



## Efficient Removal of Ni (II) by Multi Step Treated Carbon Nanotubes from Aqueous Solutions: Kinetic, Equilibrium and Thermodynamic Studies

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### ABSTRACT

NaOCl modified zeolite supported carbon nanotubes (CNTs) were treated with hydrogen peroxide, then oxidized with nitric acid finally with  $KMnO_4$ , after modification they were employed as adsorbents for Ni (II) ions removal. The CNTs were characterized by Fourier transform infrared, scanning electron microscope, transmission electron microscope, and Raman spectroscopy and thermogravimetric analysis. The adsorption characteristics were explored using well-established and effective parameters including the effect of pH, contact time, adsorbent dosage, initial metal ion concentration and temperature. Optimum adsorption of Ni (II) was observed at pH 6.0. Kinetic studies revealed that the adsorption data fit well to pseudo-second-order model with high correlation coefficient. Langmuir model gives a better fit than the Freundlich and Dubnin–Radushkevich models. Thermodynamic properties, i.e.,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  showed that adsorption of Ni (II) onto CNTs were endothermic, spontaneous and feasible in the temperature range of 293-313 K.

**Key words:** Carbon nanotubes, Nickel, Adsorption, Isotherms, Thermodynamics.

### 1. INTRODUCTION

Toxic heavy metal ions in water bring many detrimental effects on the environment and human health. They are non-biodegradable, and their concentration gets accentuated through bioaccumulation via food chain in living tissues, causing various diseases and disorders. Nickel is one of the most common toxic metals, and the US Environmental Protection Agency has established  $0.5 \text{ mg L}^{-1}$  as the permissible concentration in drinking water. In view of this, it is necessary to remove nickel from wastewater before they are discharged into natural water bodies [1,2]. Many conventional methods have been used to remove metal ions from aqueous solutions including oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Among these techniques, adsorption is found to be a promising system to remove heavy metal ions from effluents because of its low operational, maintenance costs and high efficiency, especially for the heavy metal ions with low concentration. Therefore, investigations of new promising adsorbents with high adsorption capacities, eco-friendly and efficiencies have become interesting and important for many researchers. Several adsorbents that have been used for removal of nickel include activated carbon [3], acid modified hulls [2],

agricultural waste [4] sugar beet pulp [5], crab shell [6], carbon nanotubes (CNTs) [7,8] etc., Search is being carried out for promising new adsorbents. Compared to that of prescribed adsorbents, nanostructured adsorbents exhibited remarkable advantages owing to their higher surface areas and much more surface active sites than bulk materials [1].

CNTs are a fascinating new class of nanomaterials, which have been the subject of much interest since the discovery of CNTs by Iijima, in 1991 [9]. Nowadays search is incredible on CNTs and carbon related compounds as adsorbents for trace metal removal. They have become more attractive materials due to their unique electrical, mechanical, optical and chemical properties [10]. These excellent properties make CNTs promising materials for numerous applications, such as hydrogen storage, catalyst supports, chemical sensors and nano electronic devices [11-14]. Research on CNTs has proven that CNTs possess superior potentiality as adsorbents for removing many kinds of organic, inorganic pollutants and various divalent metal ions from aqueous solutions [15]. In this study, we tested the adsorption capacity of CNTs toward Ni (II) ions removal from aqua solutions.

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In the present study the CNTs were synthesized by catalytic chemical vapor deposition (CCVD) method, then the CNTs were modified with different oxidizing agents and were used to investigate their characteristic and sorption properties of Ni (II) ions from aqua solutions. Studies relating to pH, dose, contact time, kinetics, isotherms and thermodynamics on Ni (II) sorption were carried out to determine the optimization of CNTs.

## 2. EXPERIMENTAL

### 2.1. Synthesis and Modification of CNTs

Synthesis and various methods of modification of CNTs were described in our previously published work [7,8].

### 2.2. Preparation of Sorbate

A standard solution ( $1000 \text{ mg L}^{-1}$ ) was prepared by dilution of standard Ni (II) solution (Merck Ltd., Germany). Working standards were prepared by appropriate dilution of the standard with deionized water. ACS reagent grade HCl, NaOH and buffer solutions (Merck Ltd., Germany) were used to adjust the solution pH.

