The Removal of Nickel from Waste Water by Modified Coconut Coir Pith

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Abstract

In this study, Coconut Coir Pith was used to prepare a low cost bio adsorbent through chemical modification. The effect of adsorbent dosage, contact time, initial metal-ion concentration, pH and temperature on the adsorption of nickel onto chemically modified coconut coir pith was investigated. The maximum removal was observed at pH 6.0 and adsorbent dose 2.0 g/L for initial metal-ions concentration 50 mg/L. Study of temperature effect proved that the process is endothermic. Langmuir and Freundlich isotherm models were used for equilibrium adsorption data. Langmuir isotherm proved to be a better fit. Pseudo first order and pseudo second order kinetic models were applied to analyze the kinetic mechanism of adsorption. The values of Gibbs free energy $\Delta G°$, Enthalpy $\Delta H°$ and Entropy $\Delta S°$ was calculated by the thermodynamic studies.

Keywords: Adsorption; Nickel (II); Coconut coir pith; Isotherms; Kinetics; Thermodynamics

Introduction

Excessive release of heavy metals into our environment due to increase of industrialization and urbanization has posed a great problem worldwide. The non-biodegradable and hazardous nature of the metal pollutants and their tendency to get accumulated in living organisms is causing a major threat to environmental sustainability. Generally, the metals whose density are more than 5.0 gram/m³ and atomic weights are between 63 to 200, are known as heavy metals [1]. Recently it is found that heavy metals are most considerable pollutant in water [2]. The industrial waste water contaminated with heavy metals are comes from industries such as metal plating, tanneries, mining operations, electroplating industries, fertilizers, pesticide and batteries industries [3]. Nickel is identified as one of the major heavy metal pollutants released by electroplating and metal surface treatment industries. Nickel causes Dermatitis, nausea, chronic asthma, human carcinogen and coughing if it is present in excess of natural source of water [4]. With better awareness of the problems associated with nickel came an increase in research studies related to methods of removing nickel from wastewater, a cheaper and more effective technologies have been developed over the years. Include adsorption, numerous approaches like biosorption, coprecipitation, electrocoagulation, chemical precipitation, membrane filtration, solvent extraction, reverse osmosis and ion exchange [5-17] have been employed for the removal of heavy metals from waste water and to improve the quality of the treated effluent. But in these treatments process adsorption has become one of the important methods [18,19]. Carbon black with high adsorption capacity is not suitable for waste water treatment process due to high cost. So there is a need to search for low-cost adsorbents that have metal-binding capacity. Agricultural by-products have been used as adsorbents for removal of metal ions from aqueous solution such as activated carbon obtained from peanut hull, almond shell, olive stones and peach stones [20-22]. India, the third largest producer of coconut in the world, produces approximately 8160 million coconuts every year. Therefore, in the present work, coconut coir pith has been used to prepare a good low cost adsorbent. The estimated production of coir pith in India is 0.5 million t. Coir pith is disposed of as waste and its accumulation around coir processing centers is creating a menace have used [23]. Different methods of preparation of activated carbon from coir pith for the removal of Cu, Cr, Hg, Cd and organics, including pesticides from industrial effluent have recently been reported. The objective of this study to prepare a good low cost adsorbent from coconut coir pith by chemical activation for the removal of Ni(II) from aqueous solution.

Experimental Methods

Bioadsorbent preparation

The Coconut coir pith used in this study was obtained from locally available fruit market, Lucknow, India. It was washed several times with distilled water to remove soil and dust particles and cut into small pieces then it was sun dried by exposure to the sunlight for 3 days and subsequently in a hot air convection oven at 60°C for 48 h. The dried material was ground into a powder using blender and sieved to obtain constant finer size particles (100 μm). The sieved powder of the raw bioadsorbent (100 g) was soaked in 1.0 L of 4 NH_2SO_4 (sulfuric acid) in a mechanical shaker at 200 rpm for 24 h. The activated coir pith were filtered and rinsed with distilled water, until the pH was neutral. The acid activated bioadsorbent material was sealed in plastic bags and stored in desiccators for further use. The acid treatment of bioadsorbent have been done to remove the mineral elements and to increase the acidic and hydrophilic nature of bioadsorbent surface.

