*

Temperature dependence of sorption is associated with various thermodynamic parameters. To study the thermodynamic of sorption, the sorption studies were carried out at 20, 30, 35, 40 °C. Fig. 7 shows the experimental results obtained from a series of contact time studies for metal ions sorption with an initial metal ions concentration of 25 mg/L in which temperature was varied from 20 to 40 °C. The sorption of metal ions has been found to increase with an increase in temperature from 20 to 40 °C. The increase in sorption capacity of WSC with temperature indicates an endothermic process. The increase in sorption with temperature may be attributed to either increase in the number of active surface sites available for sorption on the sorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of sorbate in the boundary layer decreases [15]. The standard Gibbs free energy was evaluated by

$$\Delta H^0 = -RTInKc \tag{5}$$

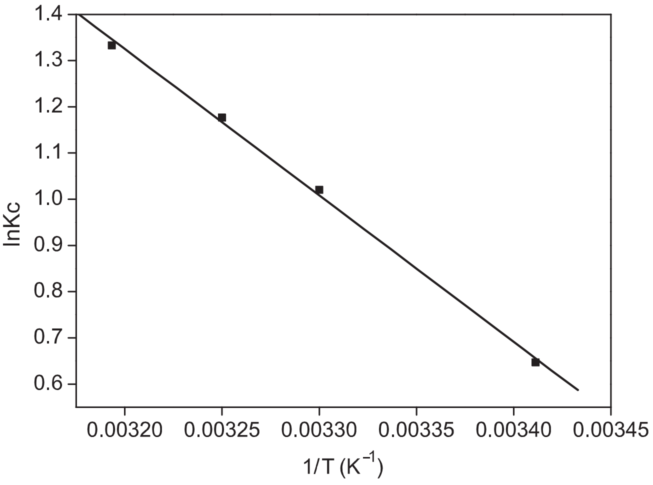

Fig. 7. Plot of InKc versus reciprocal temperature for the sorption of Ni(II) by WSC (sorbent dose: 0.15 g/100 mL ; contact time: 120 min).

The equilibrium constant K_c was evaluated at each temperature using the relationship

$$K_c = \frac{C_A}{C_e} \tag{6}$$

where C_A is the amount of Ni(II) adsorbed on the sorbent from the solution at equilibrium (mg/L), and C_e is the equilibrium concentration of Ni(II) in the solution (mg/L). Standard enthalpy (ΔH^0) and entropy (ΔS^0) were determined from the Van't Hoff equation.

$$InKc = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{7}$$

ΔH^0 and ΔH^0 were obtained from the slope and intercept of Vant Hoff plots of In*Kc* versus 1/*T*. The results are given in Table 2.

Generally, the change of free energy for physisorption is between –20 and 0 kJ/mol, however, chemisorption is a range of –80 to –400 kJ/mol [16]. The overall free energy change during the sorption process was negative for the experimental range of temperatures (see Table 2), corresponding to a spontaneous physical process of Ni(II) sorption and that the system does not gain energy from an external source. When the temperature increases from 293 to 313 K, the magnitude of free energy change shifts to high negative value (from –1.58 to –3.47 kJ/mol) suggested that the sorptionwas more spontaneous at high temperature.

Positive ΔH values of thermodynamically substantiate the assumption that the sorption of metal ions on WSC is endothermic. ΔS is estimated to be very small in the experimental conditions. Therefore, the entropic change occurring from sorption is thought to be negligible.

3.6. *Sorption isotherms*

Several mathematical models such as the standard Langmuir isotherm model and the Freundlich isotherm model can describe the distribution of metal ions between the liquid phase and the solid phase. Langmuir model is commonly used in literature for liquid phase sorption. Langmuir model assumes that the uptake metal ions

Table 2
The values of the thermodynamic of sorption at various temperatures.

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
293	–1.58	26.35	0.095
303	–2.57		
308	–3.01		
313	–3.47		

Table 3
Parameters of Langmuir isotherm model for Ni(II) ions uptake by WSC.

Temperature (K)	Q_0 (mg/g)	b (L/mg)	R^2	R_L					
				20 (mg/L)	25 (mg/L)	35 (mg/L)	45 (mg/L)	55 (mg/L)	80 (mg/L)
293	14.28	1.19	0.9977	0.040	0.033	0.023	0.018	0.015	0.010
303	15.34	1.00	0.9991	0.048	0.038	0.028	0.022	0.018	0.012
313	16.99	1.00	0.9991	0.048	0.038	0.028	0.022	0.018	0.012

occur on a homogenous surface by monolayer sorption without any interaction between adsorbed ions. The Langmuir equation is expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}, \tag{8}$$

where q_e is the amount (mg/g) of solute adsorbed per gram, C_e the equilibrium concentration of the solute (mg/L), and Q_0 and b are constants related to the sorption capacity and energy of sorption, respectively.

