

Biosorptive Removal of Ni(II) from Wastewater and Industrial Effluent

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Abstract: The objective of the present work was to investigate the removal of Ni(II) by the fresh biomass (FBM) and chemically treated leached biomass (LBM) of *Calotropis procera*. The scope of the work included screening of the biosorbents for their metal uptake potential, batch equilibrium, column mode removal studies and kinetic studies at varying pH (2-6), contact time, biosorbent dosages (1-25 g/L) and initial metal ion concentration (5-500 mg/L). The development of batch kinetic model and determination of order, desorption studies, column studies were investigated. It was observed that pH had marked effect on the Ni(II) uptake. Langmuir and Freundlich models were used to correlate equilibrium data on sorption of Ni(II) metallic ion by using both FBM and LBM at 28°C and pH 3 and different coefficients were calculated. It was found that both biomasses were statistically significant fit for Freundlich model. The biomass was successfully used for removal nickel from synthetic and industrial effluents and the technique appears industrially applicable and viable.

Keywords: Biosorption, biomaterial, nickel, industrial effluent, *Calotropis procera*

Introduction

Heavy metals have a tendency to bioaccumulate and end up as permanent additions to the environment [1]. Heavy metals like Zn, Cu, Ni, and As are known to have toxic effects at very low concentrations [2] as well as very high concentration [3]. Nickel is a toxic heavy metal found in the environment as a result of various natural and industrial activities. Nickel has been implicated as an embryotoxin and teratogen [4]. The higher concentration of Ni causes poisoning effects like headache, dizziness, nausea, tightness of the chest, dry cough, vomiting, chest pain, shortness of breath, rapid respiration, cyanosis and extreme weakness [5]. Nickel is well known heavy metal pollutant, which is present in effluents of electroplating industries to the tune of 20 – 200 ppm [6]. Studies of human cell cultures have indicated that nickel is a possible carcinogen, creating a need for the cleanup of nickel pollution. So it is very essential to remove Ni from

soil, industrial wastewater and effluents. The conventional methods which are commonly used for the removal of nickel from the industrial effluents are physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and membrane technologies. These processes may be ineffective or expensive, especially when the heavy metal ions in the contaminated media are high i.e. in order of 1-100 mg dissolved heavy metal ions/l [7]. Secondly the operational problems and the high cost of treatment necessitate the research for some newer methods. Biological methods such as biosorption/ bioaccumulation may provide an attractive alternative to physico-chemical methods for the removal of heavy metal ions [8]. In this context it may be noted that few non-conventional and less expensive adsorbents have been investigated for removal of Ni(II) such as sphagnum peat [9], blast furnace slag [10], apple waste [11], soyabean and

cottonseed husk [12], peat nut husk carbon [13], straw [14], treated saw dust and activated alumina [15] and silica gel.

The acceptable limit of Ni in drinking water is 0.01 mg/L and the industrial discharge limit in wastewater is 2 mg/L [16]. Microorganisms uptake metal either actively (bioaccumulation) and/or passively (biosorption) [17–21]. In the present study the sorption of Ni²⁺ ions by fresh biomass (FBM) and chemically treated leached biomass (LBM) were investigated. The sorption isotherm and the kinetics of the sorption were characterized and the influence of pH, biosorbent dosages, loading capacity, and effects of common background ions were investigated. The main objective of present study was to investigate the feasibility of using FBM and chemically treated LBM for the removal of Ni(II) from wastewater, aqueous solution, and industrial effluents.

Materials and Methods

Preparation of Biosorbent Material (FBM)

The root of the commonly located shrub *Calotropis procera* was collected from the different areas of Durg district of Chhattisgarh. The biomass was extensively washed with running tap water for 30 to 40 minutes to remove dirt and other particulate matter followed by washing in double distilled water. The outer part of the root was removed and cut into the small pieces. The pieced biomass was then immersed in 1:1 HCl solution for 10 minutes and then washed with double deionized water and was finally put in an electric oven at 60°C for two hours. Afterwards the biomass was kept at a temperature of 45°C for overnight. The dried biomass was ground in a laboratory blender and sorted using standard test sieves. The sample used was of particle size passing 250 µm sieve. This sample was then stored in a desiccator and used for biosorption studies.