Batch adsorption test

The adsorbate stock solution of 1000 mg/L Ni(II) was prepared from nickel nitrate $Ni(NO_3)_2.6H_2O$ in double distilled water. The standard test solutions (10-60 mg/L) of Ni(II) were prepared by diluting the stock solution as required by double distilled water. All other chemicals used in this study were AR Grade. Batch adsorption tests were carried out by shaking 0.2 g of adsorbent with 100 ml of Ni(II) solution of desired concentration at an initial pH of 6.0 in 250 ml conical flasks, which were agitated at 200 rpm and room temperature (30°C). After a predetermined contact time, the sample was removed from the mechanical shaker and filtered by using Whatman No. 4 filter paper.

The remaining concentration of Ni(II) was spectrophotometrically estimated (Systronic 2203). The effect of concentration (10-60 mg/L) of Ni(II), contact time (0-3 h), adsorbent dose (0.25-3 g/L) and pH (2-10) were observed in batch adsorption test. The optimum condition (pH 6.0, contact time 120 minutes, adsorbent dose 2.0 g/L for 100 ml) for adsorption isotherm was fixed. The amount of metal-ion adsorbed (qe) from aqueous solution and percentage removal of metal-ions were calculated by using the following Eqs. (1) and (2) respectively.

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

$$\% \text{ Removal} = \frac{(C_o - C_e)V}{C_o} \times 100 \tag{2}$$

Where, C_o is the initial concentration and C_e is the equilibrium concentration of metal-ion solution, V is the volume of metal-ion solution in L, m is the amount of adsorbent in g.

Characteristics techniques

The CCP were characterized by using BET technique (BEL Japan) to determine surface area. SEM (scanning electron microscope) used to determine surface morphology of CCP. The FT-IR spectra of CCP before and after adsorption of nickel-ions were obtained to demonstrate the functional groups on surface.

Results and Discussion

Characterization of the adsorbent

The BET technique was used to determine surface area and pore size of the CCP. The BET surface area of CCP is 4.8512 m^2/gm and mean pore diameter is 2.7011 nm. The surface morphology of CCP examined by SEM is shown in Figure 1. The irregular and porous structures on surface of adsorbent play a significant role in adsorption [24]. Fourier transform infrared spectra (FTIR) was used to investigate the changes in vibrational frequency in the functional groups of the adsorbents due to Ni(II) adsorption. The adsorbent was scanned in the spectral range of 4000-400 cm^{-1}. The Figure 2 shows the FTIR spectra of CCP before and after adsorption. The spectra indicated a number of changes in peaks, which show the complex nature of the adsorbent. The functional group is one of the key factors to understand the mechanism of metal binding process on natural adsorbents [25,26]. The shifts in the wave length showed that there was metal binding process taking place at the surface of the CCP.

Effect of pH on adsorption

The pH is one of the most important operating variables in the adsorption process because the values of pH affect the surface and binding capacity of adsorbent due to exchange of H^+ ions with metal ions. The effect of pH on the adsorption of Ni(II) by CCP was studied at pH 2.0-10 (Figure 3). The results show maximum adsorption near 6.0 pH. Therefore, remaining experiments were carried out on this pH. Lower value of pH favor the adsorption but with increase in pH from 6.0 to 8.0, the removal percentage decreased.

Effect of adsorbent dosage

Adsorbent dose is an important parameter because it determines the binding capacity of adsorbent for given initial metal ions concentration. The Figure 4 shows the removal of Ni(II) as a function of CCP added to an aqueous solution of pH 6.0. CCP granular dose ranged from 0.25 to 3.0 g/L of Ni(II) test solution and was equilibrated for 120 minutes while keeping other parameters at optimal. The

percentage metal removal was 22.8117% (at 2.0 g/L of adsorbent dosage) and increased to 75.8781% (at 5.0 g/L of adsorbent dosage). Increase in removal percentages with increasing CCP dosage is related to the increase in surface area and by extension the increased number of ion exchangeable sites available for interaction with nickel ions. The decrease in metal adsorbed (gm/g) with increase in adsorbent dose is due to the increase in surface vacant site. The experiment results show that optimal adsorbent dosage was 2.0 g/L for this experiment.

Effect of contact time

The adsorption of Ni(II) from aqueous solution on CCP increases with increase in contact time. It was observed that the general uptake rate was fast during first 2 hrs. After which adsorption was achieved a steady state. The Figure 5 shows the effect of contact time on the CCP removal of 50 mg/L Ni(II) at 30°C and pH 6.0. The initial uptake rate was fast during first 2 hrs may be due to the more availability of the surface vacant sites. Two kinetic models, Lagergren first-order and Ho's second-order were applied to analyze the adsorption rates of Ni(II) ions onto the CCP.

