

Adsorption of Toxic Ni(II) From Aqueous Solution By Activated Carbon

Mervette El Batouti , Abdel –Monem M. Ahmed and Soad M. Salam,

Chemistry Department, Faculty of Science, Alexandria University.

Abstract

In this study, the adsorption potential of activated carbon for removal of Ni^{2+} ions from wastewater has been investigated. The study involves batch type experiments to investigate the effect of initial concentration, adsorbent dose, agitation speed, contact time, temperature and pH of the solution in adsorption process and the optimum conditions were evaluated. The adsorption process has fit pseudo-second order kinetic models. Langmuir and Freundlich adsorption isotherm models were applied to analyze adsorption data and both were found to be applicable to this adsorption process. Thermodynamic parameters, e.g., ΔG° , ΔS° and ΔH° of the on-going adsorption process have also been calculated and the sorption process was found to be endothermic

* Corresponding author:

mervette_b@yahoo.com

Received 25 Sept 2016,

Revised 11 Dec 2016,

Accepted 01 Jan 2017

Keywords: Wastewater, Adsorption, Nickel, Activated carbon, Removal

I. INTRODUCTION

Industrial effluent are the major sources for contamination of water resources by heavy metals. Ni^{2+} belongs to the so-called « essential » metals and is identified as a component in a number of enzymes, participating in important metabolic reactions, such as ureolysis, hydrogen metabolism, methane biogenesis, and acidogenesis [1]. But nickel(II) ion intake over the permissible levels results in different types of disease such as pulmonary fibrosis, renal edema, skin dermatitis, and gastrointestinal distress (e.g., nausea, vomiting, diarrhea) [1]. It is, therefore, essential to remove Ni^{2+} from wastewater before disposal. Mining and metallurgy of nickel, stainless steel, aircraft industries, nickel electroplating, battery and manufacturing, pigments and ceramic industry wastewaters contain high amounts of nickel ions [2]. The commonly used techniques for removing metal ions from effluent include ion exchange, adsorption, chemical precipitation, reverse osmosis and solvent extraction [3-5]. These techniques are economically expensive and have disadvantages like incomplete metal removal, generation of toxic sludge and other disposable waste product. Recovery of heavy metals from wastewaters and industrial wastes has become a very important environmental issue. Nickel has many useful applications in our life and is harmful if discharged into natural water resources [6]. Ni^{2+} is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries. The acceptable limit of Ni in drinking water is 0.01 mg/L and for the discharge of industrial wastewater is 2.0 mg/L [7]. At higher concentrations, Ni^{2+} causes cancer of the lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and costume jewelry. Ni carbonyl $[\text{Ni}(\text{CO})_4]$ has been estimated as lethal in humans at atmospheric exposures of 30 ppm for 30 min [8]. Acute poisoning of Ni(II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness. Hence, it is essential to remove Ni^{2+} from industrial wastewater before mixing with natural water sources. In advanced countries, removal of Ni^{2+} metal ions in wastewater is normally achieved by advanced technologies such as precipitation-filtration, ion exchange and membrane separation [9]. However, in developing countries, these treatment cannot be applied because of technical levels and insufficient funds. Therefore, it is desired that the simple and economical removal method which can utilize in developing countries is established. Although, the treatment cost for the precipitation - filtration method is comparatively cheap, the treatment procedure is complicated. On the other hand, the adsorption method such as ion exchange and membrane separation is simply one for the removal of heavy metals. However, there is a limit in the generality in developing countries because chelating and ion-exchange resins are expensive. In the present study, removal of Ni^{2+} ions from wastewater was further carried out by adsorption onto activated carbon. The objectives of the present study are: 1) to study the effect of contact time on Ni^{2+} ions adsorption onto activated carbon; 2) to investigate the influence of pH on the adsorption of Ni^{2+} ions; 3) to study the adsorption of Ni^{2+} ions at different temperatures and to calculate the adsorption thermodynamic parameters (i.e., ΔH° , ΔS° and ΔG°); 4) to find the effect of adsorbent dose and initial concentration on the adsorption of Ni^{2+} ions; 5) to describe the experimental data of adsorption isotherms through Langmuir and Freundlich models; 6) to discuss the adsorption mechanism of Ni^{2+} ions onto both adsorbents.

2. Experimental

2.1. Materials and reagents

All chemicals used in this present work were either of analytical reagent (AR) or laboratory reagent (LR) grade and were used as received. NiSO_4 supplied by BDH chemicals Ltd. Distilled water was used in all preparations. Deionized water was used to prepare synthetic chromium containing waste-water. Powder activated carbon (PAC) produced from natural origin by ADWIC was used as adsorbent as well as American Wyoming used in Alexandria Company for Refractories.

Powder activated carbon (PAC) were supplied from ADWIC and Alexandria Company for Refractories, respectively. The surface area and particle size analyses for the two adsorbents were checked Table 1.