Preparation of Chemically Treated Leached Biomass (LBM)

For preparing leached biomass the fresh biomass sample was immersed in 1 L 1:1 HNO₃ for 24-h. Afterwards the biomass was filtered and washed properly with double deionized water and then dried at 50°C for 1-h in an electric oven and then at 35°C for 24-h and stored in desiccators for use.

Preparation of Nickel Solution

A synthetic solution of 5000 mg/L was prepared by dissolving 5 g ANALAR grade commercially available pure metal of Nickel in 20 ml of hot concentrated HNO₃, cooled and diluted with double distilled water up to the mark. The stock solution was further diluted with distilled water to desired concentration for obtaining the test solution.

Instrumentation

A hydride generation atomic absorption spectrophotometer with background correction facility (HG-AAS, Chemito-201) was used for Ni(II) measurement. The detection limit for nickel measurement was 0.06 mg/L. A high precision electric balance (Denver TR-104) was used for weighing and a digital pH meter was used for pH measurement.

Batch Mode Adsorption Study

Batch adsorption experiment was carried out at room temperature (28–30°C). In each experiment 100 ml of Ni(II) solution of known initial concentration (5 mg/L–500mg/L) was treated with a specified known amount (by wt) of biomass (1 g/l to 25 g/L), and known pH for a specified period of time. Batch kinetic studies were first conducted using fresh biomass and leached biomass to determine the time needed for Ni(II) binding process to reach the equilibrium state. Based on kinetic experiment results all experiments were conducted for a period of 30 minutes. After the equilibrium was reached the adsorbent was separated from the metal solution by using Whatman's filter paper no 42. Then Atomic Adsorption Spectrophotometer (CHEMITO-201) measured the concentration of Ni(II) remaining in solution. The nickel concentration was measured both in the biomass and remaining in solution and the nickel uptake by the biomass was calculated as follows:

$$q_e = \frac{C_i - C_e}{m};$$

Where, C_i–initial concentration of metal ion mg/L;

C_e – Equilibrium concentration of metal ion mg/L;

m – mass of adsorbent g/L;

q_e – Amount of metal ion adsorbed per gram of adsorbent.

Similar experiments were also carried out to evaluate the effect of process parameters such as pH (2–8), biosorbent dosage (1–25 g/L), initial concentration of Ni(II) ion (5–500 mg/L). Batch Elution experiments were also carried out to desorb binded Ni(II) from the biomass using five different eluting agents HCl, NaCl, HNO₃, NaOH and Na₂CO₃. The Industrial wastewaters contaminated with Ni(II) were treated with fresh biomass and chemically treated leached biomass in batch experiment. The experiments done without biomass were treated as blanks and they showed that no precipitation of metal ions occurred under the conditions selected. Quality control checks were carried out by inter-laboratory test using ICP-OES at Hyderabad (Varian, Australia).

Column Mode Adsorption Studies

The column used for the removal of nickel under continuous flow conditions, was made up by Borosil glass. The outer diameter of column was 4.6 cm and the

inner diameter of column was 4.1 cm. The filter used in the column was 0.5 cm thick 1 g biomass was packed into a column having a column height of 0.5 m. An aqueous solution containing 50 mg/L nickel was passed through the column. The pH of metal solution was adjusted by the addition of 0.01M NH_4OH or HCl . Effluent sample was collected for every cycle using a fraction collector and were analyzed for Ni(II) concentration by using Atomic Adsorption Spectrophotometer (CHEMITO – 201). Elution of the binded Ni (II) from biomass was carried out using an aqueous 0.1N HNO_3 solution. The eluted biomass was washed with distilled water for regeneration.

Desorption Study

A known amount of biomass was taken into a 250 ml beaker. Batch kinetic studies were first conducted using fresh biomass to determine the time needed for the Ni(II) binding process to reach the equilibrium state. After the biosorption tests the biomass was washed with deionised water for 15 minutes and left in 15 ml different eluting agents such as NaOH , NaCl , Na_2CO_3 , HCl , HNO_3 for one hour at 30°C in a beaker. The biomass was separated from the solution by filtration and washed with deionized water until the pH of the filtrate reached 7. Then the recovered biomass was dried in an electric oven at 60°C and the capacity for biosorption metal was determined. The biosorption-desorption cycle of Ni(II) metal-biomass recovery was repeated two times in order to determine the biosorption capacity of recovered biomass.