### 2.3. Batch Sorption Experiments

Batch sorption experiments were conducted using a number of 125 mL glass bottles containing 50 mL of Ni (II) solution of initial concentrations ( $C_0$ ) ranging from  $10 \text{ mg L}^{-1}$  to  $80 \text{ mg L}^{-1}$  and the solution pH was adjusted to neutral value using  $0.1 \text{ M HNO}_3$  and  $0.1 \text{ M NaOH}$ . A carefully weighed amount of  $0.05 \text{ g}$  of modified CNTs was introduced into each bottle. The glass bottles were sealed with  $20 \text{ mm}$  rubber stopper and were mounted on a shaker, which was placed in a thermostatic shaking water bath (HB-205 SW, Han Baek Scientific Company, Bucheon, Korea) and operated at  $180 \text{ rpm}$  and maintained at desired temperature for  $12 \text{ h}$ . The amount of metal ion sorbed onto CNTs,  $Q_e$ , was computed by the following equation:

$$Q_e = \frac{v}{m} (C_0 - C_e) \quad (1)$$

where,  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of metal ions in solution whereas  $v$  and  $m$  are solution volume and mass of adsorbent, respectively. All the batch experiments were carried out in triplicate, and the negative controls (with no adsorbent) were simultaneously carried out to ensure that adsorption was by adsorbent and not by the container. The resulted values were reported average of three readings.

### 2.4. Batch Mode Desorption and Reusability Studies

Desorption measurements were conducted in order to explore the feasibility of recovering both the metal ion

and the adsorbent. The CNTs saturated with Ni (II) was removed from solution and transferred into stoppered bottles ( $125 \text{ mL}$  capacity), to this  $100 \text{ mL}$  of  $0.05\text{-}0.25 \text{ M HCl}$  solution was added, and the bottles were shaken for  $4 \text{ h}$ . The metal concentrations were determined. Finally, CNTs were washed with excess of distilled water in order to reuse for the next experiment. Consecutive sorption-desorption cycles were repeated to establish the reusability of the adsorbent.

### 2.5. Characterization of CNTs

The physical properties of modified CNTs indicated that most pore volumes are in  $5.0\text{-}100 \text{ nm}$  width range, Brunauer, Emmett, and Teller (BET) surface area is  $119.469 \text{ m}^2 \text{ g}^{-1}$  (refluxion with  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ ) and  $152.31 \text{ m}^2 \text{ g}^{-1}$  (treating with  $\text{NaOCl}$ ), this suggest that oxidation of CNTs with various oxidizing agents is an effective method to remove the amorphous carbon [7], carbon nanoparticles introduced by chemical vapor deposition preparation process and review inner cavities of the CNTs, which expose their internal surface area. Average pore diameter is  $4.693 \text{ nm}$  and pore volume is  $0.039 \text{ cm}^3 \text{ g}^{-1}$ .

The concentration of Ni (II) was determined using inductively coupled plasma spectrometer (ICP-7510, Shimadzu, Kyoto, Japan). The physical properties such of CNTs were determined by  $\text{N}_2$  adsorption at  $77 \text{ K}$  using an ASAP 2020 surface area analyzer (Micromeritics Inc. Norcross, GA, USA).  $\text{N}_2$  adsorption isotherms were measured at a relative pressure range of  $0.0001\text{-}0.99$ . The adsorption data were then employed to determine surface area using the BET equation and pore size distribution using the Barrett, Johner and Halenda equation.

The surface functional groups of CNTs were determined by a Fourier transform infrared (FT-IR) spectrophotometer (Thermo-nicolet FT-IR, Nicolet IR-200, USA) and Boehm titration method [16].  $100 \text{ mg}$  of CNTs was placed in a  $100 \text{ mL}$  flask containing  $50 \text{ mL}$  of  $0.1 \text{ M NaOH}$  and  $0.1 \text{ M HCl}$  solution. The flask was sealed and shaken for  $48 \text{ h}$  at  $25^\circ\text{C}$ . The solution was then filtered through a  $0.45 \text{ }\mu\text{m}$  nylon fiber filter and  $10 \text{ mL}$  of each filtrate was pipetted. The excess of acid was titrated with  $0.1 \text{ M NaOH}$  while the excess of the base was titrated with  $0.1 \text{ M HCl}$ . The concentrations of acidic and basic sites were determined from the amount of NaOH and HCl reacted with the CNTs.