Table 1: Surface area and particle size analysis of activated carbon.

Adsorbents Analysis	Activated Carbon	
Surface Area (BET)		
Nova 2000	931.9 m ² /g	
Quantachrome		
	Size (micrometer)	Wt. %
Particle size (XRD)	32-16	2.75
Philips PW 1730	16-8	55.89
	8-4	16.03
	4-2	21.14
	< 2	4.19
Adsorbent	% removal of metal	
moss peat [5,6]	66 %	
coconut husk[7,8]	70 % removal of nickel ions	
chitosan [9]	74 % removal	
coir pith[10]	66 % removal	
rice husk[11,12]	74 % removal	
tea leaf[13]	69 % removal	
almond husk[14]	64 % removal	

2.2.Apparatus and instrumentation

Magnetic hot plate stirrer was used to stir the heavy metals ion solutions with adsorbents (activated carbon). A definite volume of heavy metal ion solution with a known initial ion concentration was stirred with a definite amount of adsorbents for a certain time at fixed temperature and agitation rate. The pH values of the solution were measured by digital pH meter (Model μ pH system-361, India). The metal ions concentrations were measured by using atomic-absorption spectrophotometer, AAS, (Model, AA55; Varian Inc., USA).

2.3.Experimental procedures

Ni^{2+} chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) , and redistilled water were used to prepare a stock solution with a concentration of 1000 ppm of the Ni^{2+} and which were diluted for preparation of test solutions. Several solutions with different initial concentrations of nickel chloride (50, 100, 200, 300 and 400 ppm) were prepared. Adjustment of pH was carried out by using 0.1 N NaOH and/ or 0.1 N HCl. All experiments, conditions were optimized to achieve maximum removal efficiency (RE) for all heavy metal ions by adding different amounts of both adsorbent (0.1, 0.3, 0.5, 0.7 and 1.0 g) to different concentrations of 250 mL of heavy metal ions solution. The agitation rate for all experiments was 200 RPM and the residence time were (0, 15, 30, 45, 60, 75, 90 and 120 min) at 25°C. 1 mL of Sample was taken from each reaction solution and diluted to 10 mL with redistilled water, adsorbents were then separated from the solution by

using filter paper (Watman No. 40) and the residual Ni^{2+} ion concentrations in the each solution was then determined by atomic-absorption spectrophotometer (AAS). The effects of several parameters, such as contact time, initial concentration, adsorbent dose, solution volume, pH value and temperature on the adsorption of Ni^{2+} ions onto activated carbon were studied.

2.4. Data analysis

The uptake of Ni^{2+} ions was calculated from the mass balance, which was stated as the amount of solute adsorbed onto the solid. It equals the amount of solute removed from the solution. Mathematically, it can be expressed by Eq. (1):

$$q_e = (C_i - C_e)/S \quad (1)$$

where:

q_e the heavy metal ion concentration adsorbed by an adsorbent at equilibrium (mg of metal ions/g of adsorbent).

C_i is the initial concentration of metal ions in the solution (mg/L).

C_e is the equilibrium concentration or final concentration of metal ions in the solution (mg/L).

S the dosage concentration and it is expressed by Eq. (2):

$$S = m/V \quad (2)$$

where V is the initial volume of metal ions solution used (L) and m is

The weight of dried used adsorbent (g). The percentage of adsorption (%) is calculated using Eq. (3):

$$\% \text{ adsorption} = [(C_i - C_e)/C_i] \times 100 \quad (3)$$

2.5. Adsorption kinetics

To investigate the mechanism of Ni^{2+} ions adsorption onto activated carbon, two kinetic models were considered as follows: Lagergren pseudo-first order model can be expressed by Eqs. (4) and (5):

$$dq/dt = k_1(q_e - q) \quad (4)$$

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (5)$$

The pseudo-second order model is given by Eqs. (6) and (7):

$$dq/dt = k_2(q_e - q)^2 \quad (6)$$

$$t/q = t/q_e + 1/k_2 q_e^2 \quad (7)$$

where q and q_e are the amount of Ni^{2+} metal adsorbed per unit weight of adsorbent (mg/g) at time t , and at equilibrium, respectively, and k_1 and k_2 are the adsorption rate constants. The applicability of the above two models can be examined by each linear plot of $\ln(q_e - q)$ vs. t , and (t/q) vs. t , respectively and are represented in Fig.(1) respectively. The kinetics study for the adsorption of Ni^{2+} was conducted at optimum pH 5.0 and completed in 2 h for the concentrations (50, 100 and 200 mg/L) Ni^{2+} ions onto (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) doses of both adsorbents at 25°C. The validity of the kinetic models is tested by the magnitude of the regression coefficient R_2 . It is important to note that for a pseudo-first order, the correlation coefficient is always less than 0.98, which is indicative of a bad correlation. In contrast, the application of a pseudo-second order model leads to much better regression coefficients, all greater than 0.99. Moreover, from **Fig (1)**, the q_e , the values estimated from the pseudo-first kinetic model gave significantly different values compared to experimental values and the correlation coefficients were also found to be lower. However, in pseudo-second order kinetic model the calculated q_e , the values is very close to q_e , exp values at various initial concentrations and various adsorbent doses.