FT-IR Method

The FT-IR Study of fresh biomass and metal loaded biomass of *Calotropis procera* using the Thermo Nicolet Nexus 670 spectrometer having a resolution of 4 cm^{-1} at the Indian Institute of Chemical Technology, Hyderabad, India.

Results and Discussion

Effect of pH on Biosorption

Metal sorption is critically linked with pH and the effect of pH of the solution is a very important controlling factor in the adsorption process. For this the role of hydrogen ion concentration was examined at different pH. The effect of pH was studied at the Ni(II) concentration of 50 mg/L, biosorbent dosage of 10 g/L at the pH range 2-8. It was observed that with the increase in the pH of the solution the percentage removal of Ni(II) increased up to the pH 3. After pH 3, further increase in pH value decreased the percentage removal of Ni(II) up to pH 5. After pH 5 the removal of Ni(II) showed a marginal increase in removal till the pH 6. After pH 7 the precipitation of Ni was evident. A similar behavior was shown by the leached biomass but the percentage of Ni removal was much higher than the fresh biomass. The increase in percentage removal of metal ion due to increase in pH may be explained on the basis of a

decrease in competition between proton (H^+) and positively charged metal ion at the surface sites and also by decrease in positive charge near the surface which results in a lower repulsion of the adsorbing metal ion. Maximum percentage removal of nickel was observed at pH 3, which can be due to the formation of $\text{M}(\text{OH})$ and $\text{M}(\text{OH})_2$ as hydrolyzed product. The lower solubility of these hydrolyzed species may be another reason for maximum adsorption. The effect of pH on the removal of Ni(II) is shown in Figure 1.

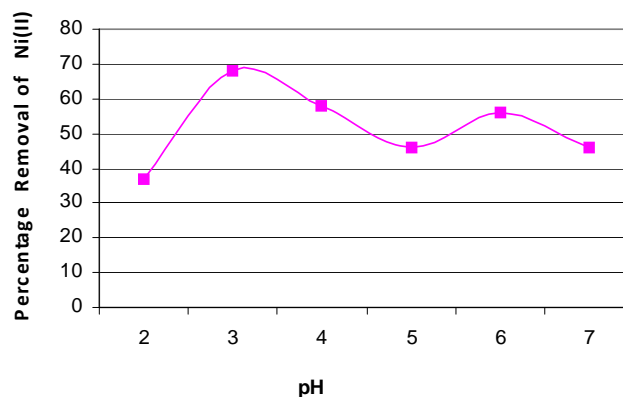


Figure 1: Effect of pH on the biosorption of Ni(II)

Effect of Biosorbent Dose

A graph was plotted between the different dosage of biosorbent FBM and LBM, and the resultant percentage removal of Ni(II). The effect of different biosorbent dosage (1–25 g/L) with percentage removal of nickel is shown in Figure 2. The graph shows a marginal increase in nickel removal with increasing biomass concentration which ranged between 68 to 72% in case of FBM and 88–92% in case of LBM.

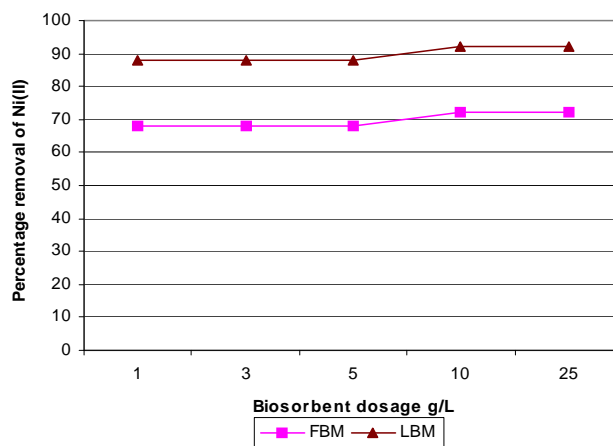


Figure 2: Effect of Biosorbent Dosage on the biosorption of Ni(II)

Effect of Initial Metal Concentration

The effect of initial metal concentration on Ni(II) removal by using fresh and leached biomass is shown in

Figure 3. The biosorbent dose, pH and standing time for the batch experiment were fixed at 10 g/L, pH 3 and 30 minutes respectively. Increasing the initial concentration of Ni(II) in a batch study resulted in decreasing percentage of Ni(II) removal because evidently the biosorbent was approaching its saturation uptake capacity. In batch study using fresh biomass percentage removal of Ni(II) decreased from 95 to 42% when the initial concentration of Ni was increased from 5 to 250 mg/L. The LBM showed a similar trend and the removal was decreased from 100% to 63% in the similar conditions.

