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Research Article

REMOVAL OF NICKEL (II) IONS FROM AQUEOUS SOLUTIONS USING A LOW COST ADSORBENT OBTAINED FROM *CENTELLA ASIATICA* LEAVES

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ABSTRACT
In the present study, the adsorbent prepared from the leaves of *Centella asiatica 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 *Centella asiatica* leaf could be employed as an effective low cost adsorbent for the removal of nickel (II) ions from waste water.

Keywords: Nickel (II) ions, Isotherm models, Adsorbent, Thermodynamic Parameters.

I. INTRODUCTION

Nickel metal is used in many industries such as storage batteries, electroplating, dying, porcelain enameling, pigment and steel manufacturing,[1,2]. These industries discharge effluents containing nickel. The maximum permissible limit of nickel in drinking water is 0.01 mg/L and for industrial wastewater it is 2.0 mg /L.[3] but, the effluents discharged from the industries are loaded with higher concentration of nickel than the permissible limit. Exposure to higher concentration of nickel leads cancer of the lungs, nose, and bones and it may also cause nausea, rapid respiration, headache, cyanosis, and dry cough.[4,5] Therefore it is necessary to treat industrial effluents with higher concentration of Ni(II) before their discharge.

Lot of techniques have been developed for the removal of metal ions from wastewater such as ion exchange[6,7,8], reverse osmosis[9,10] adsorption[11,12], precipitation[13], co-precipitation[14], filtration [15], and coagulation[16.] The adsorption technique is very popular and efficient due to simplicity and low cost.

Many reports are found in the literature relating to the removal of heavy metals from wastewater by using adsorption techniques with different low-cost materials, such as moss peat[17], coconut husk,[18] chitin[19], sawdust[20,21], green algae[22,23], fly ash[24]. In this study we employed, the adsorbent obtained from the leaves of *Centella asiatica* 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.

Preparation of adsorbent material

Centella Asiatic 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

Table 1: Characteristics of the adsorbent

pH	6.5
Moisture Content, %	13.5
Ash Content, %	10.2
Volatile Matter, %	21.3
Water Soluble matter, %	0.45
Acid Soluble Matter, %	0.89
Porosity, %	48.1
Micropore volume cm^3/g	0.194194
Average pore width ^0A	28.2065
BET Surface Area, m^2/g	604.27

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.

$$\%\ Dye\ \text{Re}moval = \frac{(C_0 - C_e)}{C_0}\ X\ 100$$

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

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

$$q_e = (C_0 - C_e)\frac{V}{M}$$

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.

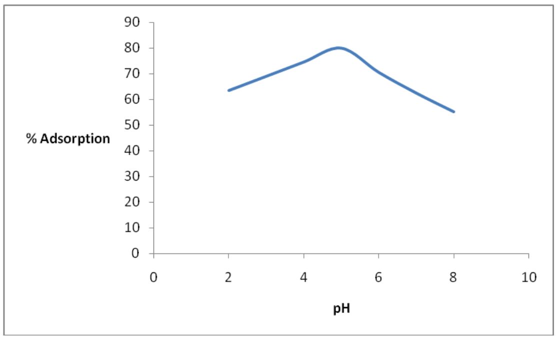

Fig. 1: Effect of pH on the adsorption of Nickel (II) ions on to the adsorbent

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.

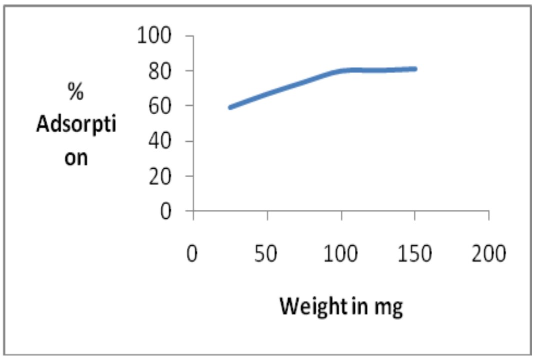

Fig. 2: Effect of adsorbent dose on the adsorption of Nickel (II) ions on to the adsorbent

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.

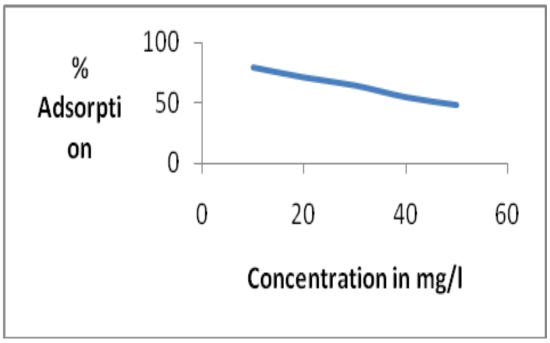

Fig. 3: Effect of dye concentration on the adsorption of Nickel (II) ions on to the adsorbent

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.

