Kinetic, Equilibrium and Mechanistic Studies of Nickel Removal by Glossocardia Linearifolia Stem

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Abstract: An adsorbent prepared from Glossocardia linearifolia Stem, by acid treatment was tested for its efficiency in removing Nickel ion. The process parameters studied include agitation time, initial nickel ion concentration, adsorbent dose, pH and temperature. The adsorption followed second order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plot at an initial pH of 6.0 and at 30, 40, 50, 60 ± 0.5^{0}C. The influence of pH on metal ion removal was significant and the adsorption was increased with increase in temperature. A portion of the nickel ion was recovered from the spent AGLS using 0.1M HCl.

Keywords: Activated Glossocardia linearifolia Stem, Nickel ion, Adsorption isotherm, Equilibrium and Thermodynamic parameters, Intra-particle diffusion.

I. INTRODUCTION

Electroplating is performed in a number of small, medium and large size industries. Metal plating and finishing on the metal are performed to improve the value of the treated metal by providing improvements such as corrosion resistance, durability, electrical properties and aesthetic appearance. The process involves metals and their compounds such as Cadmium, Chromium, Nickel, and Zinc etc. which are found to be highly toxic and accumulative in nature. The humans as well as other life forms get affected. Industrial exposure to nickel may cause Dermatitis and its high occupational exposure has been associated with renal problem and lung cancer. W.H.O. has prescribed a maximum concentration of Nickel in drinking water as 0.1 mg/L whereas the nickel plating effluent water may contain up to 50mg/L of nickel. Thus the effluent water has to be treated for the removal of Nickel. The treatment process, to remove heavy metals such as nickel, comprises of chemical precipitation, coagulation, complexing, solvent extraction, ion-change, sorption, osmosis and electrolysis[1].

II. MATERIALS AND METHODS

2.1. Adsorbent

The Glossocardia linearifolia Stem obtained from agricultural area was activated around 600°C in a muffle furnace for 5 hrs, then it was taken out, ground well to fine powder and stored in a vacuum desiccators.

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Fig. 1. Glossocardia Linearifolia

2.2. Chemicals

All chemicals used of high purity commercially available Analar grade. 1000 mg/L of stock solution of nickel was prepared by dissolving accurately weighed 6.699 gram of nickel ammonium 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. The concentration of residual nickel ion was determined with atomic absorption spectrophotometer (Perkin Elemer 2380).

2.3. Batch experiments

The effect of various parameters on the removal of nickel ion onto AGLS was studied. Batch adsorption experiments were conducted at (30-60°C). For each experimental run, 50 ml of nickel solution of known initial concentration and pH were taken in a 250 ml plugged conical flask. A 25 mg adsorbent dose was added to the solution and mixture was shaken at constant agitation speed (150 rpm) sample were withdrawn at appropriate time intervals (10-60 min) and the adsorbent was separated by filtration. The residual solutions were analyzed to determine the nickel ion concentration.

The effect of dosage of adsorbent on the removal of nickel ion was measured by contacting 50 ml of 50 mg/L of nickel ion solution with 25 mg of AGLS till equilibrium was attained. Adsorption equilibrium isotherm is studied using 25 mg of AGLS dosage per 50 ml of nickel ion solution. The initial concentrations were ranged from (25 to 125 mg/L) in all sets of experiments.

The plugged conical flask was shaken at a speed of 150 rpm for 60 minutes. Then the solution was separated from the mixture and analyzed for nickel ion concentration. The adsorption capacity was calculated by using a mass equilibrium equation as follows:

$$q_e = (C_0 - C_e) V/M \dots\dots\dots\dots\dots\dots (1)$$

Where C_0 and C_e being the initial nickel concentration (mg/L) and equilibrium concentration, respectively V is the experimental volume of nickel ion solution expressed in liters [L] and M is the adsorbent mass expressed in grams [g]. The nickel ion percentage can be calculated as follows:

$$\%R = (C_0 - C_t) \times 100/C_0 \dots\dots\dots\dots\dots (2)$$

The effect of pH on the rate of adsorption was investigated using nickel concentration of 75 mg/L and with constant AGLS dosage. The pH values were adjusted with dilute HCl and NaOH solution. The adsorbent – adsorbate mixture was shaken at room temperature using agitation speed (150 rpm) for 60 minutes. Then the concentration of nickel in solution was determined.