For the pseudo-second order kinetic model, the rate constant decreases with an increasing of initial Ni^{2+} concentration.

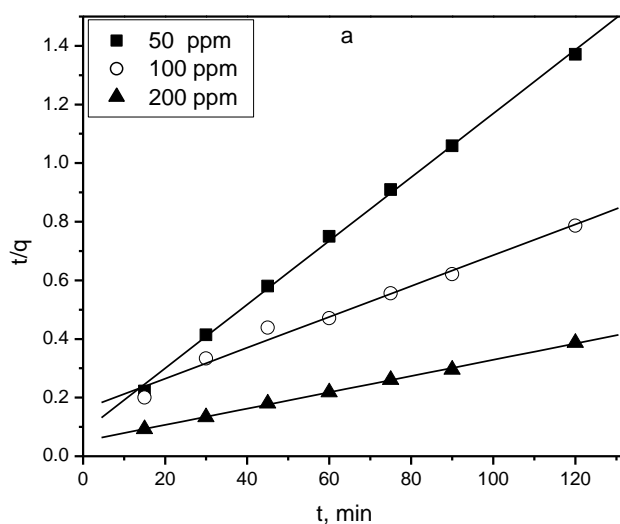


Fig. (1): Pseudo-second order kinetic plots for the adsorption of different initial concentrations: 50, 100 and 200 ppm Ni^{2+} ions onto different adsorbent doses of activated carbon: a) 0.1 g/250 mL, (pH: 5.0; agitation speed: 200 rpm; temperature: 25°C).

Table 2: The adsorption kinetics model rate constants for adsorption of Ni^{2+} ions onto activated carbon at various concentrations and constant temperature 25°C.

Adsorbent (0.1 g)	Co (mg/ L)	q _e exp. (mg/g)	Lagergren first order			Pseudo-second order		
			K1 (min ⁻¹)	q1, theo. (mg/g)	R2	k2 (gmg ⁻¹ min ⁻¹)	q2, theo. (mg/ g)	R2
Activated Carbon	50	87.5	3.4x10 ⁻²	52	0.883	1.4x10 ⁻³	88	0.998
	100	152.5	2.7x10 ⁻²	141	0.971	1.7x10 ⁻⁴	150	0.993
	200	310	3.3X10 ⁻²	268	0.988	1.5x10 ⁻⁴	308	0.998

Adsorbent (0.5 g)	Co (mg/ L)	q _e exp. (mg/g)	Lagergren first order			Pseudo-second order		
			K1 (min ⁻¹)	q1, theo. (mg/g)	R2	k2 (gmg ⁻¹ min ⁻¹)	q2, theo. (mg/ g)	R ₂
Activated Carbon	50	19	2.9x10 ⁻²	11	0.812	8.5x10 ⁻³	20	0.993
	100	34	3.3x10 ⁻²	26	0.970	2.2x10 ⁻³	32	0.996
	200	64	3.4x10 ⁻²	45	0.935	1.9x10 ⁻⁴	61	0.998

2.6.Parameters affecting adsorption process:

- *Effect of contact time.*

The effect of contact time for five different concentrations of Ni(II) (50, 100, 200, 300 and 400 mg/L) onto (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) of activated carbon doses, pH 5.0 at 25°C is shown in **Figs. (2)**. The Ni^{2+} percentage removal increased by time until the equilibrium is attained between the amounts of Ni^{2+} adsorbed onto both adsorbents and the remaining in solution. The figures showed that the adsorption of Ni^{2+} increased with time from 0 to 30 min and more and then increased slowly up to the end of the experiment. It can be concluded that the rate of Ni^{2+} binding with activated carbon is more at initial stages, which gradually decreases and becomes almost constant after an optimum period 90 min.

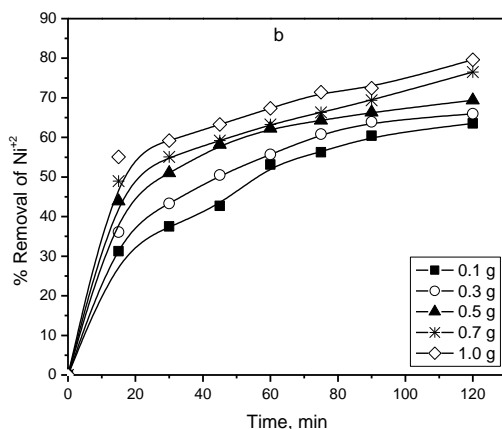


Fig. (2): Effect of contact time (min) on % removal of Ni^{2+} ions for: 100 ppm, in the presence of different amounts of activated carbon (temp. = 25°C, pH = 5.0 and equilibrium time = 2 h).