### 2.6. Scanning Electron Microscopic (SEM) and Transmission Electron Microscopic (TEM) Studies

In order to evaluate the textual structure of adsorbent surface, (SEM: Evo15, Carl Zeiss, England) was used, from the SEM images (Figure 1a and b) the CNTs are regarded as an entangled network, flexible and are not easily broken during oxidation, washing and drying process. And nano structure of CNTs was determined

by (TEM, Philips: CM200). From (Figure 1c and d), the TEM images of modified CNTs are exhibited that the CNTs have an inner diameter of 7.2 nm and an outer diameter of 25.1 nm the CNTs have 45 graphitic layers on both sides, which indicate its thickness. It is apparent comparison of the TEM images of modified CNTs with those of as-grown CNTs, that the inner and outer diameters of CNTs decreased and a large amount of carbon-containing defects appeared along the surface of CNTs after modification by  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{KMnO}_4$  and  $\text{NaOCl}$  reagents [8].

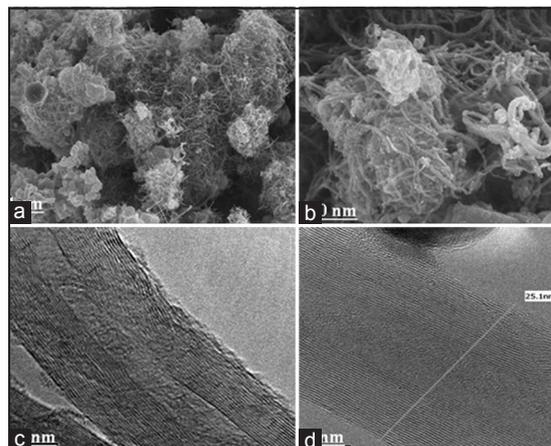
### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of pH

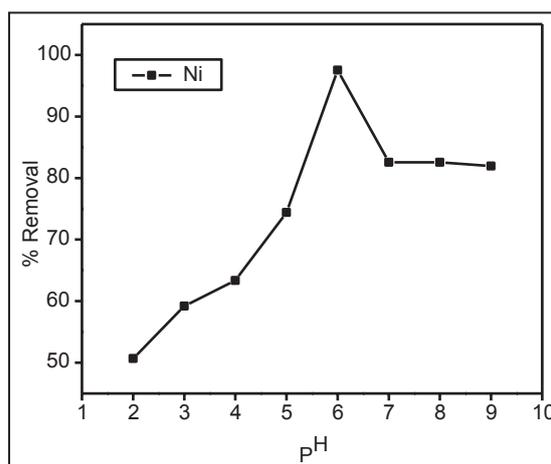
The pH of the solution is an important parameter in the adsorption process, because of the pH dictates not only the dissociation of functional groups but also the complexation reactions or electrostatic interactions at the adsorption surface [17]. The solution pH affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbates. The effect of pH can be explained in terms of  $\text{pH}_{\text{pzc}}$  and surface site distribution of the materials. The  $\text{pH}_{\text{pzc}}$  of the sorbent was found to be 3.68. At  $\text{pH} < \text{pH}_{\text{pzc}}$ , the surface charge of the sorbent is positive, sorption of metal (II) on to the surface of the sorbent may be hindered because of charge repulsion. At  $\text{pH} > \text{pH}_{\text{pzc}}$ , the surface of the sorbent is negatively charged, thereby it is easy for the positively charged metal (II) to be adsorbed on the negatively charged adsorbent surface [18]. In this study, the pH selected to remove Ni (II) is 2.0-9.0, and the maximum removal efficiency of Ni (II) ions at pH 6.0 (Figure 2) was observed as 97.52%. Therefore, the experimental work was performed at pH 6.0 in order to avoid any precipitation effect at higher pH. From the Figure 2 it is clear that as the pH increases, the adsorption uptake increases for CNTs due to an increase in the electrostatic attractive forces between  $\text{OH}^-$  and Ni (II) ions. At pH values below 4.0, the adsorption uptake was very weak due to the competition between Ni (II) ions and  $\text{H}^+$  in the solution. Results of previous study indicated that the adsorption of Ni (II) increases with an increase in solution pH from 2.0 to 6.0. This is because oxidation of CNTs with oxidized acid can introduce many functional groups such as hydroxyl, carbonyl and carboxyls on the surface of CNTs [19]. The decrease in percentage removal from pH 6.0 reflects a reduction of negative surface charge density on CNTs. Therefore, the presence of a negative charge on CNTs surface over the pH range is the main reason for Ni (II) adsorption.

#### 3.2. Effect of CNTs Mass

Dosage study is an important parameter in adsorption studies, because it determines the capacity of the adsorbent for a given initial concentration of metal ion solution. The influence of adsorbent CNTs dose on the percentage removal of Ni (II) was examined by carrying out experiments with varying CNTs mass



**Figure 1:** (a-b) Scanning electron microscopic image of modified carbon nanotubes, (c-d) transmission electron microscopic image of modified carbon nanotubes.