III. RESULTS AND DISCUSSION

3.1. Effect of agitation time and initial Nickel ion concentration

The kinetics of adsorption of nickel ion by AGLS is shown in **Fig. 1.** Smooth and single plot indicating the monolayer adsorption of metal ion on the AGLS[2]. The removal of metal ion increased with the lapse time and attains equilibrium in 60 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 AGLS is concentration dependent.
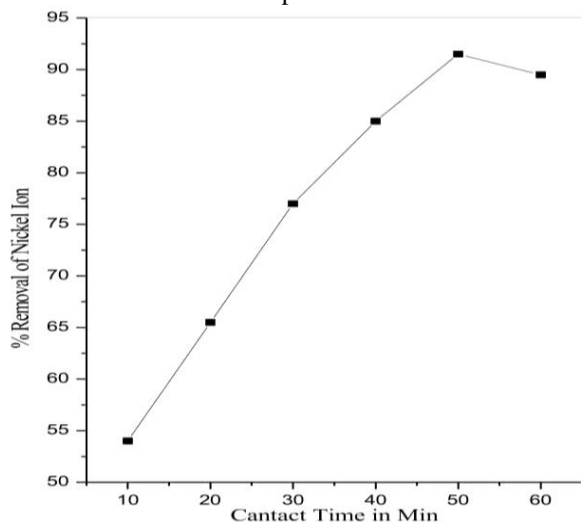

Fig: 1 Effect of Contact Time on the removal of Nickel Ion [Ni]=50mg/L; Temperature 30ºC; Adsorbent dose = 25 mg/50ml

3.2. Effect of AGLS mass

The amount of nickel ion adsorption increased with the increase in AGLS 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 AGLS dose of 125 mg. The increase

in the adsorption of metal ion with AGLS dose was due to the introduction of more binding sites for adsorption and the availability of more surface area.
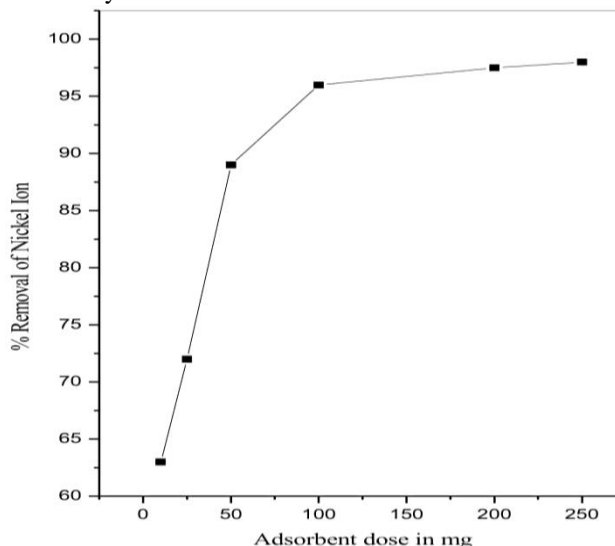

Fig: 2 Effect of Adsorbent does on the removal of Nickel Ion [Ni] =50mg/L; Contact Time 60 min; Temperature 30ºC

3.3. Effect of pH

The experience carried out at different pH show that there was a change in the percent removal of metal ion over the entire pH range. (Fig. 3). This indicates the strong force of interaction between the metal ion and AGLS that either H^+ or OH^- ions could influence the adsorption capacity. In other words, the adsorption of metal ion on AGLS does involve ion exchange mechanism that have been an influence on the metal ion adsorption while varying the pH[3] This observation is in line with the positive $\triangle H^0$ value obtained, which indicates irreversible adsorption probably due to polar interactions.
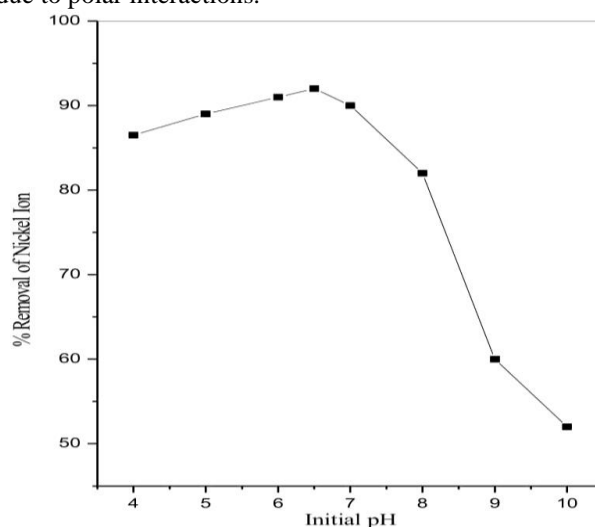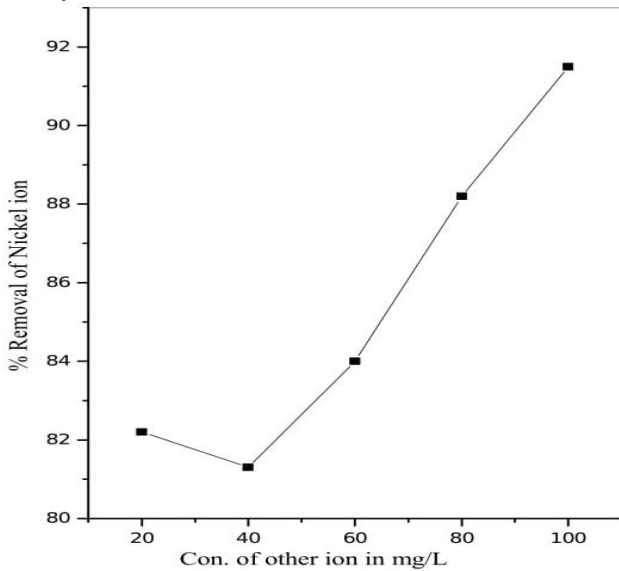