In this work, Langmuir model was used to describe the relationship between the amount of Ni(II) ions adsorbed and its equilibrium concentration in solution at three temperature (293 K, 303 K, 313 K) for 120 min. Plotting C_e versus C_e/q_e, straight lines were obtained with a slope of $1/Q_0$ and b are presented in the Table 3. It is noticed that from Table 3 that the sorption amount for Ni(II) at 313 K is greater than that at 293 K, which results from the interaction both negative temperature effect (the sorption amount decreases as temperature increases) and positive one (the sorption amount increases as the temperature rises). The Langmuir sorption equations are suitable for monolayer adsorption. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the adsorbent surface; since the Langmuir equation assumes that the surface is homogenous. The values of Ni(II) uptake by different sorbent collected from the literature along with the results of this work are given in Table 4 in the form of monolayer sorption capacity. The value of Ni(II) uptake found in this work is higher than reported elsewhere. The comparison of sorption capacities of WSC used in this study with those obtained in the literature shows that WSC is effective for the removal of Ni(II) from aqueous solution.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is defined by:

$$R_L = \frac{1}{1 + bC_0} \tag{9}$$

Table 4
Comparison of sorption capacity of Ni(II) onto various sorbents.

Sorbent	Sorption capacity (mg/g)	References
Fly ash	0.03	Rao [17]
Tea factory waste	15.26	Malkoc [18]
Sheep manure waste	7.20	Meunier [9]
Almond husk	4.89	Hasar [3]
Apricot	19.37	S. Erdoğan [4]
Grape stalks wastes	10.62	Isabel Villaescusa [12]
Olive stone waste	2.13	Furia Fiol [14]
Bagasse	0.001	Rao [17]
Baker's yeast	11.40	Patmavathy [19]
Hazelnut shell	8.46	E.Demirbas [20]
Coir pith	15.96	Parab [21]
Walnut shell carbon	15.34	This study

The parameter R_L indicates the shape of isotherm as follows:

R_L value	Type of isotherm
$R_L>1$	Unfavorable
$R_L=1$	Linear
$0<R_L<1$	Favorable
$R_L=0$	Irreversible

According to G. Mckay *et al.* [22], R_L values between 0 and 1 indicate favorable sorption. Our R_L (Table 3) were $0 < R_L < 1$ suggesting favorable sorption of Ni(II) onto WSC.

3.7. Kinetic studies

In order to investigate the mechanism of sorption, kinetics models are used to test experimental data. Pseudo-first-order and pseudo-second-order equations can be used while assuming that the measured concentrations are equal to surface concentrations.

Table 5
Pseudo first- and second-order kinetics model parameters for the sorption systems in the study

C_0 (mg/L)	Pseudo-first-order model				Pseudo-second-order model			
	$q_{e,\text{exp}}$ (mg/g)	$q_{e,\text{calc}}$ (mg/g)	k_1	R^2	$q_{e,\text{calc}}$ (mg/g)	k_2	h	R^2
15	6.49	6.59	0.1047	0.9596	6.51	0.1128	4.8690	0.9999
25	10.97	11.17	0.0678	0.9777	11.01	0.0497	6.1637	0.9998
35	14.40	14.52	0.0396	0.9704	14.47	0.0267	5.7212	0.9998

3.7.1. Pseudo-first-order model

The pseudo-first-order model is expressed as [23]

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{10}$$

where q_t and q_e are the amounts of Ni(II) adsorbed (mg/g) at time t (min) and at equilibrium time and k_1 is the rate constant of first-order sorption. Linear plot of $log(q_e - q_t)$ versus t shows the applicability of the above equation for WSC. The k_1 and q_e values were calculated from slope and intercept of the plot, respectively. The values of these constants for Ni(II) removal by WSC are given in Table 5.

3.7.2. Pseudo-second-order model

The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical sorption or chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. A pseudo-second-order model may be expressed as [24]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \, , \tag{11}$$

where k_2 (g/mg min) is the rate constant of second-order sorption determined from the plot of t/q_t vs t. The second-order rate constants were used to calculate the initial sorption rate, given by

$$h = k_2 q_e^2 \tag{12}$$

The second-order rate constants and the calculated initial sorption rate values are shown in Table 5. From Table 5, it was observed that the pseudo-second-order equation showed a good correlation of the experimental results with linearized form. The R^2 values obtained from pseudo-second-order model is higher than those of pseudo-first-order model. From these results, it is seen that the correlative coefficients of the pseudo-second-order model are obviously higher than those of the pseudo-second-order model, indicating the pseudo-second-order model a comparatively suitable model to describe the sorption.

4. Conclusions

The results obtained show that carbon preparation from walnut shell waste, an inexpensive precursor, can be used for the removal of Ni(II) from aqueous solution. The maximum Ni(II) sorption was obtained at pH 6.0. The sorption capacity was found to be 15.34 mg/g at 303 K. The removal process was affected by process parameters, namely, pH, sorbent dose, concentration of metal ion and contact time. The pseudo-second-order model provides better correlation of the sorption data than the pseudo-first-order model. The sorption obeyed Langmuir sorption for Ni(II) uptake by WSC. Based on the results of this study, we conclude that WSC is an effective sorbent for the removal of Ni(II) from aqueous solutions.

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