Figs. (3) show the relation between the amount of adsorbed ions per gram of adsorbent and contact time in the presence of different amounts of adsorbent at 25°C. At the begin, q rises rapidly and by time it increases slowly till the maximum adsorption.

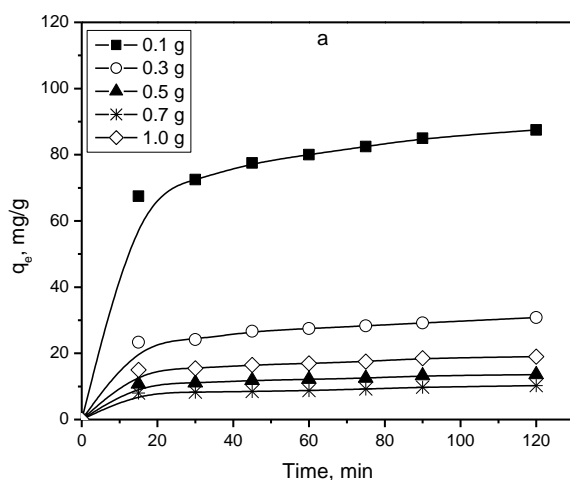


Fig. (3): Effect of contact time on adsorbed amount of Ni^{2+} for different concentrations: a) 50 ppm and b) 100 ppm, in the presence of different h).

- **Effect of adsorbent dose**

The effect of adsorbent dose on percentage removal of (50, 100, 200, 300 and 400 mg/L) Ni^{2+} ion concentrations at 25°C is shown in **Fig. (3)**. Percentage of nickel(II) ions removal increased when the adsorbent dose increased from 0.1 to 1.0 g/250 mL of activated carbon. It can be seen that, the number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal ions removal at a high dose. However, the amount of metal ions adsorbed per unit weight of adsorbent (q) decreases with the adsorbent dose. This is due to the fact that at higher adsorbent dose the solutions ion concentration drops to a lower value and the system reaches equilibrium at lower values of q indicating the adsorption sites remain unsaturated.

- **Effect of initial Ni^{2+} ion concentration**

An increase of initial Ni^{2+} concentration from 50 to 300 mg/L with different amounts of activated carbon (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) when other experimental conditions are kept constant, illustrated in **Figs. (4)**. It can be seen from the figures that, % removal of Ni^{2+} increases when the initial concentration decreased. At low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, the amount of metal adsorbed per unit weight of adsorbent, q , is higher in high concentration as shown in **Figs. (5)**.

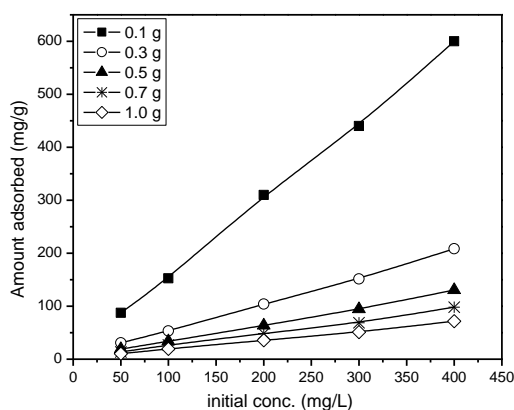


Fig. (4): The effect of initial concentration (namely 50, 100, 200 and 300 mg/L) on quantity adsorbed of Ni^{2+} ions in the presence of different amounts of activated carbon (temp. = 25°C, pH = 5.0 and equilibrium time = 2 h).

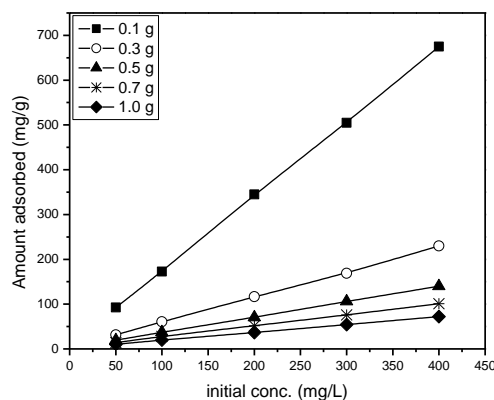


Fig. (5): The effect of initial concentration (namely 50, 100, 200 and 300 mg/L) on quantity adsorbed of Ni^{2+} ions (temp. = 25°C, pH = 5.0 and equilibrium time = 2 h).