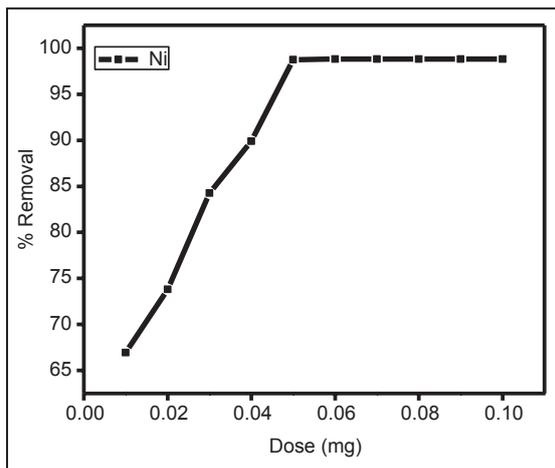


**Figure 2:** Effect of pH for the removal of Ni (II) ions by modified carbon nanotubes.

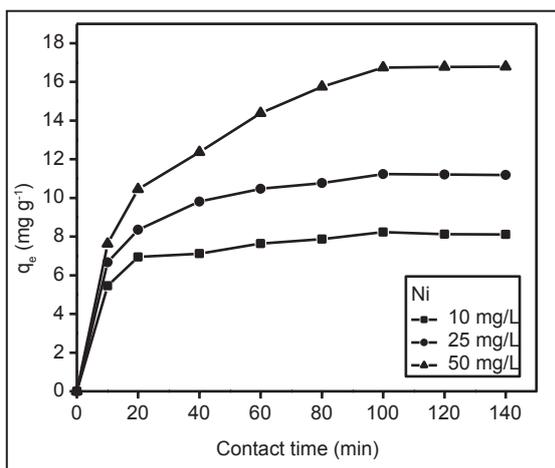
from 0.01 g to 0.120 g, while the total volume, initial concentration of the metal solution, and the pH values were kept constant. The amount of Ni (II) adsorbed is increased with an increase in the adsorbent dosage from 0.01 g to 0.12 g. This result could be explained by the fact that for optimum adsorption, extra sites must be available for adsorption reaction, whereas by increasing the CNTs mass, a number of sites available for adsorption are increased. The maximum adsorption percentage reached 98.76% for Ni (II) as a mass reached 0.05 g as shown in Figure 3. However, any further increase in sorbent mass beyond 0.05 g did not result in sufficient improvement in the percentage removal of nickel ions. Therefore, the optimum CNTs mass has been taken as 0.05 g for conducting further batch of experiments.

#### 3.3. Effect of Contact Time

The adsorption capacity of CNTs mass toward Ni (II) as a function of time at different initial concentrations was represented in Figure 4. The effect of contact



**Figure 3:** Effect of dose for the removal of Ni (II) ions by modified carbon nanotubes.



**Figure 4:** Effect of contact time for the removal of Ni (II) ions by modified carbon nanotubes.

time on the adsorption process was studied in the time range of 10-120 min at pH 6.0, and  $30 \pm 1^\circ\text{C}$  with a fixed adsorbent dose. The effect of the concentration of Ni (II) has been investigated by repeating the experiments using different initial concentrations (10, 25 and  $50 \text{ mg L}^{-1}$ ) of Ni (II). It is noted that the  $q_e$  increased quickly with the time and then slowly reaches equilibrium. From the Figure 4 it is observed that the equilibrium time for Ni (II) adsorption onto CNTs is 100 min with initial concentrations of 10, 25 and  $50 \text{ mg L}^{-1}$ . The amounts of Ni (II) sorbed onto CNTs at equilibrium ( $q_e$ ) are 8.11, 11.90 and  $16.78 \text{ mg g}^{-1}$  with the respective concentrations mentioned above.

