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# Usefulness of Biomaterial prepared from Dry leaves of *Pinus gerardiana* in the removal of Nickel(II) from aqueous solution

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## ABSTRACT

*In the present study the dry leaves powder of Pinus gerardiana has been used as metal adsorbent to remove nickel ion from aqueous solution. The adsorption characteristic of nickel(II) ion bio-sorbent were evaluated as a function of pH, contact time and initial metal ion concentration. The adsorption isotherm data confirmed to Freundlich isotherm . The percentage removal of nickel ion increases with increase in the pH from five to seven and the maximum sorption takes place at pH seven. The study has demonstrated that the easily available biomaterial can be a cost effective and environmental friendly bio-sorbent in the removal of toxic heavy metal from waste water.*

**Key Words**: Nickel; pollution; *Pinus gerardiana*; Freundlich isotherm; Biosorbent; adsorption.

## INTRODUCTION

The rapid industrialization and advancement in technology has resulted toxic heavy metal release into the environment. The release of these heavy metals is a threat to ecosystem and organism. The conventional methods of removal of metals from the aqueous system include solvent extraction [1], ion-exchange, reverse osmosis, coagulation, membrane separation etc are expensive [2]. In recent years the attention has been devoted to the removal of metal ions[3] from aqueous system using absorbent material of low cost and easily available material of biological origin like tree bark, saw dust, coconut husk and fungal biomass etc. There is also a report on arsenic (III) determination by spectrophotometry coupled with preconcentration technique in water samples [4]. The surfactants of chemical and biological origin are also investigated for their efficiency in removal of metal ions through adsorption processes[5,6]. The metal ions in various industrial effluents are copper, cadmium, chromium, cobalt, zinc, mercury, lead, iron, nickel etc. These metal ions have a tendency to bind with the biosorbents having multiple sites due to the presence of chemical species present in the biomass. The literature on metal binding by activated sludge and role of extra cellular polysaccharide produced by bacteria have been reviewed[7] and the sorption of chromate by HDTMA-exchanged zeolites has also been studied[8]. Use of micellar enhanced ultra filtration at low surfactant concentrations has also been used for metal ion removal from aqueous and soil matrix[9,10]. In biosorption several chemical processes reviewed such as adsorption, ion exchange, coordination, complexation, chelation and micro precipitation takes place through passive non directed physicochemical interaction between metal species and cellular part of biomasses[11]. There are reports on studies of biosorption of cadmium on Psidium guajava leaves powder using statistical experimental design[12] and removal of nickel(II) ion from aqueous solution using different absorbent like cotton hull, activated carbon, beads as sorbent/ adsorbent[13,14]. This article elucidates the usefulness of biodegradable and cost effective adsorbent (dry leave powder of *Pinus gerardiana* )for of nickel ion removal from aqueous system The study include the observation of influence of contact time, concentration and pH.

## EXPERIMENTAL SECTION

The stock solution of nickel sulphate was prepared by dissolving an accurately weighed amount of sample (Qualigen lab reagent). Solutions were diluted to desired strength. The leaves of *Pinus gerardiane* collected from Parder area of Kistwar district in Jammu and Kashmir. The shade dried leaves were used to prepare coarsely powdered form. The powder was used as such in the experimental studies.

Batch sorption studies were carried out at the desired concentration of adsorbate and adsorbent dosage in a 100ml stopper conical flask containing 20ml of test solution. Sorption study were performed by shaking the substrate/ adsorbate sample amount 0.5g with nickel sulphate solution of known concentration in distilled water. In general the contact time was kept constant for each set of experiments 2.5hour. After contact time of 2.5hour the contents of the flask were filtered through Whatman filter paper and the filtrate was analyzed for nickel(II) concentration in the solution. The concentration of nickel(II) determined conductometrically using digital conductivity meter 306 (Systronic) in the filtrate received after sorption by the sorbate adopting the standard procedure[6]. The effect of pH on the bio-sorption of nickel(II) by LPPG was determined in the pH range 5 to 9 with digital pH meter (Elico, model L1-120) having glass and calomel electrode assembly.