Effect of initial metal-ion concentration

Ni(II) ions adsorption on CCP was studied, using different initial metal concentrations in the range of 0-60 mg/L at optimal conditions of contact time, temperature, pH and adsorbent dosage. It was observed
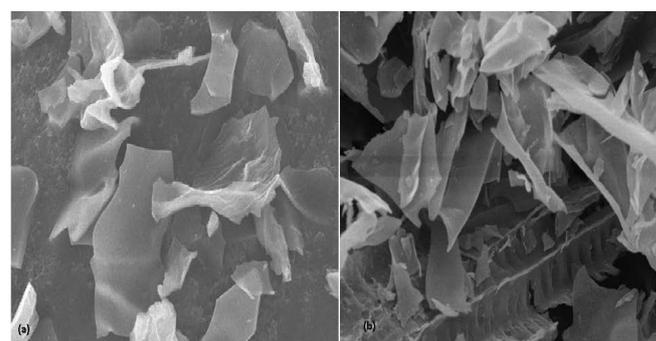

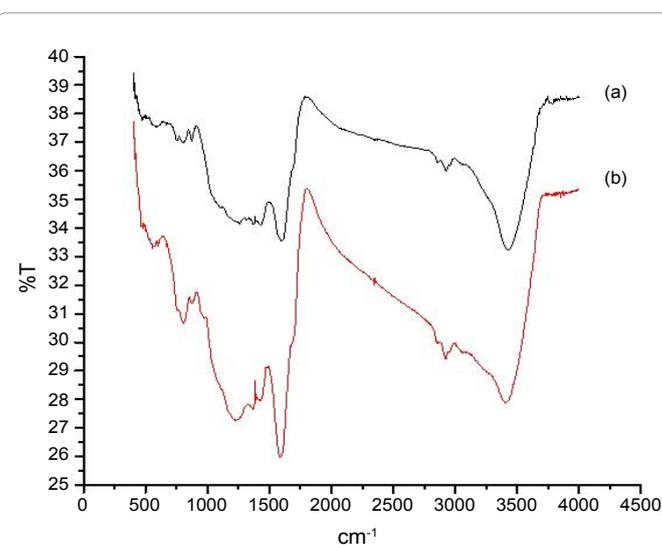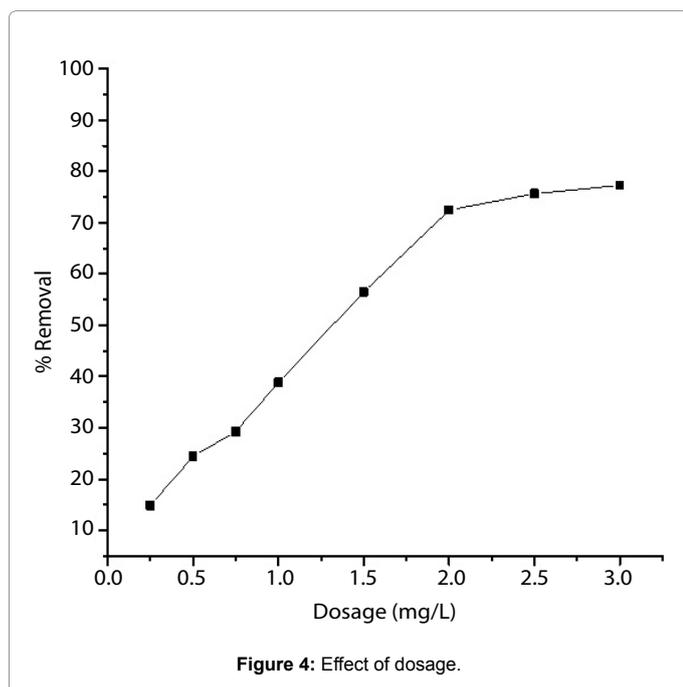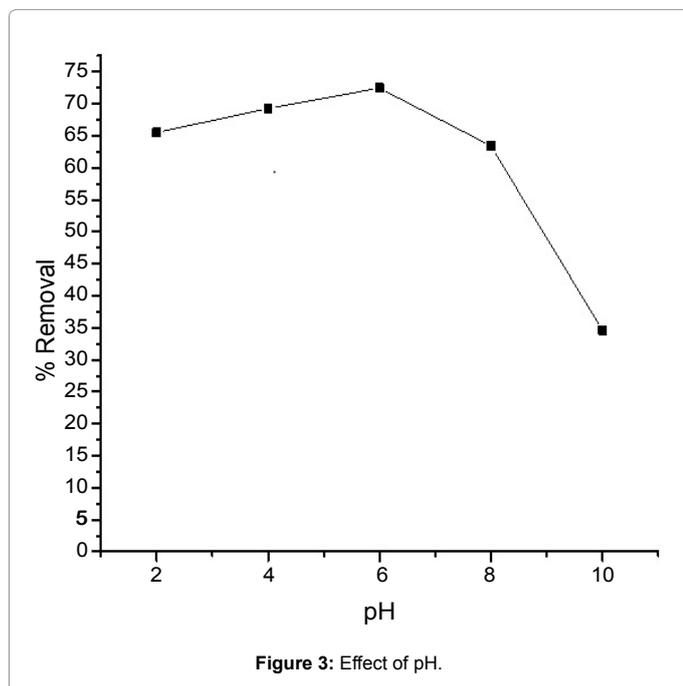**Figure 1:** SEM of coconut coir pith (a) Ni(II) loaded CCP (b) CCP.

