Removal Of Nickel (Ii) Ions From Aqueous Solutions Using Adsorbent Obtained From *Andrographis Paniculata* Leaves As A Low Cost Adsorbent

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Abstract- In the present study, the adsorbent prepared from the leaves of *Andrographis paniculata was* used for the removal of nickel(II) ions from wastewater. The adsorption process was influenced by various parameters such as contact time, adsorbent dose, temperature, pH and dye concentration. The equilibrium data fitted well to both Langmuir and Freundlich isotherm models. The results revealed that the adsorbent obtained from *Andrographis paniculata* leaf could be employed as an effective low cost adsorbent for the removal of nickel (II) ions from waste water.

Index terms -Nickel (II) ions, Isotherm models, Kinetics, Adsorbent, Thermodynamic Parameters.

I. INTRODUCTION

Environmental pollution due to metals is a major concern due to their toxic nature[1,2]**.** Nickel (II) ions is one of the toxic heavy metal when absorbed into the body[3]. Accumulation of nickel (II) ions in the body affects lungs, liver and central nervous system[4]. Hence the removal of this metal from wastewater is important.

A number of conventional techniques have been employed to remove nickel (II) ions from waste water. Granulated activated carbon[5] , Chemical precipitation[6], and crystallization in the form of nickel carbonate[7] are available for the removal of nickel (II) ions , But these methods are either ineffective or expensive.

Adsorption technique is widely used for metal removal from waste water[8]. Many low cost adsorbents were prepared from materials such as crab shell[9], bark of tree[10], waste coir fiber[11], wooden charcoal[12], pine bark[13], tree bark powder[14], wood dust[15], fly ash[16], lignin[17]. In these study we employed , the adsorbent obtained from the leaves of *Andrographis paniculata* for the removal of nickel (II) ions from the waste water.

II. EXPERIMENTAL

Preparation of adsorbate

A stock solution containing 1000mg/l of nickel (II) ions was prepared by dissolving an appropriate quantity of nickel sulphate in double distilled water. The working solutions were prepared by diluting the stock solution. The concentration of the nickel (II) ions in the solution was determined spectrophotometrically[18].

Preparation of adsorbent material

Andrographis paniculata leaves were collected and washed with tape water several times to remove soil dust and finally washed with DD water. It is dried in sun shade. The dried leaves were powdered and soaked in con.H_2SO_4(1:1,w/w), for a day, then filtered and dried. The charred mass was kept in a muffle furnace at 400^0C,for 1 hour, it was taken out, ground well to fine powder and stored in vacuum desiccators. The Characteristics of the adsorbent is presented in the table-1

pH	6.9
Moisture Content, %	11.8
Ash Content, %	9.9
Volatile Matter, %	20.8
Water Soluble matter, %	0.40
Acid Soluble Matter, %	0.92
Bulk Density, g/mL	0.43
Specific Gravity	0.91
Porosity, %	49.8
BET Surface Area, m^2/g	478.529
Fixed Carbon, %	57.5

Table-1 Characteristics of the adsorbent

Batch equilibrium studies

Batch equilibrium adsorption experiments were conducted by adding known quantity of the adsorbent to Erlenmeyer flasks containing 50ml of metal ion solution at different concentrations ranging from 10mg/l to 50mg/l at different pH. Then the flasks were kept in an orbitary shaker with a speed of 120rpm at room temperature for 90min. The adsorbent was separated from the solution by filteration. The removal efficiency of Nickel (II) ions was determined. The

percentage of Nickel (II) ions removal was calculated by using the following equation.

% Nickel (II) ions removal$= Ci - Ce/Ci * 100$

Where Ci = initial concentration(mg/l), Ce = equilibrium concentration(mg/l)

The adsorption capacity Qe (mg/g), is obtained from the following equation

$$Qe = (Ci - Ce)V/M$$

Where, Q_e = adsorbent capacity(mg/g), C_i= initial Nickel (II) ions concentration (mg/l),V = volume of the solution(l), M = mass of the adsorbent (g).