Fig: 3 Effect of initial pH on the removal of Nickel Ion [Ni] =50mg/L; Temperature 30ºC; Adsorbent dose = 25 mg/50ml

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3.4. Effect of other ions

The effect of other ions like Ca^{2+} and Cl^- on the adsorption process were studied at different concentrations. The ions added to 50mg/L of metal ion solutions and the contents were agitated for 60 min at 30^0C. The results shown in the Fig. 4 reveals that low concentration of Cl^- does not affect the percentage of adsorption of metal ion on activated AGLS, 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[4]

Fig: 4 Effect of ionic strength on the adsorption of Nickel Ion onto AGLS [Ni] =50mg/L; pH=6.5; Adsorbent dose = 25 mg/50ml

3.5. Effect of temperature

The adsorption capacity of AGLS increased with increase in the temperature of the system from 30 to 60^0 C. Thermodynamic parameters such as change in free energy ($\triangle G^0$), enthalpy ($\triangle H^0$) and entropy ($\triangle S^0$) were determined using the following equations.

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

$$\triangle G^0 = -RT \, In \, K_0 \quad \dots\dots\dots\dots\dots\dots\dots(4)$$

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

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. $\triangle H^0$ and $\triangle S^0$ were obtained from the slope and intercept of van't Hoff plot and are presented in Table 4. Positive value of $\triangle H^0$ 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[5]. As chemisorptions is mainly an irreversible process, the low positive $\triangle H^0$ value depicts that Nickel ion is both physically as well as chemically adsorbed onto AGLS. This is in agreement with the type I and II isotherm obtained, which is close to irreversible adsorption[6].

The negative values of $\triangle G^0$ (Table 4) indicate that the metal ion adsorption is spontaneous. The positive value of $\triangle S^0$ shows increased randomness at the solid-solution interface during the adsorption of metal ion on AGLS. 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 AGLS at higher temperatures may be attributed the enlargement of pore size and/or activation of the adsorbent surface[7].

3.6. Adsorption Isotherms

3.6.1. Freundlich isotherm

The linear form of Freundlich isotherm[8] is represented by the equation

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

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**. In general K_f value increases the adsorption capacity for a given adsorbate increase. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. The value of $n>1$ represents favorable adsorption condition[9] (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 AGLS was found to be around 5.0 L/g. The K_f values indicate that the saturation time for adsorption of metal ion is attained quickly slue to high affinity of activated AGLS towards adsorbate, while low K_f values indicate low adsorption rate of metal ion [10,11]. The values of $1/n$ were around 3.5 (mg/L) for Nickel ions. The high value of $1/n$ signifies that the forces which are exerted on the surface of AGLS during metal ion adsorption are strong. From the values K_f and $1/n$ it is clear that activated AGLS is more efficient for removal of Nickel ions.

Table 1. Langmuir and freundlich isotherm parameter for the adsorption of nickel ion onto AGLS

Temp. (^{0}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

3.6.2. Langmuir isotherm

The Langmuir isotherm model[12] 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

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

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 respectively and are presented in **Table 1**. 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[13,14]. By the equation

Table 2. Equilibrium parameters for the adsorption of nickel ion onto AGLS

M_0	Ce (Mg / L)				Qe (Mg / g)				Removal (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
25	1.61	1.67	1.23	1.083	46.77	46.65	47.52	47.83	93.54	93.3	95.04	95.66
50	4.27	4.62	4.096	3.273	91.45	90.75	91.8	93.45	91.45	90.75	91.8	93.45
75	12.38	11.78	10.75	9.547	125.2	126.4	128.49	130.9	83.48	84.29	85.66	87.27
100	25.68	24.76	10.75	27.87	148.6	150.46	178.49	144.24	74.31	75.23	89.24	72.12
125	44.83	39.94	22.79	31.04	160.3	170.1	204.4	187.9	64.13	68.04	81.76	75.16

$$R_L = (1/(1+bC_o)) \dots\dots\dots\dots\dots\dots(8)$$

Where C_o (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 adsorption.

