# Application of a low cost agricultural adsorbent for removal of Nickel ions

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## Abstract

*In the present study, the adsorption potential of an agricultural waste material Bengal gram husk was evaluated for the removal of $Ni^{2+}$ ions. The optimum conditions for the adsorption of $Ni^{2+}$ ions were conducted by batch experiments. Parameters studied include initial concentration, pH, adsorbent dosage and contact time. The experimental data fitted well to Freundlich and Langmuir isotherms with $R^2$ values greater than 0.9. The adsorption kinetics of $Ni^{2+}$ onto Bengal gram husk follow pseudo first order reaction. The maximum adsorption of $Ni^{2+}$ was 112.2 mg/g of the adsorbent, which is much higher than other adsorbents reported in literature.*

*Functional groups like –OH, C= O and - CN groups were found to be involved in the adsorption process as revealed by Fourier transformed infrared spectroscopy. Hence, the present adsorbent can be used at an industrial scale to remove nickel ions from the effluents before discharging into the environment.*

**Keywords:** Bengal gram husk, nickel, adsorption, isotherm studies, infrared spectroscopy, kinetics.

## Introduction

The heavy metal discharge in surface water has received widespread attention due to its toxic nature, bioaccumulation and difficulty in degradation. Hence, it becomes mandatory to remove heavy metals from wastewater before discharge[23]. Nickel is widely used in metal plating, mineral processing, paint formulation, battery manufacturing and steam electric plants[5]. Nickel is known carcinogenic and is easily absorbed by the skin. High concentration of nickel can also lead to various types of cancers. There are several conventional methods for the removal of nickel which include oxidation, electro-flotation, membrane filteration, reverse osmosis, ion exchange and precipitation. But these methods have several disadvantages like sludge generation, ineffective removal, high energy demands and are extremely expensive[6].

Hence there is an increasing need to develop environmentally friendly methods for the removal of low concentrations of heavy metals. Adsorption has proved to be the easiest, convenient and efficient technology for the removal of heavy metals[16]. Adsorption by agricultural wastes can be considered as one of the most popular methods for the removal of heavy metals from the wastewater due to its low cost, easy availability and high removal efficiency[1]. The utilization of agricultural wastes as adsorbent is desirable because of their easy availability and low-cost owing to relatively high fixed carbon content and porous structure.

Agricultural waste materials that have been evaluated for the removal of heavy metals include husks of rice, wheat bran, sugarcane bagasse, sawdust, grape stack, mango peels, coconut copra meal, black gram, peels of lemon, lime, orange, apple and banana, barks of trees, shells of groundnut, coconut, hazelnut and walnut, cotton seed hulls, waste tea and Cassia fistula leaves, maize corn cob, jatropa deoiled cakes, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans etc.[7,18,19]

Functional groups such as acetamido, alcoholic, carbonyl, phenolic, amido, amino and sulfhydryl have been implicated for the removal of heavy metals[24]. The functional groups bind with the metal either through ion exchange by transferring hydrogen ions or complex formation by sharing an electron pair, adsorption on surface and ion exchange.

In the present study, agricultural waste bengal gram husk (*Cicer arientinum*) was evaluated for the removal of nickel from synthetic aqueous solutions. The focus of this study is to use the above said agricultural waste without any pretreatment so as to make the process economically viable. The surface properties of these adsorbents have been investigated by Fourier transformation infrared spectroscopy (FTIR).

## Material and Methods

Bengal gram husk (BGH), the seed coat of *Cicer arientinum* was collected from a legume seed-splitting mill. The husk was washed extensively in running tap water and later subjected to washing and boiling in distilled water to remove colour, dirt and other particulate matter. Subsequently the husks were oven dried at 105°C for 24 hours, stored in a desiccator and used for biosorption studies in the original piece size.

**Determination of Carbon, Nitrogen and Sulphur:** The CHN analysis was carried out to understand the metal binding mechanisms of the Bengal gram husk. C.H.N. 1106 Carlo Erba MicroAnalysing device equipped with inductive furnace analyzer was used for elemental analysis. The Bengal gram husk was subjected to quick and complete combustion in an oven at 1000°C under oxygen. $N_2$, $H_2O$ and $CO_2$ were released and conducted in a copper oven at

650°C, then passed through a 2 m column with helium vector gas and analyzed by a catharometer detector.

**Fourier transformation infrared spectroscopy:** FTIR spectroscopy using an FTIR spectrophotometer (Perkin Elmer RXI spectrum) was carried out to determine the functional groups present on the surface of the adsorbent so as to evaluate the interactions between BGH and nickel ions. FTIR spectroscopy was performed for Bengal gram husk (BGH) by KBr discs (150 mg) containing approximately 2% of BGH prepared just before recording the FTIR spectra in the range of 400–4,000 cm$^{-1}$.