III. RESULTS AND DISCUSSION

Effect of pH

The pH is one of the important parameters influencing the adsorption process. The experiments were conducted over a pH range of 2 to 8. The pH of the working solution was controlled by adding 1NHCl or 1NNaOH solution. The uptake of the nickel (II) ions at pH-5 was maximum (fig.1). At low pH the adsorption is low due to the positive charge density on the surface of the adsorbent resulting in the electrostatic repulsion between the Ni(II) ions and positive charge on the surface. With the increase   in pH the adsorption also increases and reaches the maximum at pH 5. Hence the pH of the medium was maintained at 5 for further studies.
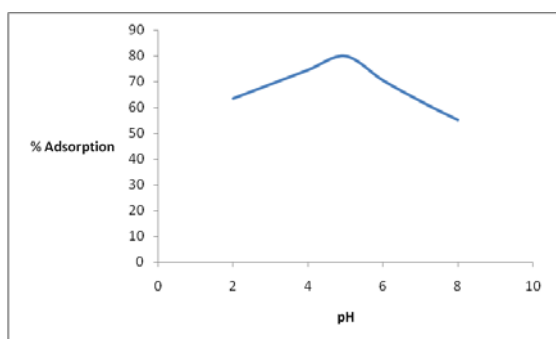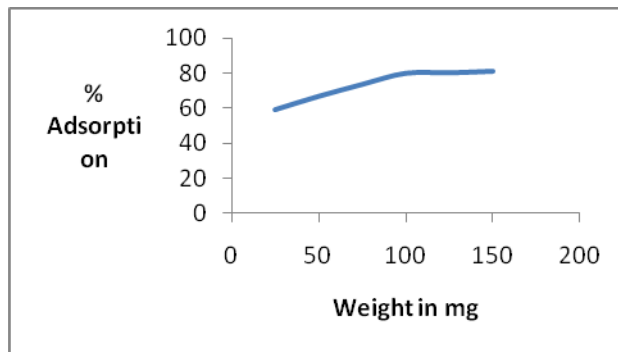

Fig:1 Effect of pH on the adsorption of Nickel (II) ions on to the adsorbent

Adsorbent dose

The effect of adsorbent dosage was studied by varying the dosage from 25mg to 150mg keeping the other parameters constant. The result is shown in fig.2. The adsorption percentage increased as the adsorbent dosage increased. The adsorption percentage increases and reaches the maximum at 100mg of adsorbent dosage thereafter, there was no appreciable increase in the percentage of nickel (II) ions removal. This is

due to greater availability of the sites for adsorption on the adsorbent surface. Therefore the adsorbent dosage was maintained at 100mg for further studies.

Fig:2 Effect of adsorbent dose on the adsorption of Nickel (II) ions on to the adsorbent

Effect of dye concentration

The experiment was carried out with 10mg/l to 50mg/l solutions with adsorbent dosage 100mg, for a contact time of 90min at pH-5, and the result is shown in fig.3. From the figure it can be seen that the percentage of adsorption decreases with increase in the nickel (II) ions concentration. This is due to less availability   of   sites   on   the   adsorbent   surface.
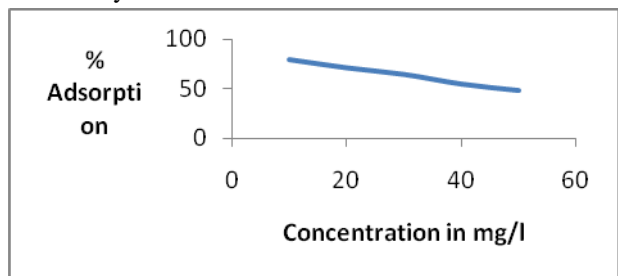
Fig:3 Effect of dye concentration on the adsorption of Nickel (II) ions on to the adsorbent

Effect of contact time

The effect of contact time on adsorption of nickel (II) ions removal is shown in fig.4. 100mg of adsorbent was used for this experiment with a contact time of 15 to 90minutes. It is observed that the percentage removal of dye increases with time and reaches the maximum at 90min, thereafter, there was no appreciable increase in the percentage of nickel (II) ions removal. This is because at the initial stage, the rate of removal of Nickel (II) ions was higher due to availability of more number of active sites on the surface of the adsorbent , and become slower after 90 minutes, due to availability of lesser number of active sites. Hence all the experiments were conducted for a period of 90 minutes.
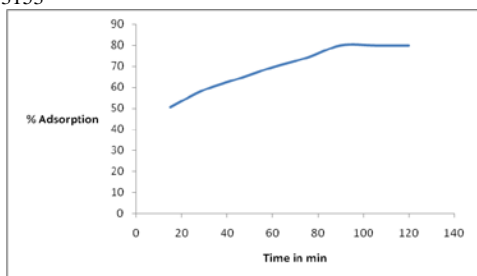
Fig:4 Effect of contact time on the adsorption of Nickel (II) ions on to the adsorbent

IV. ADSORPTION ISOTHERMS
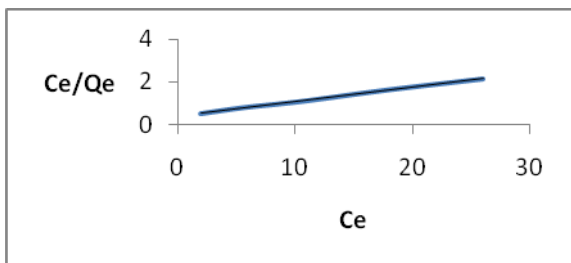
Langmuir Adsorption Isotherm

The equilibrium adsorption isotherms help to understand the mechanism of the adsorption. The Langmuir and Freundlich isotherms have been tested in this study.