Figure 2: FTIR spectra of (a) Ni(II) loaded CCP (b) CCP.

Figure 3: Effect of pH.

Figure 4: Effect of dosage.

that the removal of metal-ion decrease with increase in initial metal-ion concentration of Ni(II) (Figure 6).

Kinetic studies

In this study, the Lagergren first-order reaction rate model (pseudo-first order adsorption kinetics, Eq. (3) [27] and Ho's second-order reaction rate model (pseudo-second order adsorption kinetics, Eq. (4) [28] has been applied to the experimental data to determine the adsorption kinetics of Ni(II) ions.

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{1}{q_e} t \tag{4}$$

Where, the maximum adsorption capacity at equilibrium is q_e (mg/g) and the amount of metal-ion adsorbed at time, t is q_t (mg/g). k_1 (min^{-1}), k_2 (g/mg min) are the equilibrium rate constants for pseudo-first order and pseudo-second order kinetics respectively. Results of the kinetic data indicated that the pseudo-second order model best describes the adsorption of Ni(II) on CCP. The R^2 value for the pseudo second order was higher than that of pseudo first order kinetic model (Table 1).

Adsorption isotherms

Adsorption isotherms describe the behavior of adsorption process and interaction of the adsorbate with the adsorbent. In the present work, two adsorption isotherms, Langmuir and Freundlich, were used for fitting the obtained experimental adsorption data.
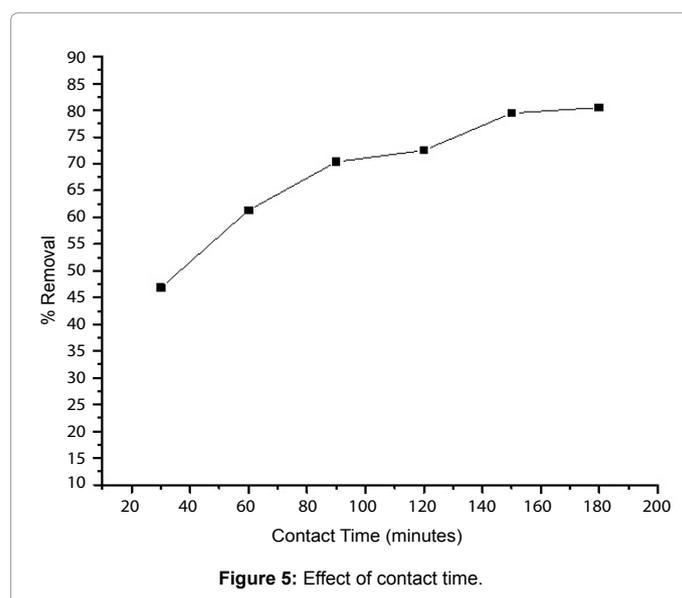
Langmuir isotherm

The Langmuir isotherm explains monolayer adsorption, linearized model of Langmuir isotherm [29] can be represented by the following equation (5).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{5}$$

Where, the equilibrium concentration is C_e (mg/L), the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium is q_e (mg/g), q_{max} is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg). The values of R_2, K_L and q_{max} were determined from the slopes and intercepts of the linear plots of C_e/q_e against C_e (Table 2).

Pseudo first-order		Pseudo second-order	
k_1 (min^{-1})	R^2	k_2 (g/mg.min)	R^2
0.025	0.922	2.97×10^{-4}	0.997

Table 1: Pseudo first-order and pseudo second-order reaction rate constants for Ni(II) adsorption by CCP.