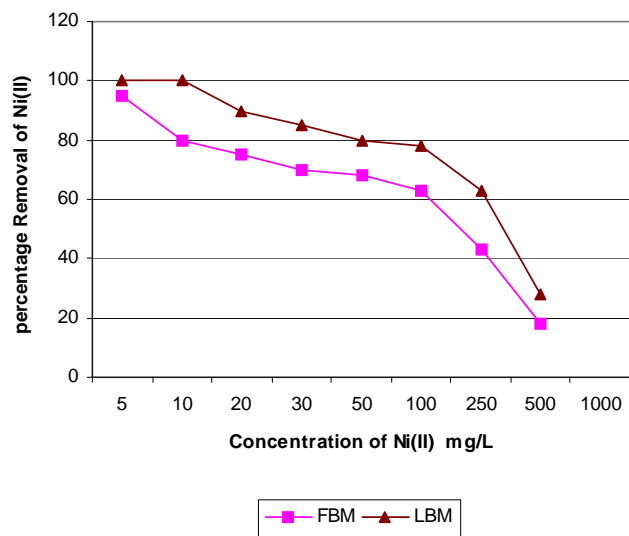


Figure 3: Effect of Initial metal ion concentration on the biosorption of Ni(II)

Analysis of the Kinetic of Ni(II) Removals

Kinetics and equilibrium are the two major parameters for evaluating adsorption dynamics. The effect of contact time on Ni(II) removal was investigated for an initial concentration of 50 mg/L. It was observed (Fig. 4) that the percentage removal of Ni(II) initially increased with contact time and the equilibrium was attained within 30 minutes. Further increase in contact time decreased the removal of Ni(II).

To determine the kinetics, Lagergren equation was applied as follows;

$$\log(q_e - q) = \log q_e - K_{ad} \times t / 2.303$$

Where, K_{ad} – is the rate constant of adsorbent
 q – is the amount of metal ion adsorbed at time t (mg/g)
 q_e is the amount of metal ions adsorbed at equilibrium (mg/g)

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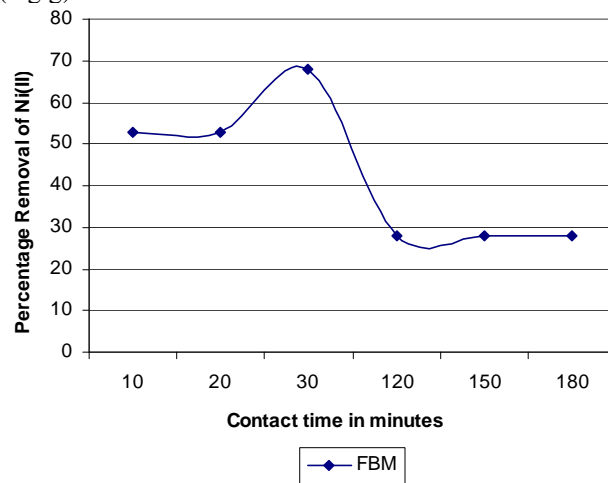


Figure 4: Effect of contact time on biosorption of Ni(II).

Values calculated based on above equation and graph plotted between $\log(q_e - q)$ and time in minutes follow a linear relation which indicates that the kinetics of biosorption of Ni(II) was of first order kinetics (Fig 5).