### 3.4. Adsorption Dynamics

In order to investigate the sorption rate law of metal sorption, the kinetic data obtained from batch experiments have been analyzed using the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. The first order equation of Lagergren [20] is expressed as:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

where  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are the amounts of metal ions adsorbed per unit weight of the adsorbent at time  $t$  and equilibrium, respectively; and  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant of the sorption process. The model is based on the assumption, that the adsorption rate is proportional to the number of free sites available. On integrating the Equation (2) linear form is obtained as:

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

Linear plots of  $\log(q_e - q_t)$  versus  $t$  have been used to evaluate the data, to determine the rate constant and  $q_e$  from the slope and intercept respectively. The experimental and calculated  $q_e$  values, pseudo-first-order rate constant and correlation coefficient ( $R^2$ ) values are given in Table 1. The theoretical values ( $q_{e, \text{cal}}$ ) are far lower than the corresponding experimental data, ( $q_{e, \text{exp}}$ ), implying that the adsorption process has not fully followed the pseudo-first-order adsorption rate expression.

The pseudo-second order kinetic rate equation [21] is based on the assumption that the adsorption follows the second order chemisorption. The linear form can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is the second order rate constant of adsorption. From the plots of  $t/q_t$  against  $t$ ,  $q_e$  and  $k_2$  are evaluated.

Plotting of  $t/q_t$  versus  $t$  at different adsorbate concentrations has provided the second-order sorption rate constant ( $k_2$ ) and  $q_e$  values from slopes and intercepts. The linear plots of  $t/q_t$  versus  $t$  for all the experimental concentrations are shown in Figure 5. The values of the correlation coefficients,  $R^2$  and  $k_2$  are presented in Table 1. The correlation coefficient for the linear plots are superior (close to 1.0), and the calculated sorption capacity values are more consistent with the experimental values of the predicted sorption capacity, which is confirming the applicability of the pseudo-second-order model.

Further, the lower correlation factors obtained for pseudo-first-order model (0.8962-0.9982) as compared with that obtained for the pseudo-second-order model (0.9991-0.9992) for the adsorption of Ni (II) ions, indicate that the pseudo-first-order model is not encouraging for explaining the kinetics of the

**Table 1:** Kinetic parameters of pseudo-first-order, pseudo-second-order and intra particle diffusion models for Ni (II) onto CNTs.

Initial Ni (II) concentration (mg L <sup>-1</sup> )	Experimental value q <sub>e, exp</sub> (mg g <sup>-1</sup> )	Pseudo-first-order			Pseudo-second-order			Weber and Morris		
		q <sub>e, cal</sub> (mg g <sup>-1</sup> )	k <sub>1</sub> (mg g <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e, cal</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> (mg g <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e, cal</sub> (mg g <sup>-1</sup> )	K <sub>id</sub> (mg g <sup>-1</sup> min <sup>-1/2</sup> )	R <sup>2</sup>
10	8.11	8.01	3.33×10 <sup>-2</sup>	0.9982	8.40	3.79×10 <sup>-2</sup>	0.9992	2.54	0.5762	0.7392
25	11.19	7.84	2.64×10 <sup>-2</sup>	0.9912	11.33	3.26×10 <sup>-2</sup>	0.9991	2.91	0.8435	0.8151
50	16.78	11.41	2.55×10 <sup>-2</sup>	0.8966	17.15	1.74×10 <sup>-2</sup>	0.9991	2.59	1.3798	0.9264

CNTs=Carbon nanotubes

adsorption of the metal. Therefore, the option exercised in favour of the pseudo-second-order model better represents the sorption kinetics and thus supports the assumption behind the model.

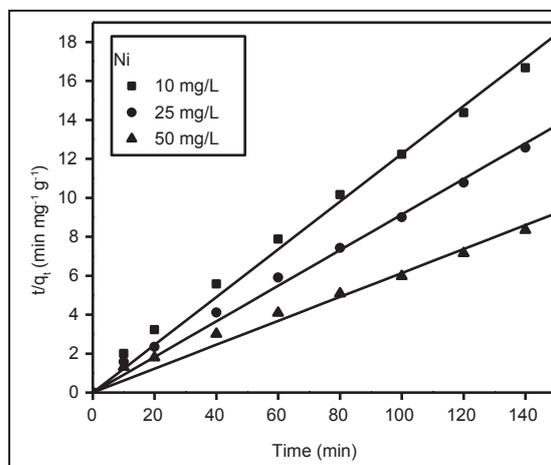
Since neither the pseudo-first-order nor the pseudo-second-order models could identify the diffusion mechanism, the kinetic results are analyzed by the intraparticle diffusion model. In many cases, there is a possibility that intra-particle diffusion would be the rate limiting step, and this normally is determined using the equation described by Weber et al. [22].