**Batch Mode Adsorption Studies:** The chemical reagents used in the present study were of analytical grade. Nickel sulphate of concentration 1000mg/L was prepared as the stock solution. The required working standards were prepared from the stock solution using distilled water. pH was adjusted using sodium hydroxide and sulphuric acid. Batch mode adsorption studies were conducted to optimize different factors i.e. pH (2–10), BGH dosage (0.1–1.0 gm.), $Ni^{2+}$ concentration (20-100 mg/l). The various isotherm and kinetic studies were completed by altering the metal concentration (50–200 mg/L) and time (5–600 min.) at optimum pH and BGH dosage.

## Results and Discussion

The approximate percentage of total carbon, nitrogen and hydrogen in the BGH is 38.7%, 0.86 and 6.31% respectively. The high percentage of carbon content in BGH reveals that carbon compounds might be responsible for adsorption of nickel (II). The percentage nitrogen in BGH is less, hence it can be inferred that the protein content is low. Low percentage of protein shows that BGH is unlikely to putrefy under moist conditions and this is advantageous over protein rich adsorbents.

**Infrared spectroscopic studies**: The different functional groups present on BGH were analysed with the aid of FTIR. The peak at 3000 and 3750 cm$^{-1}$ indicates the presence of OH group and the peak at 2918.18 cm$^{-1}$ and 893.25 cm$^{-1}$ indicates the presence of C-H groups. The 1634.34 cm$^{-1}$ band is a result of CO groups which are conjugated to a NH deformation mode and indicate an amide 1 band. The peak at 1115.57 cm$^{-1}$ can be attributed to CO or CN groups.

**Effect of equilibrium time:** The role of equilibrium time (0 – 300 minutes) on the uptake of $Ni^{2+}$ was carried out at different adsorbent dosages (10-100 mg/L) at pH 5.5 and is given in figure 1. As seen from the figure, the uptake of $Ni^{2+}$ increased with the contact time, but the percentage adsorption decreased with increase in metal concentration. It is seen that for the low initial concentrations, the percent uptake of the nickel was high. The uptake of nickel was rapid and the equilibrium was attained within 15 minutes of contact between the BGH and the metal solution. The equilibrium time required by BGH to remove Ni (II) is very less compared to other adsorbents[25,31]. This result is significant as one of the important considerations for economical water and wastewater applications is equilibrium time.

**Effect of pH:** pH is an important factor for the adsorption process as it affects the chemistry of the adsorbent and the adsorbate. The experimental results revealed that the optimum pH for nickel adsorption by BGH is 5 (Figure 2). The percentage of $Ni^{2+}$ adsorbed is highest at pH 5.0 and the adsorption rate decreases as pH increases or decreases. The $H^+$ ions compete with $Ni^{2+}$ for the adsorption sites in adsorbent, thereby partially releasing the metal cations at low pH[3]. At increasing pH, functional groups such as amino and carbonyl groups would be exposed on the adsorbent leading to attraction between these negative charges and $Ni^{2+}$ increasing the adsorption on to the surface of adsorbent[22].

The reaction of nickel ions in the solution with the biomass can be described by the following equilibrium:

$$\mathrm{H}n\mathrm{B} + \mathrm{M}n+ \longleftrightarrow \mathrm{MB} + n\mathrm{H}+,$$

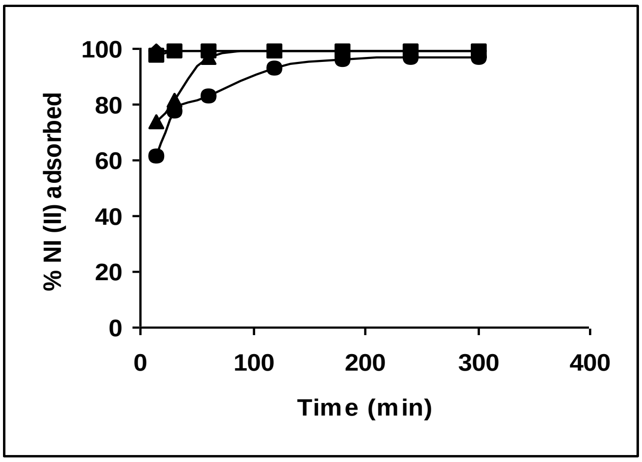

**Figure 1: Effect of agitation time on the Nickel biosorption by BGH**
**(♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)**

where M represents the metal, n is its charge and B is the biosorptive active centers. The pH dependency is both related to the surface properties of BGH and nickel species in solution. In addition, at higher pH, more than 7, the lower binding is attributed to reduced solubility of the $Ni^{2+}$ and consequently precipitation as metal hydroxides.