## RESULTS AND DISCUSSION

**Effect of nickel(II) ion concentration:**
The effect of nickel(II) ion concentration was studied at constant temperature 297K by taking the concentration range of 0.04 $moldm^{-3}$ to 0.08 $moldm^{-3}$ at pH 7.0 The equilibrium concentration of nickel(II) ions in aqueous solutions has been calculated with the help of calibration curve for the variation of conductance with concentration under experimental solution conditions. In each case the equilibration time taken was 150 minutes. The sorption studies were carried out in 20 ml of solution with a fixed amount of sorbent 0.5gm in each case. The experimental results are presented in Table1.

The nickel(II) removal by dry leaves powder of Pinus gerardiana (LPPG) data is analyzed to determine the percentage uptake by the sorbent. The following equation used for the calculation of percentage sorption.

$$\% \text{ sorption} = \frac{c_0 - c_e}{c_0} \times 100 \qquad \text{---------------(1)}$$

where $c_o$ = Initial concentration of metal ion
$c_e$ = Equilibrium concentration of metal ion after equilibrium time of 150 minutes.

**Table 1: Initial and equilibrium conductance for various concentration of nickel (II) ion in aqueous solution at 297K**

| Sorbent | Flask No. | Initial [Ni] | Initial Ni conductance | Equilibrium Ni conductance | Amount of sorbent |
|---|---|---|---|---|---|
| | | $c_o$ | | | |
| | | moldm$^{-3}$ | mS | mS | g |
| LPPG | 1 | 0.04 | 4.41 | 2.77 | 0.5 |
| | 2 | 0.05 | 5.19 | 3.1 | 0.5 |
| | 3 | 0.06 | 5.88 | 3.44 | 0.5 |
| | 4 | 0.07 | 6.65 | 3.84 | 0.5 |
| | 5 | 0.08 | 7.37 | 4.25 | 0.5 |

The calculated percentage uptake by the sorbent is given in Table 2. The effect of nickel ion concentration on sorption is also shown graphically in Fig.1.