$$q = k_{id}t^{1/2} + c \tag{5}$$

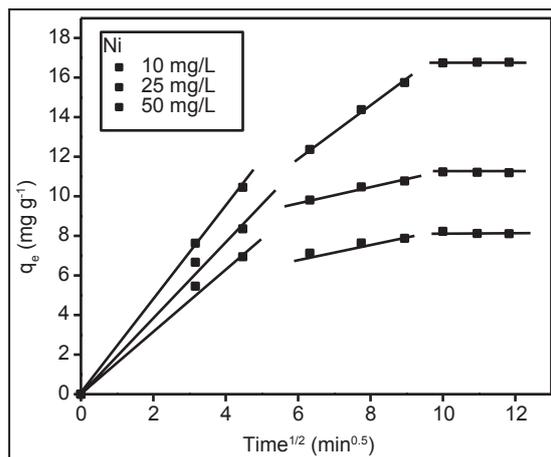
where q (mg g<sup>-1</sup>) is the amount adsorbed at time t, c (mg g<sup>-1</sup>) the intercept, and k<sub>id</sub> (mg g<sup>-1</sup> min<sup>-1/2</sup>) is the intraparticle diffusion rate constant. Figure 6 shows the amount of metal sorbed versus t<sup>1/2</sup> at three different concentrations with a fixed adsorbent dose. It can be deciphered that these plots have three distinct regions. The initial region of the curve relates the adsorption on the external surface. The second region corresponds to the gradual uptake, which reflects the intraparticle diffusion as the rate limiting step. The final plateau region indicates the equilibrium uptake. It denotes that the intraparticle diffusion is not the only rate controlling step [23]. The k<sub>id</sub> values are obtained from the slope of the linear portions of the curve of different initial concentrations and are indicated in Table 1.

### 3.5. Equilibrium Sorption Isotherm Models

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. Great numbers of expressions were given to describe adsorption data; we selected well known Langmuir [24], Freundlich [25], and Dubinin–Radushkevich (D–R) [26] isotherm models. Isotherm plots were drawn for the experimental data of the amount of Ni (II) adsorbed per unit mass (mg g<sup>-1</sup>) versus equilibrium concentration of Ni (II) concentration ranging from 10 mg L<sup>-1</sup> to 80 mg L<sup>-1</sup> at selected temperatures of 293, 303 and 313 K keeping other conditions as constant.



**Figure 5:** Pseudo-second-order kinetic plots for the removal of Ni (II) ions by modified carbon nanotubes.



**Figure 6:** Intra particle diffusion model plots for the removal of Ni (II) ions by modified carbon nanotubes.

#### 3.5.1. Langmuir isotherm

The Langmuir model assumes that adsorption occurs at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. This model can be written as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

Where  $q_e$  is the amount of metal ion adsorbed per unit mass of adsorbent in ( $\text{mg g}^{-1}$ ),  $C_e$  the equilibrium concentration of the metal ion in solution ( $\text{mg L}^{-1}$ ),  $q_m$  is the maximum metal uptake,  $K_L$  is the Langmuir adsorption constant ( $\text{L mg}^{-1}$ ) relating the free energy of adsorption. The data obtained with the correlation coefficients ( $R^2$ ) and Chi-square ( $\chi^2$ ) are listed in Table 2. The essential characteristics of the Langmuir isotherm can be conveniently expressed in terms of a dimensionless term  $R_L$ , which is a constant separation factor or equilibrium parameter for a given isotherm. This is defined as

$$R_L = 1/(1+bC_o) \tag{7}$$

Where,  $C_o$  is the initial concentration of metal ion. The  $R_L$  value indicates the type of the isotherm. According to McKay and Gardener [27],  $R_L$  values between 0 and 1.0 indicate the isotherm favorable, and it is unfavorable if  $R_L > 1.0$ . Isotherms are linear or irreversible if  $R_L$  values are equal to 1.0 or 0 respectively. The  $R_L$  for Ni (II) is 0.15 which indicates favorable adsorption of Ni(II) onto CNTs.

### 3.5.2. Freundlich isotherm

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich model is given by

$$q_e = k_f C_e^{1/n} \tag{8}$$

where  $q_e$  and  $C_e$  are the equilibrium concentrations of metal ions in the adsorbed and liquid phases in  $\text{mg g}^{-1}$  and  $\text{mg L}^{-1}$ , respectively.  $k_f$  and  $n$  are the Freundlich's constants characteristic of the system, indicating the adsorption capacity and adsorption intensity, respectively. The  $k_f$  and  $1/n$  values were found in the range 0.66-10.83 and 0.361-0.379. The Freundlich correlation coefficients ( $R^2$ ) and Chi-square ( $\chi^2$ ) values are listed out in Table 2. On comparison of Langmuir model, the  $R^2$  values of Freundlich model are lower hence this model could not properly describe the relationship between the adsorbate and adsorbent at equilibrium concentration in the solution.