Figure 5: Effect of contact time.

Figure 6: Effect of initial metal-ions concentration.
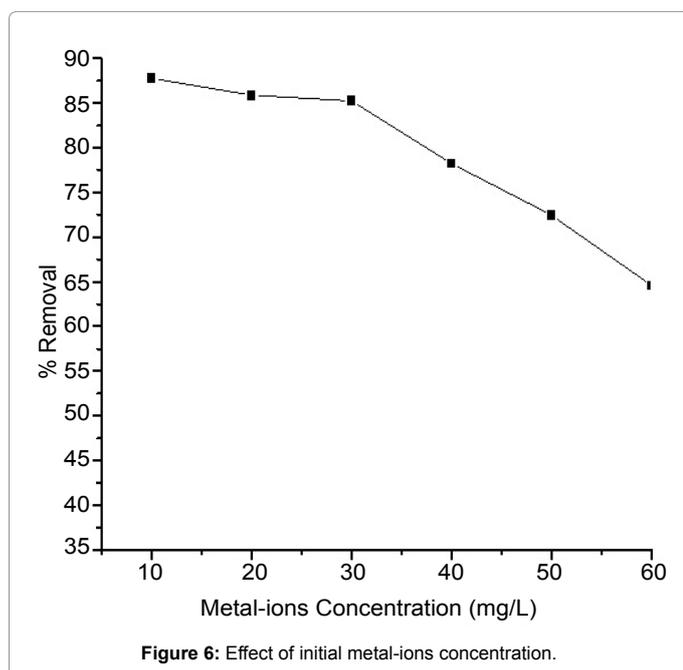
Langmuir isotherm			Freundlich isotherm		
q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)	R^2
24.3902	0.0206	0.994	1.9531	1.9699	0.923

Table 2: Langmuir and freundlich isotherm constants for the adsorption of Ni(ii) ion onto CCP.

Freundlich isotherm

Freundlich isotherm explains heterogeneous surfaces and multilayer adsorption, the linearized model of Freundlich isotherm [30] can be represented by the following equation (6).

$$Log q_e = Log K_F + \frac{1}{n} Log C_e \qquad (6)$$

Where, K_F is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent (mg/g) (mg/L). 1/n and n are dimensionless constants of the adsorbents, which can be used to explain the adsorption intensity between the solute concentration and adsorbent respectively. The values of R_2, K_F and n were determined from the slopes and intercepts of the linear plots of Log q_e against Log C_e (Table 2).

The details of comparative study of adsorption of Ni(II) by different adsorbents reported by earlier workers, along with present study are provided in Table 3, in the form of adsorption capacity (q_{max}).

Thermodynamic studies

The effects of temperatures on the adsorption of Ni(II) onto CCP surface have been presented in Figures 7 and 8. The graph shows slight increase in adsorption on increase in temperature. This may be due to a greater kinetic energy acquired by the metal-ions with increase in temperature. The correlation of standard Gibbs free energy (ΔG°) and thermodynamic equilibrium constant K_c can be expressed by following equation.

$$\Delta G° = -RT \, Ln \, Kc \qquad (7)$$

Adsorption enthalpy (ΔH°), and adsorption entropy (ΔS°), is related to the standard Gibbs free energy (ΔG°) presented by Van't Hoff equation [36], shown in Eq. [8].

$$Ln \, Kc = -\left(\frac{\Delta G°}{RT}\right) = -\left(\frac{\Delta H°}{RT}\right) + \left(\frac{\Delta S°}{R}\right) \qquad (8)$$

Kc is defined by Eqs. [9].

$$Kc = \frac{C_a}{C_e} \qquad (9)$$

Where: C_a is the amount of metal-ions adsorbed at equilibrium and C_e is the equilibrium concentration. The values of ΔH° and ΔS° were calculated from the slope and intercept of the plot (ln Kc versus 1/T) and the calculated thermodynamic parameter values are presented in Table 4. The ΔS°, ΔH° and ΔG° represent the entropy, enthalpy and free energy changes during the process of adsorption in the present study respectively. The positive value of ΔH° support endothermic nature of adsorption for the system at hand. Whereas, the positive value of ΔS° favors the enhanced character of randomness at the solid/solution interface during the adsorption of Ni(II) on coconut coir pith. The negative values of ΔG° at all temperatures as shown in Table 4, exhibit spontaneous nature of adsorption.