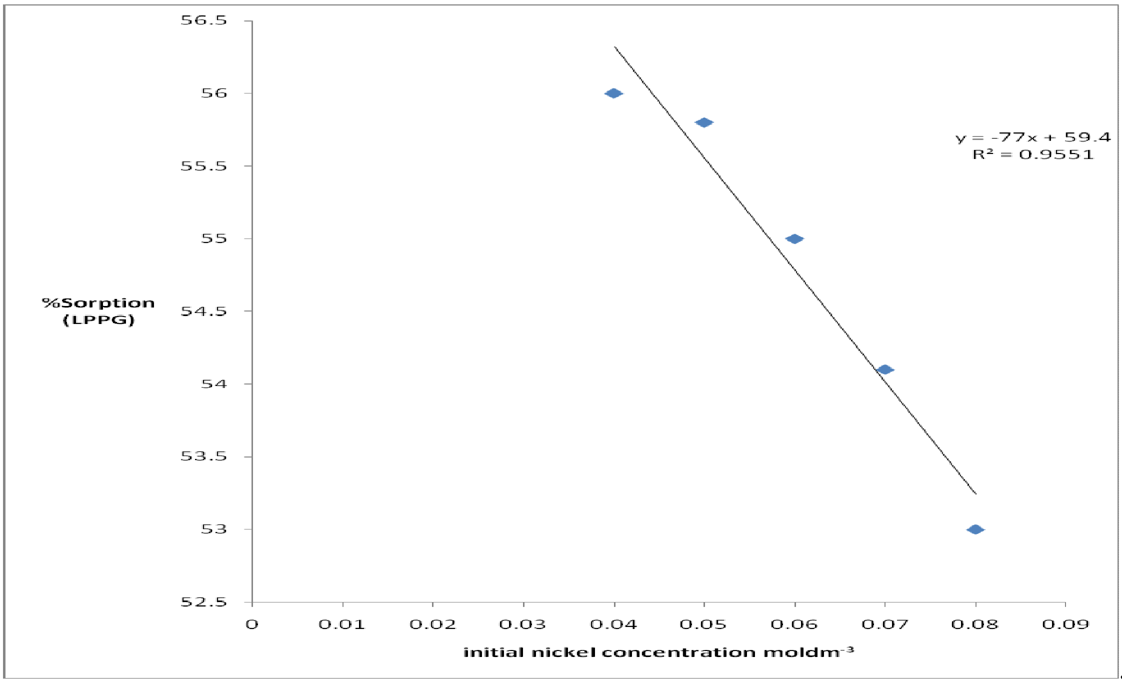


**Fig 1: Plot for % removal with initial [nickel(II)] at 297K**

From the figure it is clear that the percentage removal decreased with the increase of initial concentration of nickel(II) ion and become almost constant at 0.08 moldm$^{-3}$ .This decrease indicates the lack of available active sites on sorbent for the adsorption of higher initial concentration of nickel(II) ion. The diffusion coefficient gives an idea about the sorption process because the diffusion of the sorbate into the pores of the sorbent, basically related to the sorption process. The experimental data is also used to calculate the distribution coefficient. The distribution coefficient is computed with the help of reported[15] relation given by equation 2.

Distribution coefficient,

$$K_d = \frac{c_o - c_e}{c_e} \times \frac{V}{m} \qquad \text{--------------(2)}$$

where V is volume of solution(ml) and m is the mass of the sorbent (g).The value for LPPG is also given in Table 2.

**Table 2: The values of %removal and distribution coefficient of Ni(II) ion for sorbent at 297K**

| Sorbent | Flask No. | Initial [Ni] | Equilibrium [Ni] | Amount of Ni(II) sorbed | %sorption by 0.5g of an adsorbent | Distribution coefficient | |
|---|---|---|---|---|---|---|---|
| | | $c_o$ | $c_e$ | $c_o$-ce | [1-ce/$c_0$]X100 | $K_d$ | [1-$c_e$/$c_o$] |
| | | moldm$^{-3}$ | moldm$^{-3}$ | | | | |
| LPPG | 1 | 0.04 | 0.0176 | 0.0224 | 56.0 | 22.4 | 1.27 |
| | 2 | 0.05 | 0.0221 | 0.0279 | 55.8 | 22.32 | 1.26 |
| | 3 | 0.06 | 0.0270 | 0.0330 | 55.0 | 22.0 | 1.22 |
| | 4 | 0.07 | 0.0321 | 0.0379 | 54.1 | 21.7 | 1.18 |
| | 5 | 0.08 | 0.0376 | 0.0424 | 53.0 | 21.2 | 1.27 |

In the present study the dry leaves powder of *Pinus gerardiane* (LPPG) was first choice as biomaterial for proposed sorption study to measure its efficiency for the removal of nickel(II) ion. The results obtained were used to calculate the adsorption capacity of the adsorbent, the result obtained are given in Table 3.

**Table 3: The value of adsorption capacity (q) at 297K and pH 7**

| Sorbent | Flask No. | Initial [Ni] | Conductometric | |
|---|---|---|---|---|
| | | | Equilibrium [Ni] | Sorption capacity |
| | | $c_o$ | $c_e$ | q |
| | | mgl$^{-1}$ | mgl$^{-1}$ | mg g$^{-1}$ |
| LPPG | 1 | 10510.96 | 4624.75 | 235.44 |
| | 2 | 13138.50 | 5807.22 | 293.25 |
| | 3 | 15766.44 | 7094.79 | 346.86 |
| | 4 | 18393.90 | 8434.92 | 398.36 |
| | 5 | 21021.60 | 9880.15 | 445.66 |

*q = mg of metal ion adsorbed per gram of sorbent.*

It clearly shows that methods used for sorption studies are efficient.

## Effect of pH:

The effect of pH on sorption of nickel(II) ion on LPPG was studied in the range 5.0 to 9.0 pH. The results of percentage adsorption are summarized directly in Table 4 obtained from the experimental data.