### 3.5.3. D-R isotherms

The D-R isotherm model is used to determine the adsorption type, physical or chemical. The D-R isotherm equation is represented as:

$$q_e = Q_m \exp\left(-K\left[RT\ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) = Q_m \exp(-K\varepsilon^2) \tag{9}$$

where  $Q_m$  is the maximum amount of the ion that can be sorbed onto unit weight of sorbent ( $\text{mg/g}$ ),  $\varepsilon$  is the polanyi potential which is equal to  $RT \ln (1+1/C_e)$ , where "R" and "T" are the universal gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ) and "K" is the absolute temperature respectively.

The correlation coefficients, " $R^2$ " and the Chi-square ( $\chi^2$ ) test were also carried out to find the best fit among the adsorption isotherm models that are used. The equation for evaluating the best fit model is to be evolved as:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{10}$$

where  $q_e$ ,  $m$  is the equilibrium capacity obtained by calculating from a model ( $\text{mg/g}$ ) and  $q_e$  is the experimental data of equilibrium capacity ( $\text{mg g}^{-1}$ ). The results of the non-linear " $R^2$ " and ( $\chi^2$ ) for the three adsorption isotherms (Table 2) indicate that the Langmuir isotherm model appears to be a best fitting model for the adsorption isotherm data of the CNTs because it has displayed the highest  $R^2$  (0.9998) and a lowest Chi-square, ( $\chi^2$ ) (0.5380) values.

### 3.6. Thermodynamic Analysis

When the thermodynamic parameters were properly assessed, they could provide in-depth information regarding the inherent energy and structural changes after adsorption. Thermodynamically, in an isolated system, energy cannot be gained or lost; the entropy change is the driving force. In the practice of environmental engineering, both energy and entropy factors ought to be considered in order to determine the processes that occur spontaneously. The thermodynamic parameters, the Gibbs free energy change of adsorption  $\Delta G^\circ$  ( $\text{kJ mol}^{-1}$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) for the adsorption of Ni (II) onto CNTs is calculated using the following equations:

$$\Delta G^\circ = -RT\ln K \tag{11}$$

**Table 2:** Langmuir, Freundlich and Dubnin-Radushkevich isotherms constants of Ni (II) adsorption onto CNTs.

Metal ion	Temperature K	Langmuir				Freundlich				D-R				
		$q_{\max}$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R^2$	$\chi^2$	$K_f$ ( $\text{mg g}^{-1}$ )	1/n	n	$R^2$	$\chi^2$	Q ( $\text{mg g}^{-1}$ )	K	$R^2$	$\chi^2$
Ni (II)	293	50.09	5.5072	0.998	0.487	10.43	0.3613	2.52	0.978	4.738	38.76	0.022	0.901	16.83
	303	52.13	5.0540	0.997	0.600	10.57	0.3678	2.67	0.989	2.996	40.09	0.022	0.926	22.65
	313	54.75	4.9440	0.996	0.965	10.74	0.3790	2.71	0.991	1.894	41.24	0.023	0.913	24.86

CNTs=Carbon nanotubes, D-R=Dubinin-Radushkevich

Where  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ mol<sup>-1</sup>K<sup>-1</sup>), “ $T$ ” is the absolute temperature and “ $K$ ” (L g<sup>-1</sup>) is an equilibrium constant obtained by multiplying the Langmuir constant  $q_m$  and  $K_L$  [28].

The enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) values are estimated from the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

The values of  $\Delta G^\circ$  were calculated from equation (11). The reciprocal of temperature ( $1/T$ ) was plotted against  $\ln K$ , which is found to be a straight line. The values of  $\Delta H$  and  $\Delta S$  are evaluated from the slope and intercept of the line. The values of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the adsorption of Ni (II) onto CNTs are given in Table 3. The negative values of  $\Delta G$  imply that the adsorption of Ni (II) ions onto CNTs was spontaneous. The magnitude of  $\Delta G$

also increased with an increase in the temperature indicating that the adsorption was more favorable at higher temperatures. The value of  $\Delta H^\circ$  was positive, indicating the endothermic nature of the adsorption of Ni (II) onto CNTs in the temperature range of 293-313 K. One possible explanation of endothermicity of the enthalpy of adsorption is a well-known fact that ions like Ni (II) are well solvated in water. When these ions get adsorbed, they are to some extent denuded of their hydration sheath. This dehydration process of ions requires energy. The investigators assumed that this energy of dehydration exceeds the exothermicity of the ions attaching to the surface. The implicit assumption is that after adsorption, the environment of the metal ions is less aqueous than it was in the solution state. The removal of water from ions is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of the enthalpy of adsorption to a considerable extent. The positive value of  $\Delta S^\circ$  suggested an increase in randomness at the solid/liquid interface during the adsorption of Ni (II) onto CNTs [29].

