



Studies on the isotherms, kinetics and thermodynamics of adsorption of nickel (II) on low cost material

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ABSTRACT

The removal of divalent nickel from aqueous solutions on Acid Activated was studied at varying contact times, pH, initial divalent nickel concentrations, adsorbent dose and temperature. The adsorption followed second order kinetics and the rate is mainly controlled by intra-particle diffusion. Experimental equilibrium and kinetics data were fitted by Langmuir and Freundlich isotherms. The kinetics and thermodynamics of adsorption process were evaluated and the data followed pseudo kinetic model. The thermodynamic parameters for the present system including Gibbs free energy of adsorption ΔG° , changes in enthalpy of adsorption ΔH° , and changes in entropy of adsorption ΔS° were calculated using van't Hoff equation. Negative value of ΔG° suggests that adsorption is spontaneous. The positive value of ΔH° may suggest endothermic process of adsorption.

Key words: Acid Activated Vitex Negundo Stem, Nickel ion, Adsorption isotherm, Equilibrium, Thermodynamic parameters, Intra-particle diffusion.

INTRODUCTION

The natural environment received a high volume of wastewater containing heavy metals as a result of increase in industrial activities. Due to toxicity, accumulation in food chain and persistence in nature, heavy metals pose a significant threat to public health and environment. The most immediate concern of heavy metals include lead, cadmium, zinc, nickel, cobalt, chromium, copper and mercury according to the World Health Organization (WHO). The effluents of various industries like electroplating, ceramic, metallurgy, mining, stainless steel, pigments, enameling, porcelain and accumulator manufacturing of nickel contain undesirable amount of nickel ions [1-4]. The trace amount of nickel is beneficial due to the activation of some enzymatic systems but higher intake than the permissible level causes various diseases like lung cancer, pulmonary fibrosis, skin dermatitis, renal edema, diarrhea, nausea and vomiting [5]. According to the Water Sanitation and Hygiene (WSH) under the World Health Organization (WHO), the permissible concentration of Ni (II) as insoluble compounds of Ni (II), soluble compound of Ni (II), nickel carbonyl, nickel sulphide are 1.0, 0.1, 0.05–0.12 and 1.0 mg L⁻¹ respectively [6-11]. Removal of heavy metals from wastewater is very important for the protection of environment and public health before going to natural water because of its toxicity. Various methods have been used for removal of divalent nickel from industrial wastewater, including filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange process [12]. Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water and wastewater, but the high cost of activated carbon inhibits its large scale use as adsorbent [13] to solve these problems, in recent years, investigations have been carried out for the effective removal of large quantities of divalent nickel from wastewater using low cost adsorbents [14].

MATERIALS AND METHODS

2.1. Adsorbent

The Vitex Negundo Stem collected from nearby Thiruvavur district was Carbonized with concentrated Sulphuric Acid and washed with water and activated around 400°C in a muffle furnace for 5 hrs the it was taken out, ground well to fine powder and stored in a vacuum desiccators.

2.2. Chemicals and reagents

All chemicals used of high purity commercially available Analar grade. 1000 mg/L of stock solution of nickel was prepared by dissolving accurately weighed 1 gram of nickel sulphate in 1000 ml distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration. The pH of each experimental solution was adjusted to the required initial pH value using dilute HCl (or) NaOH before mixing the adsorbent.

Batch Adsorption procedure

Batch adsorption studies were carried out in 250 mL glass-stoppered Erlenmeyer flasks with 50 mL of the working Ni(II) ion solution of different concentrations ranging from 25mg/L to 125 mg/L. A weighed amount (0.025 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 1 hours. The influence of pH (2.0–10.0), initial Ni(II) concentration (50, 75, 100, 125 mgL⁻¹), contact time (10, 20, 30,40, 50, 60min) , adsorbent dose (0.05, 0.010, 0.15, 0.2, 0.25 and 0.3 g/50 mL) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual Ni(II) concentration in the solution. The amount of Ni(II) ions adsorbed in milligram per gram was determined by using the following mass balance equation:

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

Where C_i and C_e are Ni(II) concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in liter and m is the weight of the adsorbent in grams.