**Effect of adsorbent dosage**: Figure 3 shows the relationship between the BGH concentration and the amount of $Ni^{2+}$ adsorbed at various initial nickel concentrations. An adsorbent dosage of 1g – 2g/L was sufficient for adsorption of 90% of the initial $Ni^{2+}$ ions (Figure 3). The percentage of nickel adsorbed increased with increase in BGH concentration due to increased adsorption surface area. Further increase in the adsorbent dosage did not show an increased removal of Ni (II). However, the adsorbent dosage required for maximum percent removal varied with the concentration of initial metal ions. This is mainly due to the fact that a larger mass of adsorbent could adsorb larger amount of adsorbate due to the availability of more surface area of the adsorbent.

**Adsorption Kinetic Studies:** The kinetic data was treated with Lagergren first order rate reaction and the rate constant was determined from the expression:

$$\log_{10} (qe-q) = \log_{10} q_e - Kad\ t / 2.303$$

where q and qe are amounts of adsorbate adsorbed (mg/g) at time, t (min) and at equilibrium respectively, Kad is the rate constant of adsorption (l/min). The linear plots of log10 (qe-q) vs t for Ni(II) were studied at different concentration (Figure 4). The value of $K_{ad}$ calculated from the slope of the linear plots is 2.07 X $10^{-2}$l/min for 100mg/l of Ni (II) and is comparable with those in literature[11].

**Adsorption isotherms**: The adsorption isotherm models of Langmuir and Freundlich were used to describe the adsorption mechanism. The Langmuir isotherm model assumes that the metal ions binding occurs on a homogeneous solid surface such that all binding sites on the surface have uniform energies of adsorption without any interaction between adsorbed molecules.

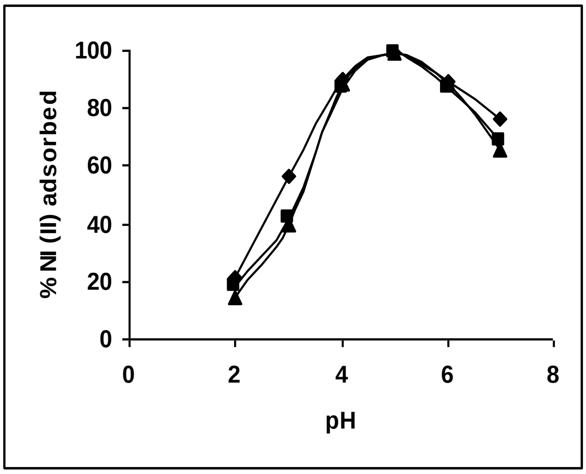

**Figure 2: Effect of pH on the Nickel biosorption by BGH (♦ 10 mg/L□■ 20 mg/L□▲□50 mg/L ● 100mg/L)**

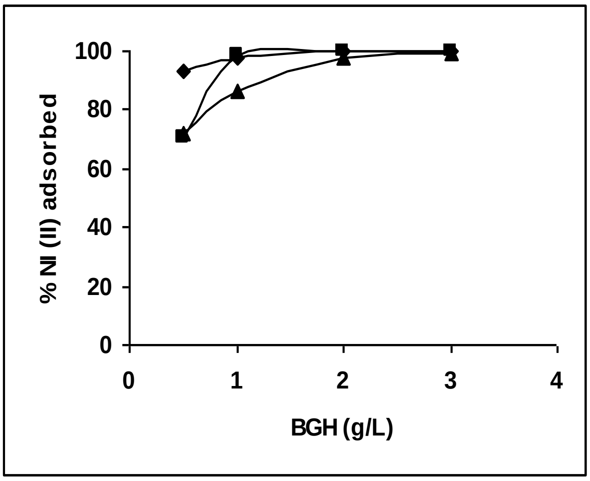

**Figure 3: Effect of adsorbent dose on the Nickel biosorption by BGH**
**(♦ 10 mg/L□■ 20 mg/L□▲□50 mg/L ● 100mg/L)**

The following linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is given by the following equation:

$$C_{eq}/q = 1/q_{max}.b + C_{eq}/q_{max}$$

Thus a plot of $C_{eq}/q$ vs $C_{eq}$ should be linear if Langmuir adsorption was operative, permitting calculation of qmax. The comparison of sorption capacities of BGH used in this study with those obtained in the literature is effective for the removal of $Ni^{2+}$from aqueous solution. The adsorption capacities of the adsorbents for the removal of $Ni^{2+}$were compared with those of other adsorbents reported in literature and the values of adsorption capacities are presented in table 1. The experimental data of the present investigations are comparable with the reported values.