The Langmuir isotherm was based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption was constant and there was no transmigration of adsorbate in the surface.

The linear form of Langmuir equation[19] is expressed as follows

$$\frac{Ce}{Qe} = \frac{Ce}{Q_0} + \frac{1}{Q_0 b}$$

The values of Q_0 and b were calculated from the slope and intercept respectively, of the linear plots of C_e/Q_e verses C_e. Langmuir adsorption isotherm is presented in fig.5. Higher value of correlation co-efficient (R^2-0.999) indicates that the experimental data fits well with the Langmuir equation. The values of Q_0 and b are given in Table-2.

Fig:5 Langmuir isotherm for the adsorption of Nickel (II) ions on to the adsorbent

Qo(mg/g)	b	R^2
14.4927	0.1815	0.999

Table-2. Langmuir constants

The essential characteristics of the Langmuir adsorption isotherm are expressed by a dimensionless constant called separation factor. This value indicates whether the adsorption is favorable or not. R_L is defined by the following equation

$R_L = 1/ (1+bCo)$

Where, R_L _ dimensionless separation factor[20], Ci – intial concentration , b – Langmuir constant (Lmg-[1]),The parameter R_L indicates the type of the isotherm.

Values of R_L	Types of isotherms
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irrevisible

The R_L value obtained using the above equation for 10mg/l Nickel (II) ions concentration is 0.3552. This R_L value lies between 0 and 1 indicating the favorability of the adsorption.
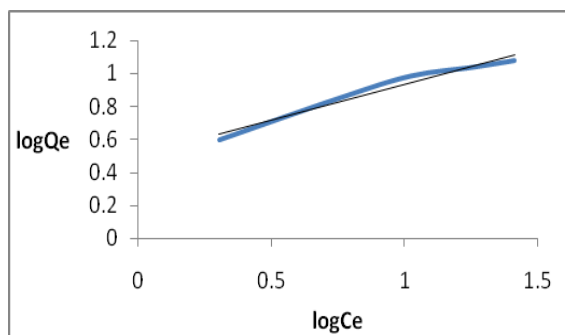
Freundlich Adsorption Isotherm

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer sorption.

The linear form of the Freundlich equation[21] is as follows

$$logQe = logK_f + 1/nlogCe$$

Where Qe , amount of dye adsorbed (mg/g),K_f ,adsorption capacity, n, adsorption intensity. By ploting logQe Vs logCe, the values of n and K were calculated from slope and intercept respectively (fig.6). The values of K_f and n are given in table-3. The value of linear regression co-efficient (R^2) was found to be 0.969. This indicates that the adsorption process follows Langmuir adsorption isotherm more than Freundlich adsorption isotherm.

Fig:6 Freundlich isotherm for the adsorption of Nickel (II) ions on to the adsorbent

n	K_f(mg/g)	R^2
2.3094	3.1550	0.969

Table-3. Freundlich constants

The value of n in the range 2-10 represents favourable adsorption[22].

V KINETIC STUDY

Pseudo First Order Kinetics

In the present study, Pseudo first and second order kinetic models have been tested at different concentrations. The linear form of Pseudo first order kinetic equation[23] is given as,

$$\log (q_e - qt) = \log q_e - (k_1/2.303)t$$

Where q_e is the amount of dye adsorbed at equilibrium. k_1 is the first order rate constant.