The percentage of removal of Ni(II) ions was calculated from the following equation:

$$\text{Removal (\%)} = (C_i - C_e)/C_i \times 100 \quad (2)$$

RESULTS AND DISCUSSION

3.1 Effect of agitation time and initial Nickel ion concentration:

The kinetics of adsorption of nickel ion by AAVNS is shown in (fig. 1) with smooth and single plots indicating monolayer adsorption of metal ion on the AAVNS. The removal of metal ion increased with the lapse time and attains equilibrium in 50 min for 50 mg/ L. With increase in metal ion concentration from 25 to 125 mg/L, the amount of metal ion adsorbed increased while the percent removal decreased, indicating that the metal ion removal by adsorption on AAVNS concentration dependent.

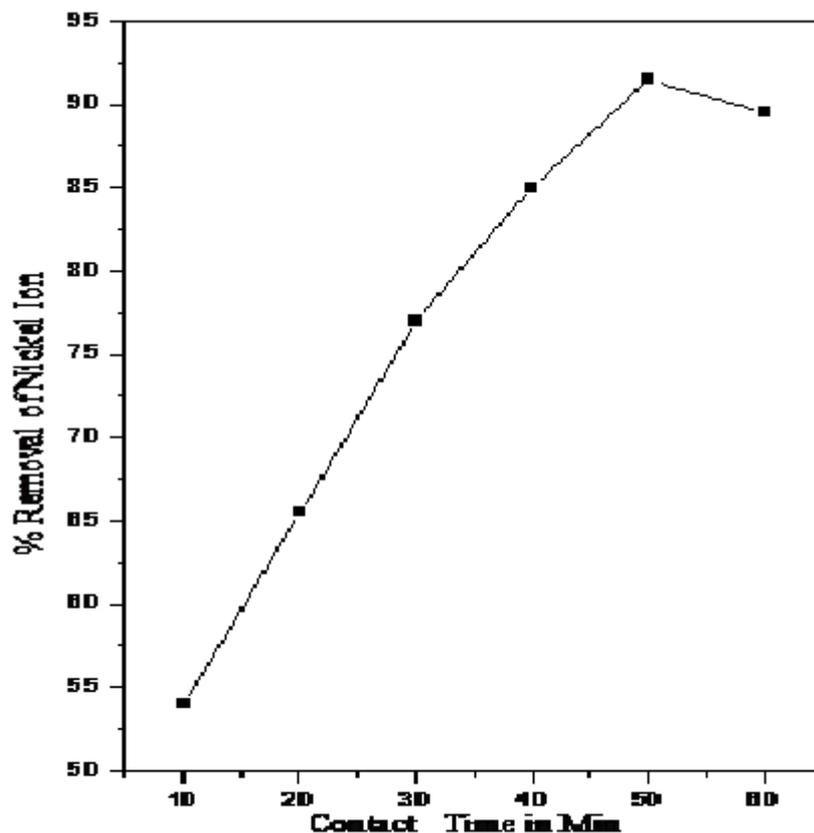


Fig. 1- Effect of Contact Time on the Removal of Nickel Ion
[Ni]=50 mg/L; Temperature 30°C; Adsorbent dose=25mg/50ml

3.2 Effect of AAVNS mass:

The amount of nickel ion adsorption increased with the increase in AAVNS dose and reached a maximum value after a particular dose (fig.2). Taken an initial metal ion concentration of 50 mg/L, complete metal ion removal was obtained at a maximum AAVNS dose of 125 mg. The increase in the adsorption of metal ion with AAVNS dose was due to the introduction of more binding sites for adsorption and the availability more surface area.