- *Effect of pH on the uptake of Ni^{2+}*

The pH value of the solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH, which influences both the adsorbent surface metal binding sites and the metal chemistry in water [10]. Hence, the influence of pH on the adsorption of Ni^{2+} onto activated carbon was examined in the range of 2-9, the results are shown in **Fig. (6)**. The figures show that, the sorption of Ni^{2+} increases with increasing pH at pH 2-7, then increases sharply with increasing pH at pH >7 and at least maintains a high level at pH >8.5. The abrupt increase of Ni^{2+} sorption may be attributed to the surface precipitation of $\text{Ni}(\text{OH})_2(\text{S})$ onto both activated carbon. It is well known that Ni^{2+} can easily form precipitation because of the low solubility of $\text{Ni}(\text{OH})_2$ ($K_{\text{sp}} = 2.0 \times 10^{-15}$). It is clear that Ni^{2+} ions start to form precipitation at pH ~8.6. However, one can see that more than 90% Ni^{2+} has been adsorbed to activated carbon at pH >8.6.

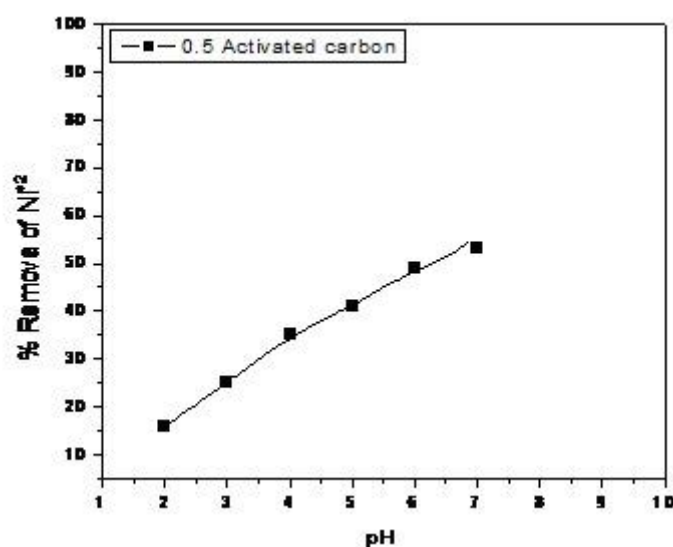


Fig. (6): Effect of pH for the adsorption of Ni^{2+} ions onto activated carbon (conditions; Ni^{2+} ions initial concentration: 100 mg/L; adsorbent dose: 0.5 g/250 mL; agitation speed: 200 rpm; contact time: 2 h) at 25°C.

- *Effect of temperature*

The effect of the temperature on the efficiency of adsorption of Ni^{2+} was studied at different temperatures in the range of 25-40°C. The adsorption experiments were carried out with (50, 100, 200, 300 and 400 mg/L) initial concentrations of Ni(II) onto 0.5 g/250 mL for both activated carbon at pH 5.0.

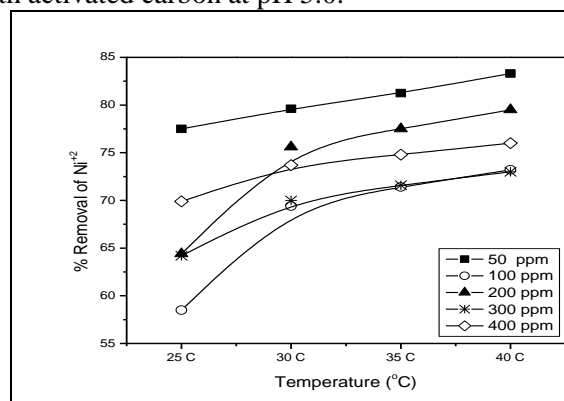


Fig. (7): The effect of temperature between 25 and 40°C for the % removal of different initial Ni^{2+} ions concentrations onto activated carbon (conditions; pH: 5.0; adsorbent dose: 0.5 g/250 mL; agitation speed: 200 rpm; contact time: 2 h).

The adsorption of Ni²⁺ onto both adsorbents increases by increased temperature from 25 to 40°C **Figs. (7)**, this indicates that the Ni(II) uptake by adsorption onto activated carbon favors at higher temperature. This may be due to availability of the more active sites of both adsorbent at higher temperature.

2.7 Adsorption isotherm

Adsorption isotherm is an expression that shows the relationship between the amount of adsorbate adsorbed per unit weight of adsorbed (q_e , mg/g) and the concentration of adsorbate in bulk solution (C_e , mg/L) at given temperature under equilibrium conditions. Adsorption equilibrium is established when the amount of adsorbate being adsorbed is equal to the amount being desorbed from the adsorbent. At this stage, the equilibrium concentrations in both phases are constant. Adsorption isotherm is very useful in giving information about adsorption mechanisms, surface properties and affinity of an adsorbent towards heavy metal ions [11]. The isotherm data were further analyzed with two most commoner isotherm models:

The Langmuir and Freundlich models (Langmuir, 1916; Freundlich, 1906), are the most frequently employed to describe equilibrium for the adsorption of (50, 100 and 200 mg/L) Ni²⁺ ion concentrations onto (0.1, 0.3, 0.5, 0.7, and 1.0 g/250 mL) for activated carbon at 25 °C . The Langmuir isotherm is probably the most widely applied isotherm models in many adsorption studies. The model was developed based on assumptions that adsorption occurs at specific homogeneous sites on the adsorbent and was used successfully in many monolayer adsorption processes. It also assumes no transmigration of the adsorbate in the plane of adsorbent surface.