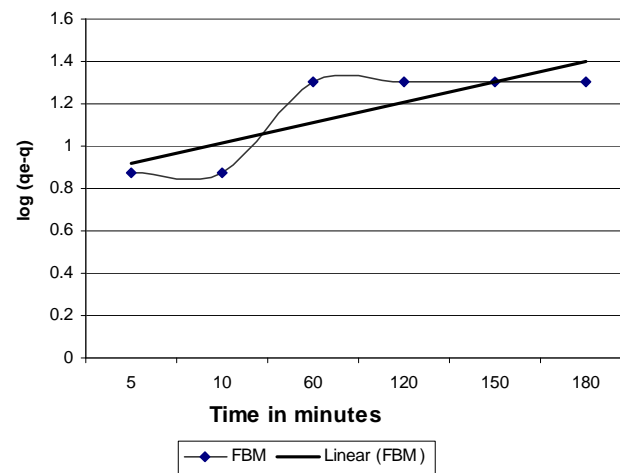


Figure 5: Lagergren equation fitting showing a linear relationship

Effect of Background Ions

Large number of ions could be present in groundwater, wastewater or industrial effluents. Out of these some of the common ions were investigated with chemically treated leached biomass and their findings are presented in Figure 6. The concentration of sulphate, fluoride, arsenate, chromium, mercury and lead ions were varied within the range of 5 to 500 mg/L. The results indicate that the percentage removal of Ni(II) was initially decreased on increasing sulphate ion concentration from 5-20 mg/L but beyond 20 mg/L no significant changes was observed up to the concentration of 500 mg/L. In

case of fluoride the maximum removal of Ni(II) was observed at 200 mg/L of fluoride ion concentration where the Ni removal was more than 93%. The complete removal of Ni(II) was noted in the presence of even a small amount of arsenate as well as chromium ions (studied range was 5-500 mg/L). The presence of mercury was not found to play any significant role. Percentage removal of nickel decreased on increasing concentration of lead ion from 5 to 100 mg/L. Nickel removal was completely blocked if the lead concentration was greater than 100 mg/L. The FBM showed similar results but with lower removal efficiency.

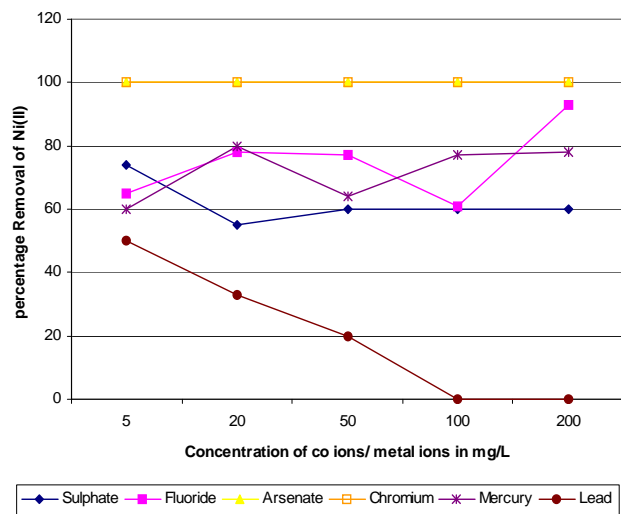


Figure 6: Effect of common ions on the biosorption of Ni(II) with chemically leached biomass at pH 3

Column Study

The effect of initial concentration on the overall removal of Ni(II) was studied with both fresh and leached biomass by using column technique. An aqueous solution containing a definite concentration of Ni(II) (5–1000 mg/L) was passed through the column and the pH of the solution was adjusted by the addition of 0.01M NaOH or HCl, as the case may be.

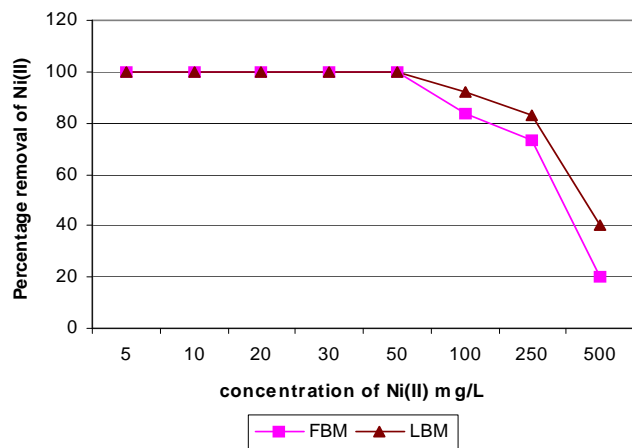


Figure 7: Loading capacity determination of Ni(II)

The percentage removal of 50 mg/L of Ni(II) was 100% with using both fresh and chemically treated leached biomass. The percentage removal of 100 mg/L of Ni(II) was about 82% with FBM and 92% with LBM. For 250 mg/L Ni(II) the removal was about 78% with FBM and 83% with LBM. The results establish the efficacy of the LBM over FBM (Fig. 7). Similarly the column technique was found to be more effective than the batch mode removal.