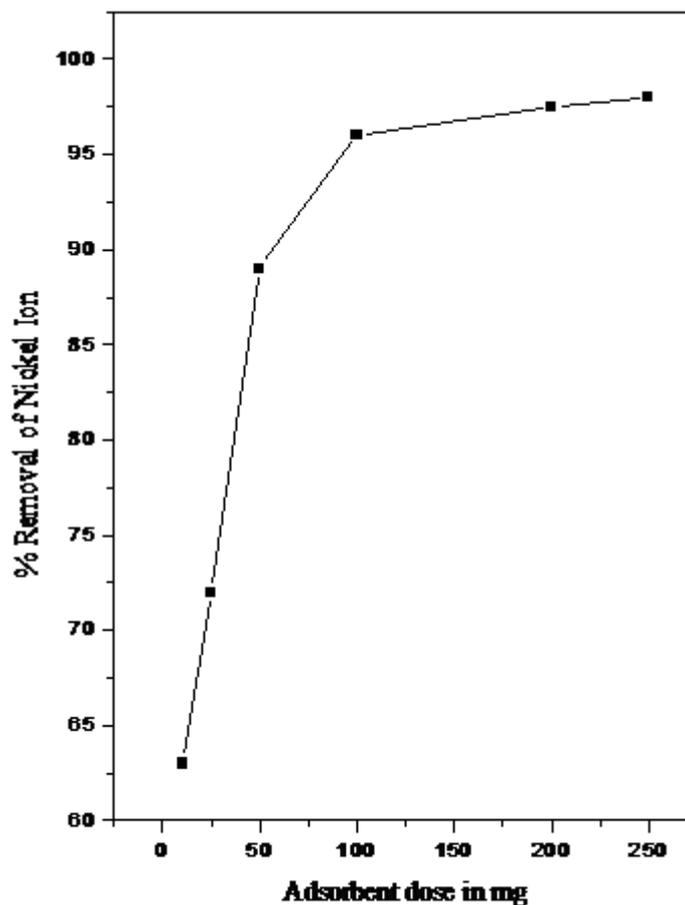
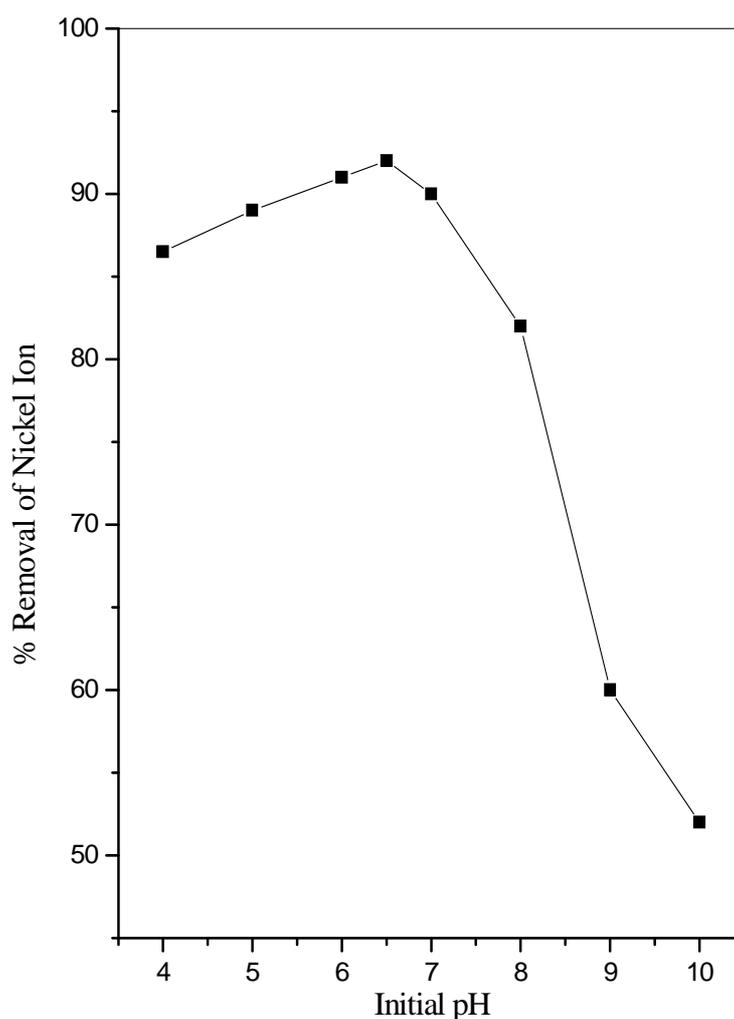


Fig2- Effect of Adsorbent dose on the removal of Ni Ion
[Ni]=50mg/L; Contact Time 50min; Temperature 30°C