The Langmuir isotherm for adsorption can be obtained from Eq. (8):

$$C_e/q_e = 1/(q_{\max}b) + (1/q_{\max}) C_e \quad (8)$$

Where q_{\max} is the maximum metal ion uptake per unit mass of adsorbent (mg/g), which is related to the adsorption capacity and b is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity. Therefore, a plot of C_e/q_e versus C_e gives a straight line of the slope $1/q_{\max}$ and intercept $1/(q_{\max} b)$ as shown in Fig.(8).

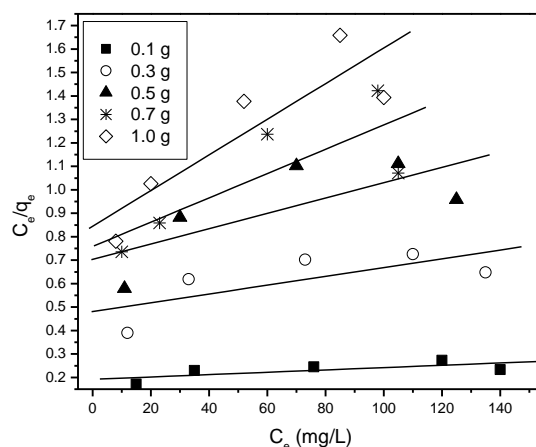


Fig. (8): Langmuir adsorption isotherm for Ni²⁺ ions adsorption onto different amounts of activated carbon at constant temperature 25°C and contact time 2 h.

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. It also assumes that the stronger adsorption sites are occupied first and the binding strength decreases with the increasing degree of site occupation. The Freundlich model is given by (Freundlich, 1906) the classical empirical isotherm, Eq. (9):

$$\ln q_e = \ln KF + 1/n \ln C_e \quad (9)$$

The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface, where the Freundlich constants KF and n, which respectively, indicating the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ as shown in Figs.(9).

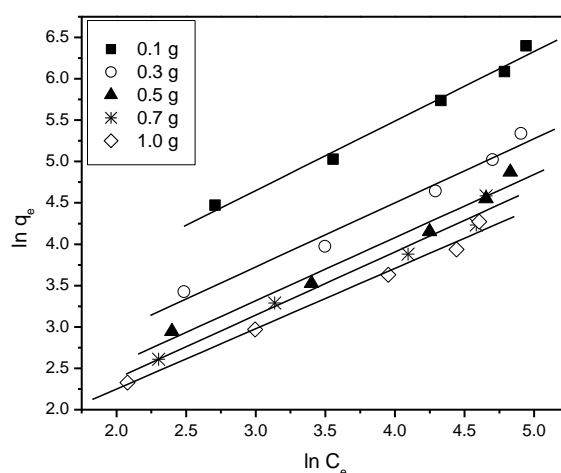


Fig. (9): Freundlich adsorption isotherm for Ni^{2+} ions adsorption onto different amounts of activated carbon at constant temperature 25°C and contact time 2 h.

This Freundlich type behavior is indicative of surface heterogeneity of the adsorbents, i.e the adsorptive sites (surface of activated carbon) are made up of small heterogeneous adsorption patches that are homogeneous in themselves. The activation of adsorption sites takes place, leading to increased adsorption probability through the surface exchange mechanism. The calculated results of Langmuir and Freundlich isotherm constants are given in Table 8. It can be seen that, the Freundlich model yields a much better fit than the Langmuir model, when the correlation coefficient (R^2) values are compared in Table 3 (R^2 values of Freundlich plot > 0.99 was close to unity, indicating isotherm data fitted well to Freundlich model). The Freundlich constant (KF) indicates the sorption capacity of the sorbent. From Table 8, It is noted that the values of (n) are bigger than 1, reflecting the favourable adsorption. The plots of (q_e) versus (C_e) are presented in **Figs. (9)**, it is seen that (q_e) increased by increasing (C_e) with a higher slope at the initial stages which indicates that, initially, there are numerous readily accessible sites for adsorption processes. Eventually (q_e) reaches a maximum value at higher (C_e), indicating that the adsorption is saturated at this level.

Table 3: Langmuir and Freundlich isotherm for the adsorption of Ni^{2+} ions onto different doses of activated carbon at constant temperature (25°C).