Conclusions

The study successfully demonstrated the application of modified coconut coir pith as a low cost adsorbent for the removal of Ni(II) ions. An increase in pH was favorable up to 6.0 where an increase in adsorbent dosage resulted in increased removal efficiencies and

Adsorbent	q_{max} (mg g^{-1})	Reference
Testa of Groundnut Shell	18.79	[31]
Bagasse fly ash	12.82	[32]
Banana peel	6.88	[33]
Orange peel	6.01	[33]
Tea factory waste	15.26	[34]
Eutrophic peat	11.15	[35]
Coconut coir pith	24.39	Present study

Table 3: Comparison of adsorption capacity q_{max} (mg/g) Ni(II) onto various bioadsorbent.
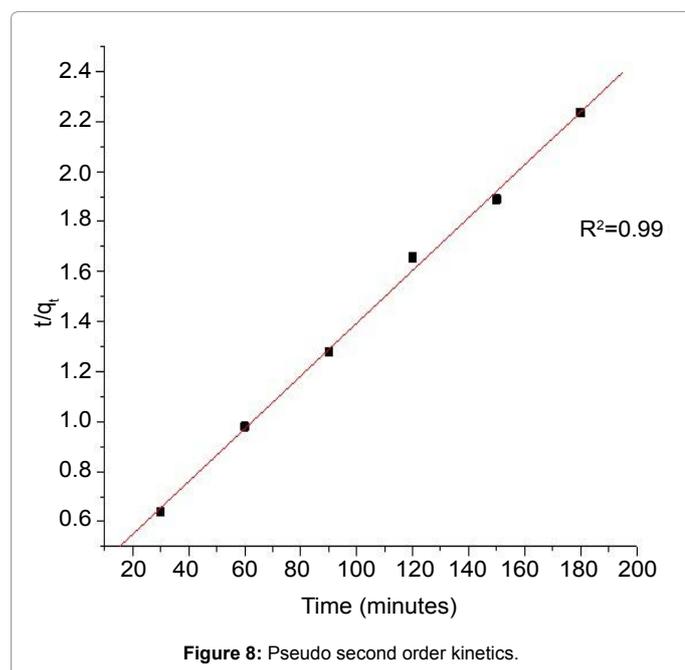

Figure 7: Pseudo first order kinetics.
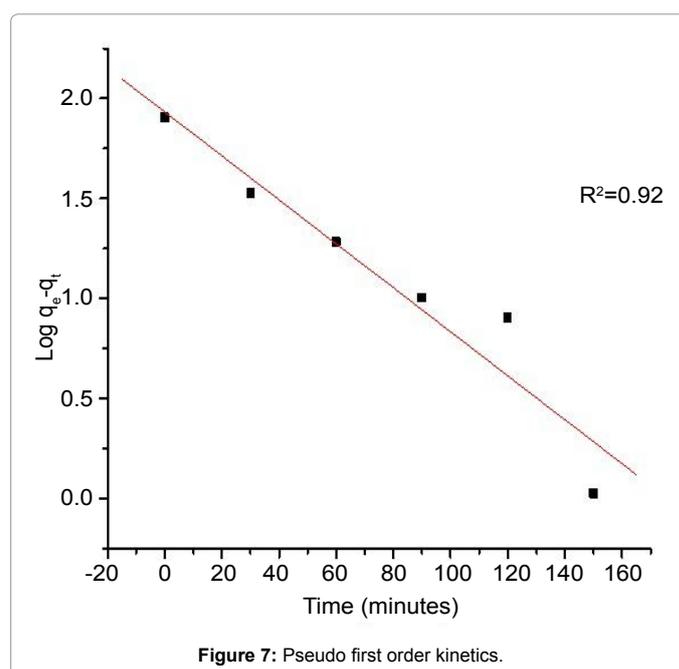
Figure 8: Pseudo second order kinetics.

T (K)	K_c	ΔG^0(kj/mol)	ΔH^0	ΔS^0	R^2
293	1.6553	-1.2019	22.93	82.92	0.990
303	2.6333	-2.3889			
313	3.1115	-2.8921			
323	4.1231	-3.7245			

Table 4: Thermodynamic parameters for the adsorption of ni(ii) from solution onto CCP.

decreased uptake capacities. The Langmuir isotherm was demonstrated to provide the best fit for the equilibrium adsorption data confirming a monolayer adsorption pattern. The pseudo-second order model fitted well (R^2=0.99) for the kinetic data. From this study, we conclude that activated coconut coir pith powder can be used as adsorbent for the removal of Ni(II) from aqueous solution.

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