3.3 Effect of pH

The pH of the solution is one of the most critical parameters in the adsorption process, which affects surface charge of the adsorbent material and the degree of ionization and specification of adsorbate[15]. The effect of pH on the removal efficiency of Ni(II) ion was studied at different pH values ranging from 4.0 to 10.0, the results are given in Figure 3. It was observed that a sharp decrease in the Ni(II) ion removal occurred when the pH value of the solutions changed from 4.0 to 10.0. The maximum adsorption of Ni(II) ions are obtained at pH 6.5 So pH 6.5 was selected as optimum pH for Ni(II) ion adsorption onto AAVNS. As seen in fig 3. Ni(II) removal by all studied adsorbents decreased significantly with increasing pH, especially between pH 4.0 to 6.5, the maximum removal percentages of Nickel onto AAVNS, were 86 to 92% respectively.



Fig;3- Effect of Initial pH on the removal of Ni Ion

[Ni]=50 mg/L; Temperature 30°C; Adsorbent dose=25mg/50ml

3.4 Effect of other ions:

The effect of other ions like Ca^{2+} and Cl^- on the adsorption process studied at different concentrations. The ions added to 50mg/L of metal ion solutions and the contents were agitated for 50 min at 30°C. The results had shown in the Fig. 4 reveals that low concentration of Cl^- does not affect the percentage of adsorption of metal ion on AAVNS, because the interaction of Cl^- at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion Ca^{2+} increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases that, decreases the percentage adsorption. The interference was more in the presence of Ca^{2+} compared with Cl^- ion. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions [16].

3.5 Effect of temperature:

The adsorption capacity of AAVNS increased with increase in the temperature of the system from 30 to 60°C. Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined using the following equations.

$$K_0 = C_{\text{solid}}/C_{\text{liquid}} \quad (3)$$

$$\Delta G^0 = -RT \ln K_0 \quad (4)$$

$$\log K_0 = \Delta S^0/(2.303R) - \Delta H^0/(2.303RT) \quad (5)$$

Where K_0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. ΔH^0 and ΔS^0 were obtained from the slope and intercept of van't Hoff plot and are presented in Table 4. Positive value of ΔH^0 shows the endothermic nature of adsorption. This rules the possibility of both physical as well as chemical adsorption. Because in the case of physical adsorption alone, while increasing the temperature of the system the extent of metal ion adsorption decreases, as desorption increases with temperature [17]. As chemisorptions is mainly an irreversible process, the low positive ΔH^0 value depicts that Nickel ion is both physically as well as chemically adsorbed onto AAVNS. This is in agreement with the type I and II isotherm obtained, which is close to irreversible adsorption [18].