Adsorbent g/250 mL)	(0.1	Langmuir Isotherm constants			Freundlich Isotherm constants		
		q_{\max} (mg/g)	b (L/mol)	R^2	KF (mg/g)	n	R^2
Activated Carbon		77	2.8×10^{-2}	0.911	8.39	1.189	0.994

Adsorbent g/250 mL)	(0.3	Langmuir Isotherm constants			Freundlich Isotherm constants		
		q _{max}	b (L/mol)	R ²	KF (mg/g)	n	R ²
Activated Carbon		84	3.8x10 ⁻³	0.889	4.12	1.290	0.991

Adsorbent g/250 mL)	(0.5	Langmuir Isotherm constants			Freundlich Isotherm constants		
		q _{max} (mg/g)	b (L/mol)	R ²	KF (mg/g)	n	R ²
Activated Carbon		94	4.61x10 ⁻³	0.886	2.80	1.309	0.998

Adsorbent g/250 mL)	(0.7	Langmuir Isotherm constants			Freundlich Isotherm constants		
		q _{max} (mg/g)	b (L/mol)	R ²	KF (mg/g)	n	R ²
Activated Carbon		193	6.8x10 ⁻³	0.872	2.34	1.308	0.998

Adsorbent g/250 mL)	(1	Langmuir Isotherm constants			Freundlich Isotherm constants		
		q _{max} (mg/g)	b (L/mol)	R ²	KF (mg/g)	n	R ²
Activated Carbon		201	8.99x10 ⁻³	0.875	2.21	1.369	0.993

2.8. Thermodynamic parameters

The determination of thermodynamic parameters has a great importance to evaluate spontaneity and heat change for the adsorption reaction. The apparent equilibrium constant (K_c) of the adsorption is defined as:

$$K_c = CA_e/C_e \quad (9)$$

The standard Gibb's energy was evaluated by:

$$\Delta G^\circ = -RT \ln K_c \quad (10)$$

Where R is the ideal gas constant (8.314 J mol⁻¹K⁻¹) and T is the temperature (K).

Where CA_e and C_e (both in mg/L) are the equilibrium concentrations of Ni²⁺ ions onto the sorbent and in the solution, respectively. In this case, the activity should be used instead of concentration in order to obtain the standard thermodynamic equilibrium constant (K_c) of the adsorption system.

$$\ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (11)$$

The plot of lnK_c as a function of 1/T yields a straight line is shown in **Figs. (9)** from which ΔH° and ΔS° can be calculated from the slope and intercept, respectively.

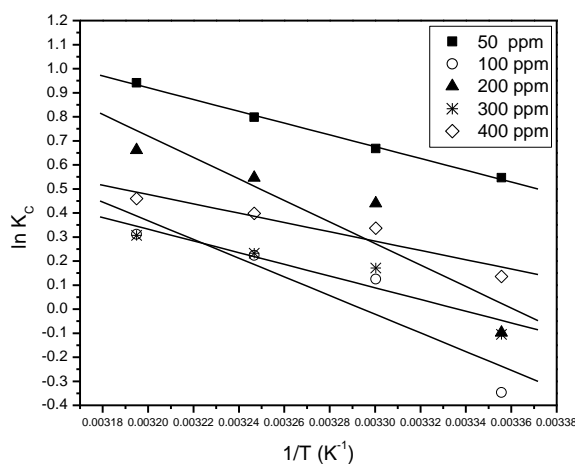


Fig. (9): A plot of $\ln K_C$ versus $1/T$ for Ni^{2+} ions adsorption onto activated carbon for different initial Ni^{2+} concentrations at a constant adsorbent dose: 0.5 g/250 mL.

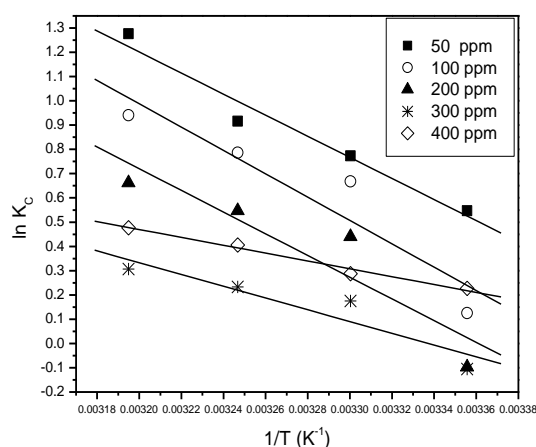


Fig. (10): A plot of $\ln K_C$ versus $1/T$ for Ni^{2+} ions adsorption for different initial Ni^{2+} concentrations at a constant adsorbent dose: 0.5 g/250 mL.

The negative values of ΔG° at all temperatures (25, 30, 35 and 40°C) indicate the spontaneous nature of the adsorption of (50, 100, 200, 300 and 400 mg/L) of $\text{Ni}(\text{II})$ onto 0.5 g/250 mL of both activated carbon. The change of the standard free energy decreases with increasing temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperature. It has been reported that, ΔG° values up to -20 kJ/mol are consistent with the electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG° values more negative than -40 kJ/mol involve charge sharing or transfer from the surface of the metal ion to form a coordinate bond (chemical adsorption). The ΔG° values obtained in this study for Ni^{2+} ions are < -10 kJ/mol, which indicates that physical adsorption was the predominant mechanism in the sorption process.[12]. The positive value of ΔH° suggests the endothermic nature of adsorption. The positive value of ΔS° shows the increased randomness at the solid/solution interface during the adsorption process. Table (4) summarizes the values of these thermodynamic properties.