$R_L > 1$	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_o) and temperatures studied. The calculated R_L values are given in **Table 3**. The values of b were increased with increasing the dose of adsorbent for AGLS.a High b values indicate high adsorption affinity the monolayer saturation capacity Q_m were around 139 mg/L for AGLS.

Table 3. Dimensionless seperation factor (RL) for the adsorption of nickel ion onto AGLS

(Ci)	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

3.7. Thermodynamic treatment of the adsorption process

Thermodynamic parameters associated with the adsorption, via standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant K_0 is given by the equation

$$\Delta G° = -RT \ln K_0 \dots\dots\dots\dots\dots..\dots (9)$$

Where $\Delta G°$ 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_O 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[15] The adsorption distribution coefficient may be expressed in terms of enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) as a function of temperature,

$$\ln K_o = (\Delta H_o/RT) + (\Delta S_o/R) \dots\dots\dots.(10)$$

Where $\Delta H°$ is the standard heat change of sorption (kJ/mol) and $\Delta S°$ is standard entropy change (kJ/mol). The value of $\Delta H°$ and $\Delta S°$ 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**. The thermodynamic treatment of the sorption data indicates that $\Delta G°$ 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 $\Delta H°$ show the endothermic nature of adsorption and it governs the possibility of physical adsorption[23]. 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 $\Delta H°$ value depicts metal ion is physisorbed onto adsorbent AGLS.

Table 4. Thermodynamic parameters for the adsorption of nickel ion onto AGLS

C₀	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 negative ΔG° values were confirm the spontaneous nature of adsorption of Ni (II) ions onto AGLS. The lesser values of ΔG° suggest that adsorption is a 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 activated AGLS.

3.8. Adsorption kinetics

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 AGLS were analyzed using pseudo second-order Elovich and intra-particle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation co-efficient (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

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

Where: K_2 is the rate constant of pseudo second- order adsorption. 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:

$$1/(q_e - q_t) = 1/q_e + K_2t \quad \dots\dots\dots\dots. (12)$$

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:

$$t/q_t=(1/k_2q_e^2)+ ((1/q_e)t \quad \dots\dots\dots\dots.(13)$$

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

$$h=k_2q_e^2 \quad \dots\dots\dots\dots\dots\dots\dots.(14)$$

Equation (11) and (12) becomes,

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

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

Table 5. The kinetic parameters for the adsorption of nickel ion onto AGLS

C₀	Temp °C	Pseudo Second Order				Elovich Model			Intra-particle Diffusion		
		qₑ	K₂	γ	h	α	β	γ	Kᵢd	γ	C
25	30	51.8	205×10⁻³	0.994	7.72	56.482	0.12	0.998	1.64	0.992	0.18
	40	49.1	153×10⁻³	0.995	13.89	2313.4	0.22	0.991	1.78	0.994	0.1
	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	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	0.105	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	0.1
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	0.12
	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	1.6	0.991	0.14
	40	162.42	237×10^{-3}	0.991	28.8	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	948023	0.1	0.997	1.74	0.992	0.06
125	30	177.52	253×10^{-3}	0.992	24	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	193.1	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	0.04	0.997	1.6	0.995	0.145

3.8.2. The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / dt = \alpha \exp(-\beta q_t) \quad \ldots\ldots..(16)$$

Where; α is the initial adsorption rate (mg g^{-1} 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.(12) becomes:

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

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 in the number of pore or active site on the AGLS 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[16] based on the following equation for the rate constant:

$$q_t = k_{id} t^{(1/2)} + C \ldots\ldots\ldots\ldots(16)$$

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) verses 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 AGLS was determined using the following rate expression given by Lagergren[17].

$$\log(Q_e - Q) = \log Q_e - (K_{ad}/2.303) t \ldots..(17)$$

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 adsorption. 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[18]. It shows that a direct linear relationship does not exist in the adsorption of metal ion on to AGLS. 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[16]. 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

$$Q = K_p t^{1/2} \ldots\ldots\ldots.(18)$$

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[19].

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 were studied. 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 activated AGLS through physisorption as well as by chemisorption mechanisms

IV. CONCLUSION

AGLS prepared from waste Glossocardia linearifolia 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 AGLS 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 $\triangle H^0$ value, pH dependent results and desorption of metal ion in mineral acid suggest that the adsorption of metal ion on AGLS involves chemisorptions as well as physisorption mechanism.

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