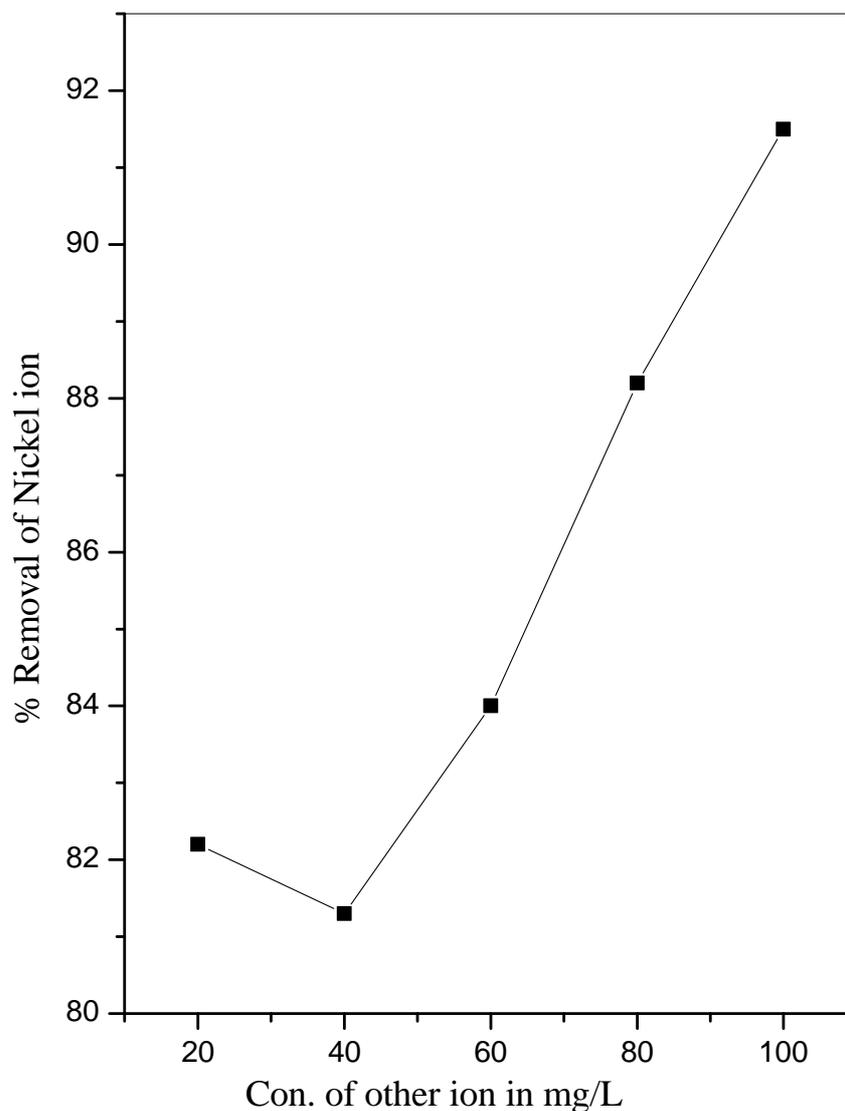


Fig.4-Effect of ionic strength on the adsorption of Nickel ion
[Ni]=50 mg/L;pH=6.5;Dose=25mg/50 ml

The negative values of ΔG^0 (Table 4) indicate that the metal ion adsorption is spontaneous. The positive value of ΔS^0 shows increased randomness at the solid-solution interface during the adsorption of metal ion on AAVNS. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity of AAVNS at higher temperatures may be attributed the enlargement of pore size and/or activation of the adsorbent surface [19].

3.6 Adsorption Isotherms

3.6.1 Freundlich isotherm

The linear form of Freundlich isotherm [20] is represented by the equation

$$\log q_e = \log K_f + (1/n) \log C_e \quad (6)$$

Where q_e is the amount of Ni (II) ions adsorbed per unit weight of the sorbent (mg/L), K_f is a measure of adsorption capacity and $1/n$ is the adsorption intensity. The value of K_f and n are calculated from the intercept and slope of the plot of $\log q_e$ vs $\log C_e$ respectively. The constant K_f and n values are given in (table-2).

TABLE: 2. LANGMUIR AND FREUNDLICH ISOTHERM PARAMETER FOR THE ADSORPTION OF NICKEL ION ONTO AAVNS

Temp. (°C)	Langmuir Parameter		Freundlich Parameter	
	Q_m	B	K_f	n
30°	175.46	0.22	5.27	2.79
40°	190.46	0.18	5.13	2.53
50°	258.99	0.14	5.16	1.96
60°	185.21	0.28	5.60	2.82

In general K_f value increases the adsorption capacity for a given adsorbate increases. The magnitude of the exponent $1/n$ gives an indication of the favourability of adsorption. The value of $n > 1$ represents favorable adsorption condition [21] (or) the value of $1/n$ are lying in the range of 1 to 10 confirms the favorable condition for adsorption. The adsorption co-efficient K_f of Nickel on activated AAVNS was found to be around 5.0 L/g. The K_f values indicates that the saturation time for adsorption of metal ion is attained quickly due to high affinity of activated AAVNS towards adsorbate, while low K_f values indicates low adsorption rate of metal ion [22,23]. The values of $1/n$ were around 3.5 (mg/L) for Nickel ions. The high values of $1/n$ signifies that the forces which are exerted on the surface of AAVNS during metal ion adsorption are strong rate from the values K_f and $1/n$ it reveals that AAVNS is more efficient for removal of Nickel ions.