Table 4: Thermodynamic parameters for different concentrations of Ni²⁺ ions onto activated carbon.

Adsorbent	Co (mg/L)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
				25°C	30°C	35°C	40°C
Activated carbon	50	20.4	73	- 1.1	- 1.5	- 1.8	- 2.2

Adsorbent	Co (mg/L)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
				25°C	30°C	35°C	40°C
Activated carbon	100	32	106	- 0.1	- 0.2	- 0.4	- 0.9

Adsorbent	Co (mg/L)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
				25°C	30°C	35°C	40°C
Activated carbon	200	35	120	- 0.6	- 0.8	- 1.2	- 2.3

Adsorbent	Co (mg/L)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
				25°C	30°C	35°C	40°C
Activated carbon	300	21	67	- 0.2	- 0.3	- 0.4	- 0.7

Adsorbent	Co (mg/L)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
				25°C	30°C	35°C	40°C
Activated carbon	400	16	55	- 0.6	- 0.7	- 1.1	- 1.2

3. Conclusion

It included the results of the ability of selected adsorbents such as activated carbon to remove Ni(II) ions from wastewater at different conditions as contact time, amount of adsorbent, temperature, initial concentration, solution volume and pH. In order to find out thermodynamic and kinetic parameters, equilibrium adsorption models were applied. Although experimental data was confirmed with both Langmuir and Freundlich isotherm models. Adsorption rate constant was determined from Lagergren equation and pseudo-second order equations.

It is found that, both of activated carbon capable of removing Ni(II) ions from wastewater. The adsorption was dependent on contact time, initial Ni(II) ions concentration, adsorbent dosage and temperature. The sorption of Ni(II) onto activated carbon and bentonite is strongly dependent on pH value. The sorption increased with increasing the pH value at pH <8.5, and then maintains a high level at pH >8.5.

Freundlich model has better correlation coefficient (R^2) than the Langmuir model for the studied concentrations at 25°C. Other important result withdrawn from value of thermodynamic parameters can be stated as, negative value of ΔG° and positive value of the ΔS° show that the adsorption of Ni(II) ions onto both adsorbents is a spontaneous process and positive value of ΔH° indicates that the adsorption is endothermic in nature. Finally, it can be seen that the pseudo-second order equation provided the best correlation coefficient (R^2) for the adsorption data.

References

- 1-Akhtar N, Iqbal J. Iqbal M. Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: characterization studies. *J Hazard Mater* 2004, *Mater* 2004, 108:85-94.
- 2-Ozer A, Gurbuz G. Calimili A., Korbahti BKJ. Investigation of nickel(II) biosorption on *Enteromorpha prolifera*; optimization using response surface analysis. *J Hazard Mater* 2008; 152: 778-88.
- 3-Yu Q. Kaews P. Adsorption of Ni^{+2} from aqueous solutions by pre-treated biomass of marine macroalgae *Durvillaea potatorum*, *Sep Sci. Technol.* 2000; 35:689-701.
- 4-Juang RS, Shiau RC, Metal removal from removal from aqueous solutions using chitosan enhanced membrane filtration. *J. Membr Sci* 2001; 165:159-67.
- 5-Yan G. Viraraghavan T, Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass. *Bioresour Technol.* 2001; 78:243-9.
- 6- Al-Asheh S., Duvnjak Z., (1997). Adsorption of metal ions by moss. *Adv. Environ. Res.* 2, 194-212.
- 7- Sharma Y. C., Prasad G., Rupasingh D. C., (1992). Heavy metal pollution of river Gang in Mirzapur. *Int. J. Environ. Stud.* 40, 41-535.
- 8-Beliles, The lesser metals, in: F.W. Oehme (Ed.), (1979). *Toxicity of Heavy metals in the Environment*, part 2, Marcel Dekker, New York, p. 383.
- 9- Dean J. D., Bosqui F. L., Lanouette K. H., (1972). Removing heavy metals from waste water. *Environ. Sci. Technol.* 6, 518-522.
- 10- Waranusantigul, Pokethitiyook P., Kruatrachue M., Upatham E. S., (2003). Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*), *Environ. Pollut.* 125, 385-392.
- 11- Ho YS, Porter JS, McKay G., (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component system. *Water, Air, and Soil Pollution.* 141, 1-33 (2002).
- 12- Horsfall, M.; Spiff, A.I. and Abia, A.A. (2004). Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (*Manihot esculenta* cranz) waste Biomass on the adsorption of Cu^{2+} and Cd^{2+} from aqueous solution. *Bull. Korean Chem. Soc.*, 25(7), 969-976