A plot of $\log (q_e-qt)$ verses $t(min)$ gives a straight line fig.7 From the slope k_1 and from the intercept q_e were determined. These values are presented in the table-4.

q_e	k_1	R^2
13.0918	0.0299	0.999

Table-4 Pseudo First order kinetic parameters

The value of R^2 indicates that the first order kinetics was followed by Nickel (II) ions adsorption.
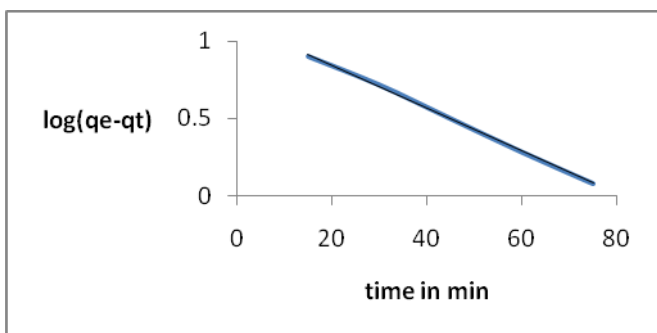
Fig:7 Pseudo first order kinetics for the adsorption of Nickel (II) ions on to the adsorbent

Pseudo Second Order Model

The linear form of pseudo second order kinetic equation[24] is

$$t/qt = 1/k_2 qe^2 + t/qe$$

Where k_2 is the rate constant of second order adsorption. The qe and k_2 can be determined from the slope and intercept of a linear plot of t/qt verses t shown in fig-8. These values are presented in the table-5.

Qe	k_2	R^2
18.8679	0.0012	0.997

Table-5 Pseudo Second order kinetic parameters

The result shows that first order kinetics is more favoured than second order kinetics.
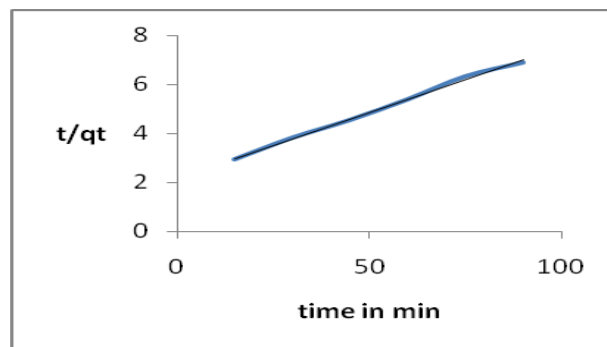
Fig:8. Pseudo second order kinetics for the adsorption of Nickel (II) ions on to the adsorbent.

VI . THERMODYNAMIC PARAMETERS

Thermodynamic studies related to the adsorption process is essential to conclude whether a process will occur spontaneously or not. The fundamental criteria for spontaneity is the standard Gibbs free energy change ΔG^o, if the ΔG^o value is negative, the reaction will occur spontaneously. The thermodynamic parameters, standard free energy (ΔG^o), change in standard enthalpy change (ΔH^o) and change in standard entropy(ΔS^o) for the adsorption of nickel (II) ions onto the adsorbent were calculated using the following equations.

$$K_0 = C_{solid} / C_{liquid}$$

$$\Delta G^o = -RT \ln K_0$$

$$\log K_0 = \frac{\Delta S}{2.303 R} - \frac{\Delta H}{2.303 RT}$$

Where Ci is the concentration of the dye at equilibrium and Ce is the amount of dye adsorbed on the adsorbent

The values of ΔG^o (KJ/mol), ΔH^o(KJ/mol^{-1}) and ΔS^o (J/K/mol) can be obtained from the slope and intercept of a linear plot of $\log K_o$ verses $1/T$ and are presented in table-6.

Conc.of Nicke dye (mg/l)	$-\Delta G^o$ (KJ/mol)				ΔH^o (KJ/mol)	ΔS^o (J/k/mol)
	30^0 C	40^0 C	50^0 C	60^0 C		
10	3.473	4.015	4.491	4.932	11.145	48.28
20	2.310	2.857	3.436	3.837	13.244	51.37
30	1.518	1.978	2.554	2.938	13.043	48.02
40	0.476	0.973	1.460	1.922	14.013	47.81
50	0.199	0.233	0.672	1.122	13.410	43.55

Table-6. Thermodynamic parameters for the adsorption of nickel (II) ions on to the adsorbent.

The negative values of ΔG^o indicates that the adsorption process is spontaneous and highly favorable . The positive values of ΔS^o indicates the increased randomness at the solid solution interface. The values of ΔH^o indicates that the adsorption process is endothermic and physical in nature.

VII. CONCLUSION

The adsorption behavior of Nickel (II) ions on the adsorbent obtained from the *Andrographis paniculata leaves* was investigated in batch equilibrium method. The adsorption was found to be highly dependent on various parameters like contact time, pH, initial concentrations, adsorbent dose and temperature. The optimum pH for Nickel (II) ions adsorbent was found to be 5. The experimental data were correlated well by the Langmuir adsorption isotherm. The adsorption process was well described by pseudo first order kinetics. The result of this study indicates that this adsorbent can be successfully utilized for the removal of nickel (II) ions from aqueous solution.

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