3.6.2 Langmuir isotherm

The Langmuir isotherm model [24] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$C_e/q_e = (1/Q_m b) + (C_e/Q_m) \quad (7)$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate per unit mass of adsorbent, Q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. Q_m is the amount of adsorbate at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption (or rate of adsorption). The linear plot of specific adsorption capacity C_e/q_e against the equilibrium concentration (C_e). The Langmuir constant Q_m and b were determined from the slope and intercept of the plot and are presented in table 2. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L [25,26] By the equation

$$R_L = 1/(1 + bC_0) \quad (8)$$

Where C_0 (mg/L) is the highest initial concentration of adsorbent and b (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

$R_L > 1$	Unfavorable adsorption
$0 < R_L < 1$	Favorable adsorption
$R_L = 0$	Irreversible adsorption
$R_L = 1$	Linear adsorption

The R_L values between 0 to 1 indicate favorable adsorption for all initial concentration (C_0) and temperatures studied. The calculated R_L values are given in table 3.

TABLE: 3. DIMENSIONLESS SEPERATION FACTOR (R_L) FOR THE ADSORPTION OF NICKEL ION ONTO AAVNS

(C _i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.15	0.18	0.21	0.12
50	0.08	0.09	0.12	0.06
75	0.05	0.06	0.08	0.04
100	0.04	0.05	0.06	0.03
125	0.03	0.04	0.05	0.02

The values of b were increased with increasing the dose of adsorbent for AAVNS High b values indicate high adsorption affinity the monolayer saturation capacity Q_m were around 258.99 mg/L for AAVNS.

3.7. Thermodynamic treatment of the adsorption process

Thermodynamic parameters associated with the adsorption, via standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant K_0 is given by the equation

$$\Delta G^\circ = -RT \ln K_D \quad (9)$$

Where ΔG° is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J mol/K). The adsorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot of $\ln(q_e/C_e)$ against C_e at different temperature and extrapolating to zero C_e according to the method suggested by Khan and Singh[27]. The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature,

$$\ln K_0 = (\Delta H^\circ/RT) + (\Delta S^\circ/R) \quad (10)$$

Where ΔH° is the standard heat change of sorption (kJ/mol) and ΔS° is standard entropy change (kJ/mol). The value of ΔH° and ΔS° can be obtained from the slope and intercept of plot of $\ln K_0$ against $1/T$. The value of thermodynamic parameter calculated from equation 9 and 10 are shown in table 4.

TABLE: 4. THERMODYNAMIC PARAMETER FOR THE ADSORPTION OF NICKEL ION ONTO AAVNS

C ₀	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
25	-6736.37	-6857.63	-7934.39	-8567.66	13.15	65.03
50	-5971.37	-5942.97	-6488.86	-7359.88	8.18	45.97
75	-4082.32	-4371.87	-4801.07	-5329.62	8.52	41.40
100	-2676.69	-2891.17	-5683.66	-2631.38	6.23	30.52
125	-1464.13	-1966.71	-4028.83	-3065.51	19.76	70.42

The thermodynamic treatment of the sorption data indicates that ΔG° values were negative at all temperature. The results point out that physisorption is much more favorable for the adsorption of Ni (II) ions. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption increases, this rules out the possibility of chemisorptions. The low ΔH° value depicts metal ion is physisorbed onto adsorbent AAVNS.

The negative ΔG° values table 4 were conform the spontaneous nature of adsorption Ni (II) ions onto AAVNS. The lesser values of ΔG° suggest that adsorption is physical adsorption process. The positive value of ΔH° further confirms the endothermic nature of adsorption process. The positive values of ΔS° in table 4, showed increased randomness of the solid solution interface during the adsorption of nickel ion onto AAVNS.

3.8. Adsorption kinetics.

Three common kinetic models that are pseudo- second-order, intraparticle diffusion and Elovich equations were used for adsorption kinetics of Ni (II) on AAVNS. The study of adsorption dynamics describes the solute up take rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Ni (II) ions adsorption on the AAVNS were analyzed using pseudo second-order Elovich and intraparticle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (γ) and the values are close or equal to 1. A relatively high correlation

coefficient (γ) value indicates that the pseudo second-order model successfully describes the kinetics of Ni (II) ions adsorption.