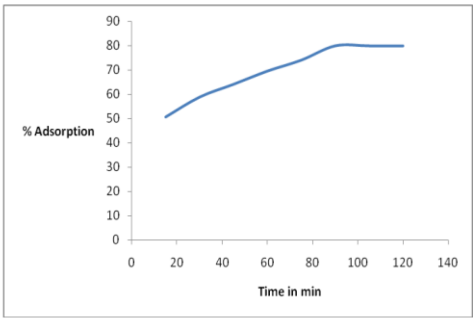

Fig. 4: Effect of contact time on the adsorption of Nickel (II) ions on to the adsorbent

Effect of Temperature

Effect of temperature on the adsorption of nickel is shown in fig.5. As the temperature was increased from $30C^0$ to $60C^0$, the percentage of adsorption also increased. The increase in temperature may be accompanied with an increase in the porosity and in the total pore volume of the adsorbent. This may also be attributed an increase in the mobility of the dye molecules with the increase of temperature.

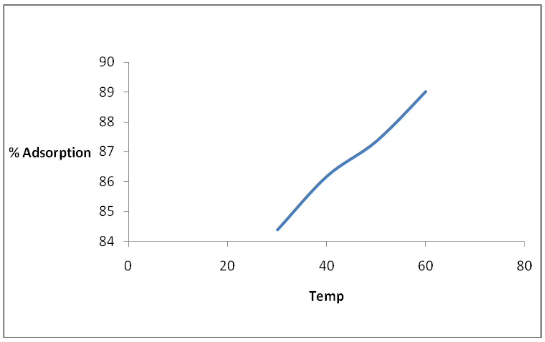

Fig. 5: Effect of temperature on the adsorption of nickel on to the adsorbent

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[25] 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.6. 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.

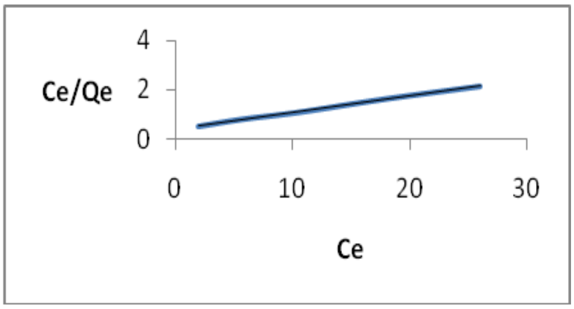

Fig. 6: Langmuir isotherm for the adsorption of Nickel (II) ions on to the adsorbent

Table 2: Langmuir constants

Qo(mg/g)	b	R^2
18.8679	0.2630	0.999

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 – initial 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 0.2754. 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[26] is as follows

$$\log \mathrm{Qe} = \log \mathrm{K}_{\mathrm{F}} + \frac{1}{n} \log Ce$$

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.7). 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.

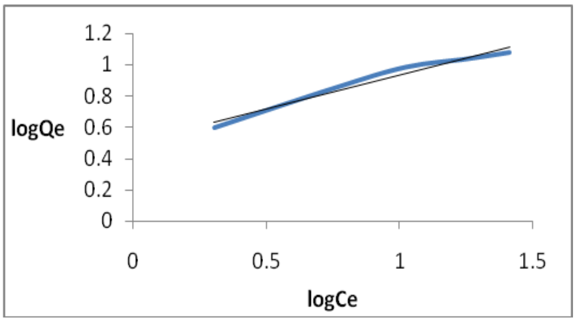

Fig. 7: Freundlich isotherm for the adsorption of Nickel (II) ions on to the adsorbent

Table 3: Freundlich constants

n	K_f(mg/g)	R^2
2.0491	3.8636	0.959

The value of n in the range 2-10 represents favourable adsorption

V. 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.

$$K_0 = \frac{C_{solid}}{C_{liquid}}$$

$$\Delta \mathrm{G}^0 = -RT \ln K_0$$

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

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-4.

Table 4: Thermodynamic parameters for the adsorption of nickel (II) ions on to the adsorbent

Conc.of Nickel dye (mg/l)	$-\Delta G^o$				ΔH^o	ΔS^o
	30^0 C	40^0 C	50^0 C	60^0 C		
10	4.1251	4.5183	4.8552	5.0285	6.571	35.32
20	3.3771	2.8103	4.1011	4.4663	7.339	35.44
30	2.4523	2.8949	3.2319	3.7464	10.197	41.72
40	1.5535	2.0150	2.2853	2.6457	9.117	35.30
50	0.7462	1.0333	1.3465	1.6968	8.738	31.22

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.

VI. CONCLUSION

The adsorption behavior of Nickel (II) ions on the adsorbent obtained from the *Centella asiatica 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 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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