The percentage removal of nickel(II) ion increases with increase in the pH from 5 to 7 and the maximum sorption takes place at pH 7. The percentage removal decreases beyond this value due to the precipitation of metal as hydroxide in basic medium. The Plot between sorbate initial pH and percentage removal is shown in Fig. 2**.**

**Table 4: Effect of pH on %removal of nickel ion at temperature 297K**

[Adsorbate]=0.04mol $dm^{-3}$ ; Adsorbent= 0.5g

| S.No. | pH | %removal LPPG |
|---|---|---|
| 1 | 5.5 | 20.1 |
| 2 | 6.0 | 39.5 |
| 3 | 6.5 | 44.8 |
| 4 | 7.0 | 54.1 |
| 5 | 7.5 | 52.5 |
| 6 | 8.0 | 17.2 |
| 7 | 9.0 | 11.2 |

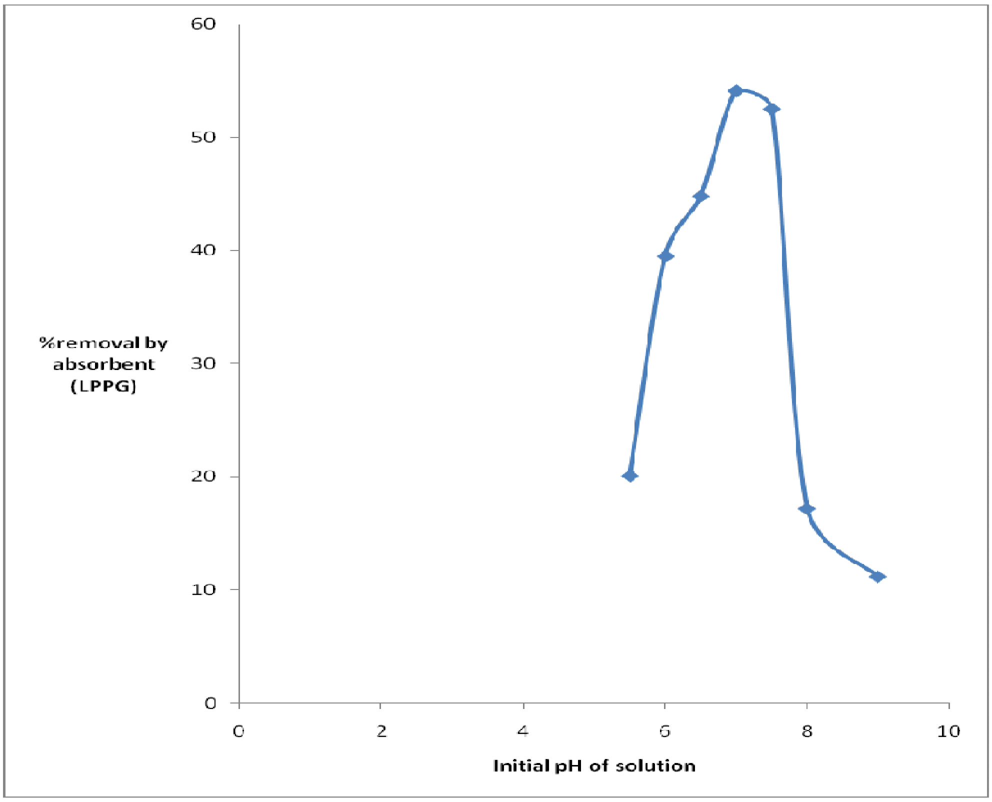

**Fig 2: Plot between initial pH and % removal**

It is observed that the change in pH is significance up to pH 7.0 and there is no considerable data after the pH 7.0. It is possible that the hydrolysis/ hydroxide formation processes are responsible above the pH 7.0. Similar observations have been reported in the adsorption process on activated carbon prepared from simarouba shells[16]. This study indicates that the functional groups available on the sorbent and the surface active charges changes from acidic to basic region due to the change in the polarity.

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log c_e \qquad \text{----------(3)}$$

**Adsorption isotherm:**

To understand the nature of the adsorption process the Freundlich isothermal equation was used. The adsorption studies conducted at fixed initial concentration of sorbate and known amount of sorbent. The results were fitted to the linearised Freundlich isotherm equation given by equation 3.

where x/m is the amount of the nickel sorbed per unit mass of the sorbent (mg/g) and $c_e$ is the concentration of nickel in aqueous solution (mg/l), $K_F$ is the measure of adsorption capacity where as 1/n is a measure of sorption intensity. This isotherm is applicable for adsorption studies the representative plots of this study are depicted in Fig.3 and related data have been summarized in Table 5.