3.8.1 The pseudo second- order equation

The pseudo second-order adsorption kinetic rate equation is expressed as

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (11)$$

Where: K_2 is the rate constant of pseudo second- order adsorption (g mg/min). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ the integrated form of Eq. (9) becomes:

$$1/(q_e - q_t) = 1/q_e + K_2 t \quad (12)$$

This is the integrated rate law for a pseudo second-order reaction. Equation (12) can be rearranged to obtain Eq.(13), which has a linear form:

$$t/q_t = (1/k_2 q_e^2) + ((1/q_e)t \quad (13)$$

If the initial adsorption rate (h)(mg g⁻¹ min⁻¹) is :

$$h = k_2 q_e^2 \quad (14)$$

Equation (11) and (12) becomes,

$$t / q_t = 1 / h + 1 / q_e t \quad (15)$$

The plot of (t/q_t) and t of Eq. (15) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-second order rate constants K_2 , the calculated h values, and the correlation coefficients (γ) are summarized in Table (5).

TABLE: 5. THE KINETIC PARAMETERS FOR THE ADSORPTION OF NICKEL ION ONTO AAVNS

C ₀	Temp °C	Pseudo Second Order				Elovich Model			Intra-particle Diffusion		
		q _e	K ₂	γ	H	α	β	γ	K _{id}	γ	C
25	30	51.80	205×10 ⁻³	0.994	7.72	56.482	0.12	0.998	1.64	0.992	0.18
	40	49.10	153×10 ⁻³	0.995	13.89	2313.4	0.22	0.991	1.78	0.994	0.10
	50	50.34	143×10 ⁻³	0.997	11.79	1622.7	0.21	0.993	1.78	0.991	0.107
	60	52.26	160×10 ⁻³	0.999	7.86	91.607	0.14	0.992	1.67	0.992	0.16
50	30	101.0	228×10 ⁻³	0.998	13.49	118.16	0.06	0.991	1.63	0.991	0.18
	40	96.65	186×10 ⁻³	0.997	20.07	1907.0	0.105	0.992	1.74	0.992	0.11
	50	97.76	179×10 ⁻³	0.998	21.23	1987.3	0.103	0.991	1.75	0.991	0.11
	60	98.93	160×10 ⁻³	0.992	22.43	2909.2	0.106	0.993	1.77	0.993	0.10
75	30	134.41	224×10 ⁻³	0.994	25.51	1173.8	0.068	0.997	1.68	0.991	0.12
	40	135.52	219×10 ⁻³	0.991	26.83	1384.2	0.069	0.994	1.69	0.992	0.124
	50	137.35	211×10 ⁻³	0.992	28.32	1854.2	0.07	0.994	1.71	0.991	0.120
	60	140.19	210×10 ⁻³	0.991	28.76	1591.5	0.06	0.9953	1.71	0.991	0.123
100	30	161.52	250×10 ⁻³	0.992	25.35	549.98	0.05	0.997	1.60	0.991	0.14
	40	162.42	237×10 ⁻³	0.991	28.80	876.94	0.053	0.999	1.62	0.992	0.13
	50	167.05	112×10 ⁻³	0.993	30.68	951.25	0.052	0.998	1.64	0.993	0.136
	60	150.16	125×10 ⁻³	0.991	94.26	948.23	0.10	0.997	1.74	0.992	0.06
125	30	177.52	253×10 ⁻³	0.992	24.00	403.69	0.04	0.998	1.52	0.993	0.15
	40	184.46	237×10 ⁻³	0.994	31.53	673.76	0.04	0.999	1.56	0.992	0.14
	50	193.10	154×10 ⁻³	0.991	31.93	686.28	0.042	0.996	1.58	0.998	0.146
	60	203.66	248×10 ⁻³	0.992	32.26	742.99	0.040	0.997	1.60	0.995	0.145

At all studied initial Nickel concentrations, the straight lines with extremely high correlation co-efficient (>0.99) were obtained. From table 5, the values of the rate constant k decrease with in increasing initial Nickel concentration for AAVNS. This is shows that the sorption of Ni (II) ions on AAVNS follows pseudo second order kinetic model

3.8.2 The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / d_t = \alpha \exp (-\beta q_t) \quad (16)$$

Where; α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation. Chien and Clayton (1980) assumed $\alpha\beta t \gg t$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq.(16) becomes:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (17)$$

If Ni (II) ions adsorption fits with the Elovich model, a plot of q_t vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The Elovich model parameters α , β , and correlation coefficient (γ) are summarized in table 5. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase the pore or active site on the AAVNS adsorbent.