**Table 3:** Thermodynamic parameters for the adsorption of Ni (II) ions onto CNTs at different temperatures.

T (K)	$-\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	R <sup>2</sup>
293	4.0289	0.005731	5.7080	0.9992
303	4.1432			
313	4.1013			

CNTs=Carbon nanotubes

**3.7. Comparison of CNTs with Other Adsorbents**

The adsorption capacities of various adsorbents for Ni (II) adsorption as reported in the literature are presented in Table 4. A comparison between this work and the reported data from the literature [2,3,15,30-34] shows that CNTs are better and promising adsorbents for Ni (II) removal than other adsorbents. Therefore, it could be safely concluded that the oxidized CNTs has a considerable potential for the removal of Ni (II) from aqueous solutions.

**Table 4:** Comparison of maximum adsorption capacities of some adsorbents for Ni (II) ion.

Adsorbent	$q_e$ (mg g <sup>-1</sup> )	Temperature (K)	pH	Isotherm followed	Reference
ZCNTs	54.75	313	6.0	Langmuir	This work
CPH (treated)	34.34	293	5.0	Langmuir	[2]
GAC	26.39	293	7.0	Langmuir	[3]
MWCNT	38.46	293	7.0	Langmuir	[3]
SWCNT	47.85	293	7.0	Langmuir	[3]
Granular biomass	26.00	294	4.0-5.5	Langmuir	[30]
Sugar beet pulp	11.86	293	4.7	Langmuir	[31]
RS 1301	5.10	293	5.0	Freundlich	[32]
AC Clothes: CS 1501	5.80	293	5.0	Freundlich	[32]
Triphenylphosphine-MWCNT (2)	100.00	273	6.0	Langmuir	[33]
Triphenylphosphine-MWCNT (1)	83.33	273	6.0	Langmuir	[33]
Purified MWCNT	55.55	273	6.0	Langmuir	[33]
MWCNT (HNO <sub>3</sub> )	9.80	273	6.55	Langmuir	[15]
As produced CNTs	18.08	293	6.0	Langmuir	[34]
Oxidized CNTs	49.26	293	6.0	Langmuir	[34]

CNTs=Carbon nanotubes, MWCNT=Multi-walled carbon nanotubes, GAC=Granular activated carbon, CPH=Coca Pod husk

### 3.8. Desorption and Regeneration

The repeated usability is an important factor for a good adsorbent. The better adsorbent should not only possess higher adsorption capacity, but also show better desorption efficiency, which will significantly reduce the cost of adsorbent. A successful desorption process requires the proper selection of the eluents, which strongly depends on the type of adsorbent and the mechanism of adsorption. Dilute solutions of mineral acids could be employed for desorption studies. In our study, desorption experiments were carried out through various concentrations of 0.05-0.25 M HCl, respectively. Four consecutive cycles of sorption/desorption experiments were carried out then it was found that desorption efficiencies were nearly 86-95% with 0.25 M HCl, at the end of desorption cycle the per cent removal was decreased, that may be attributed to the inevitable weight loss of adsorbent.

### 4. CONCLUSION

Oxidized CNTs synthesized by the CCVD method using combinations of iron and cobalt salts. The CNTs were treated with H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub> and NaOCl reagents it has been observed the increase their surface area, functional groups and acidic sites on oxidation. Kinetic studies revealed that pseudo-second-order model was better suitable than a pseudo-first-order model with the correlation coefficients >0.99. Adsorption isotherms suggest that Langmuir isotherm better explained the experimental data of Ni (II) than Freundlich and D-R isotherms. The thermodynamic studies confirm that adsorption of Ni (II) ions onto CNTs are endothermic and spontaneous. This reflects that the zeolite supported CNTs treated with oxidizing agents could enhance the Ni (II) uptake from aqueous solutions and possess good potential as sorbents for removing Ni (II) from aqua solutions.

### 5. ACKNOWLEDGMENTS

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