**Table 5: Conductometric data related to Freundlich adsorption isotherm at 297K**

| Sorbent | Flask No. | Initial [Ni] | Equilibrium [Ni] | Equilibrium [Ni] | log $c_e$ | x/m | log x/m |
|---|---|---|---|---|---|---|---|
| | | $c_o$ | $c_e$ | $c_e$ | | | |
| | | mol $dm^{-3}$ | mol $dm^{-3}$ | $mgl^{-1}$ | | mg $g^{-1}$ | |
| LPPG | 1 | 0.04 | 0.0176 | 4624.75 | 3.6650 | 235.44 | 2.3718 |
| | 2 | 0.05 | 0.0221 | 58807.22 | 3.7640 | 293.25 | 2.4672 |
| | 3 | 0.06 | 0.027 | 7094.79 | 3.8509 | 346.86 | 2.5402 |
| | 4 | 0.07 | 0.0321 | 8434.92 | 3.9261 | 398.36 | 2.6003 |
| | 5 | 0.08 | 0.0376 | 9880.15 | 3.9948 | 445.66 | 2.6490 |

$K_F$=0.1993 ; 1/n=0.8401

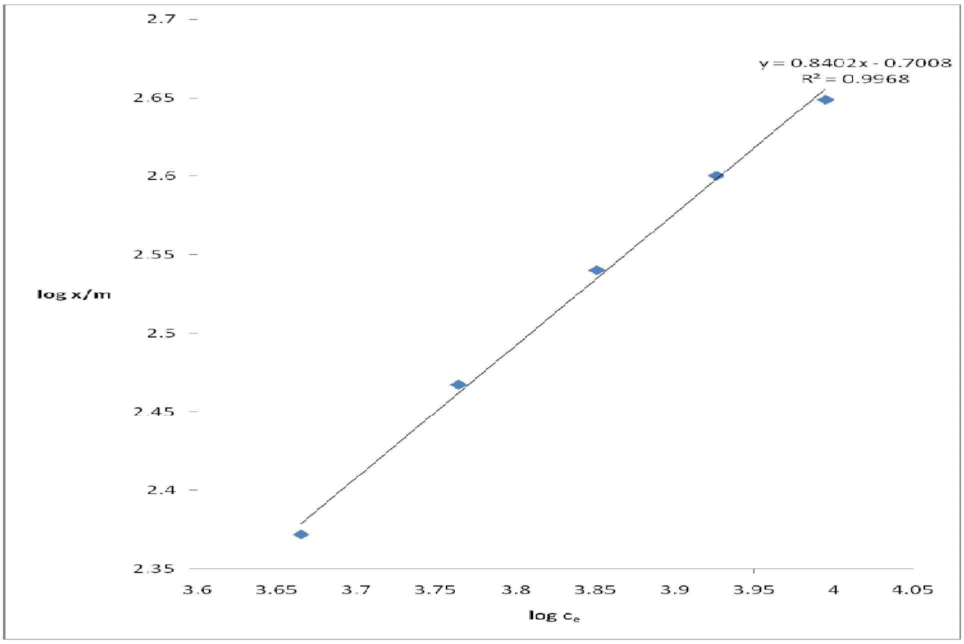


**Fig 3: Plot of log $c_e$ and log x/m, conductivity data**

The experimental data gave a straight line showing the applicability of linearised Freundlich adsorption isotherm. The values of Freundlich constant $K_F$ and 1/n were determined from the slope and intercepts of the linear plots of log x/m versus log $c_e$ for LPPG sorbent and values are given in Table 5. The fractional value of 1/n indicates that LPPG is of heterogeneous type having exponential distribution of energy sites[17]. The values of 1/n in the range of 0.7317– 0.8401 represents good adsorption potential of the sorbent[18].

## CONCLUSION

The results obtained in the study clearly shows that the dry leaves powder of *Pinus gerardiana* is able to remove nickel(II) effectively from the aqueous solution. The process of adsorption is well known in case of activated charcoal[19] . The method used in the study is well known as it has been used in adsorption studies. The study indicated that bio-sorption can be a useful alternative solution to conventional methods for removal of toxic metals from aquatic systems. To obtain a fundamental technological process for the removal of heavy toxic metals, the above study may be extended with actual industrial effluents.

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