3.8.3 The intra particle diffusion model

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris based on the following equation for the rate constant:

$$q_t = k_{id} t^{(1/2)} + C \quad (18)$$

Where k_{id} is the intra-particle diffusion rate constant (mg/g/min) and C is the constant. If the rate limiting step is intra-particle diffusion, then the graph drawn between (q_t) (mg/g) versus square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin. The slope of the will give the value of the intra-particle diffusion coefficient (k_{id}) and correlation coefficient (γ) indicate the fitness of this model. The value of C gives an idea about the thickness of the boundary layer. From these data the intercept value indicate that the line were not passing through origin, there are some other process affect the adsorption. But the correlation coefficient (γ) value is very high, so that the intra-particle diffusion takes place along with other process that may affect the adsorption. The values are given in table 5.

3.9 Adsorption rate constant:

The rate constant of adsorption of Nickel ion on AAVNS was determined using the following rate expression given by Lagergren [28].

$$\log(Q_e - Q) = \log Q_e - (K_{ad}/2.303) t \quad (19)$$

Where Q_e is the amount of solute adsorbed per unit weight of the adsorbent (mg/g) at equilibrium time, Q is the amount adsorbed (mg/g) at time t (min) and K_{ad} is the rate constant (min^{-1}). Linear plots of $\log(Q_e - Q)$ versus t suggest the applicability of the Lagergren equation. The rate constants (K_{ad}) were calculated from the slope and are presented in Table 5. K_{ad} was found to decrease with the increase in the initial concentration from 25 to 125 mg/L . An examination of the effect of metal ion concentration on the rate constant (K_{ad} , K_1 , K_2) helps to describe the mechanism of removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of reaction will not be linear [29]. It shows that a direct linear relationship does not exist in the adsorption of metal ion AAVNS. It seems likely that pore diffusion limits the overall rate of adsorption.

The contact-time experimental results can be used to study the rate-limiting step in the adsorption process, as shown by Weber and Morris [30]. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. One might then postulate that the rate-limiting step may be either film or intra-particle diffusion. As they act in series, the slower of the two will be the rate-determining step.

The rate constant for intra-particle diffusion is obtained using the equation

$$Q = K_p t^{1/2} \quad (20)$$

Here, K_p (mg/g/min) is the intra-particle diffusion rate constant. The nature of the plots suggests that the initial curved portion is attributed to the film or boundary layer diffusion effect and the subsequent linear portion to the intra-particle diffusion effect [31]. Also depicts that the intra-particle diffusion is the slow and the rate-determining step. K_p values were obtained from the slope of the linear portions of the curves at each metal ion concentration

(Table 5). The K_p values increased with increase in the metal ion concentration, which reveals that the rate of adsorption is governed by the diffusion of adsorbed metal ion within the pores of the adsorbent.

3.10 Desorption studies:

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. If the adsorbed metal ions can be desorbed using neutral pH water, then the attachment of the metal ion of the adsorbent is by weak bonds. The effect of various reagents used for desorption studies. The results indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed metal ion. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the AAVNS through physisorption as well as by chemisorptions mechanisms [32]

CONCLUSION

AAVNS prepared from acid activated vitex negundo stem was found effective in removing Nickel ion from aqueous solution. The adsorption is faster and the rate is mainly controlled by intra-particle diffusion. Using the sorption equation obtained from the Langmuir and Freundlich isotherms, it was found that AAVNS is an effective one for the removal of metal ion. The equilibrium data conformed well to the Langmuir and Freundlich isotherm models. The temperature variation study showed that the metal ion adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the metal ion solution. The type I and II isotherm obtained, positive ΔH^0 value, pH dependent results and desorption of metal ion in mineral acid suggest that the adsorption of metal ion on AAVNS involves chemisorption as well as physisorption mechanism.

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