The Freundlich isotherm model is based on the non-ideal sorption on the heterogeneous surface. The linearised forms of Freundlich adsorption isotherm were used to evaluate the sorption data and represented as:

$$\ln q = \ln K_f + 1/n \ln C_{eq}$$

where $C_{eq}$ is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and $K_f$ and n are constants incorporating all parameters affecting the adsorption process such as adsorption capacity and intensity respectively. $K_f$ and n were calculated from the slopes of the Freundlich plots. The parameters calculated from Langmuir and Freundlich isotherms are represented in the table 2.

According to literature[17], $R_L$ values between 0 and 1 indicate the isotherm favourable and it is unfavourable if $R_L > 1$. Isotherms are linear or irreversible if $R_L$ values are equal to 1 or 0 respectively. The $R_L$ for Ni(II) adsorption is $8.4 \times 10^{-1} – 1.5 \times 10^{-1}$ which indicates favourable biosorption of Ni(II) on Bengal gram husk.

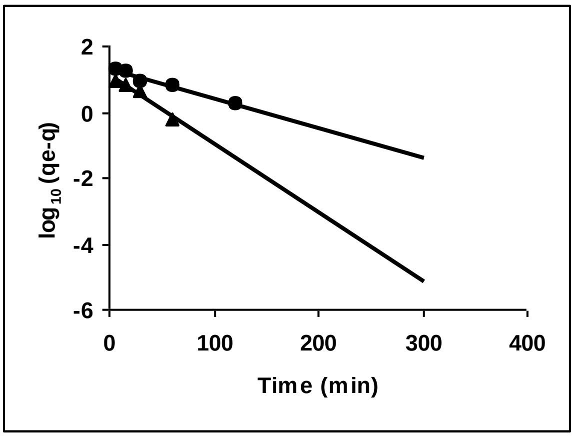

**Figure 4: Lagergren plots for Nickel adsorption by BGH (♦ 10 mg/L□■ 20 mg/L□ ▲□50 mg/L ● 100mg/L)**

**Table 1**
**Comparison of Adsorption capacity of BGH with other adsorbents**

| Adsorbent | Adsorption Capacities (mg/g) |
|---|---|
| Sugarcane bagasse[2] | 2.234 |
| Oil cake[15] | 3.248 |
| Modified riverbed sand (MRS)[30] | 0.86 |
| Lignocellulose/Montmorillonite Nanocomposite[32] | 94.86 |
| *Acacia leucocephala* bark[26] | 294.1 |
| *Ceiba pentandra* hulls[29] | 34.34 |
| *Fucus vesiculosus*[21] | 70.1 |
| Activated carbon of Duom seed[8] | 3.24 |
| Sand absorbent[28] | 6.527 |
| Algal species[20] | 9.848 |
| *Bengal gram husk* * | 112.2 |

*Present study

**Table 2**
**Isotherm Parameters of Nickel Adsorption on BGH**

| Equilibrium models | Parameters | |
|---|---|---|
| Langmuir | $q_m$ (mg/g) | 112.22 |
| | b (L/mg) | 0.009 |
| | $R^2$ | 0.98 |
| Freundlich | $K_F$ $(mg/g)(L/mg)^{1/n}$ | 9.19 |
| | nF | 1.56 |
| | $R^2$ | 0.97 |

## Conclusion

The present study evaluated the potential of using Bengal gram husk for the removal of $Ni^{2+}$ from synthetic aqueous solutions. The removal of $Ni^{2+}$ was dependent on pH, contact time, adsorbent dosage and initial metal concentration. The FTIR analysis revealed that functional groups like carboxyl, amide and hydroxyl ions play a significant role in the adsorption of $Ni^{2+}$. As the Bengal gram husk (BGH) contains very less amount of protein (N = 0.63), it will prove to be advantageous over the protein-rich algal and fungal biomass projected as $Ni^{2+}$ adsorbents, since materials rich in protein are likely to putrefy under moist conditions.

The high correlation constant reveals that adsorption of $Ni^{2+}$ follows both Langmuir and Freundlich isotherms. The kinetic study reveals that the adsorption follows a pseudo first order rate reaction. Hence, the present adsorbent can be used at an industrial scale to remove nickel ions from the effluents before discharging into the environment. These results suggest that Bengal Gram husk is an attractive adsorbent for removal of $Ni^{2+}$from aquatic medium.

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