Study on the Regeneration of Impregnated Biomass

The batch elution result is presented in Figure 8. It was evident that NaOH and NaCl performed poorly as eluting agent. On the other hand almost complete elution of the loaded Ni(II) could be achieved using 0.1N HNO₃. The percentage elution of Ni on using 0.1 N HCl and 0.1M Na₂CO₃ was 65% and 20% respectively.

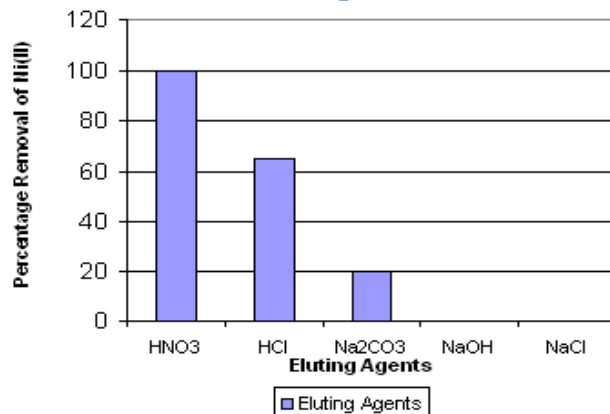


Figure 8: Effect of different eluting agents on desorption of Ni(II)

Adsorption Isotherms

Two important physicochemical aspects of evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationship between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. Most often Biosorption equilibria are described with adsorption isotherms of Langmuir or Freundlich types.

The linear form of Freundlich isotherm is:

$$\text{Log}S = \text{log}K_F + (1/N) \text{log}C$$

Where, S = moles sorbed at equilibrium per mass of sorbent (mg/g) i.e. (Ce/m)

K_F = Freundlich isotherm constant (L/g)

N = Freundlich isotherm constant; N ≥ 1

C_s = Sorbate concentration in solution at equilibrium (mg/L)

The constant K_F is the measure of adsorption capacity and $1/N$ is the measure of adsorption intensity.

The linear form of Langmuir isotherm is:

$$S = (K_L * A_M * C) / (1 + K_L C)$$

Where, S = moles sorbed at equilibrium /mass of sorbent (mg/g) i.e. Ce/m

A_M = maximum sorption capacity of the sorbent (mg/g)

K_L = Langmuir adsorption constant, related to binding energy of the Sorbate (l/mg)

C_s = Sorbate concentration in solution at equilibrium (mg/L)

A_m = the maximum sorption capacity of the sorbent

A plot of $\log Ce/m$ against $\log C_s$ provides a straight line with a slope of $1/N$ and an intercept of $\log K_F$. Based on the least squares fit of the points, the coefficient of determination of the least-squares best line of Ni(II) using both fresh and leached biomass are shown in Figure 9 and 10 respectively.

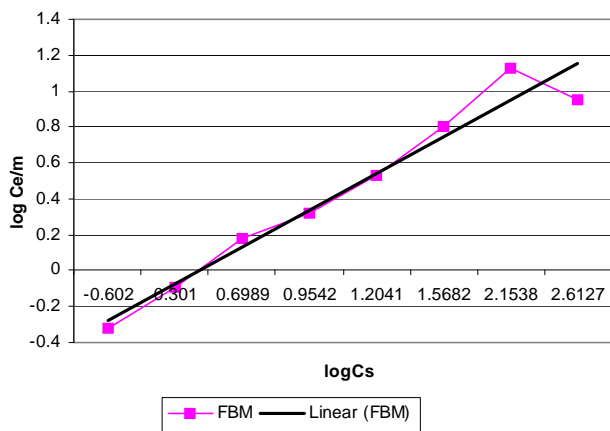


Figure 9: Freundlich Adsorption Isotherm for Batch Study for using FBM

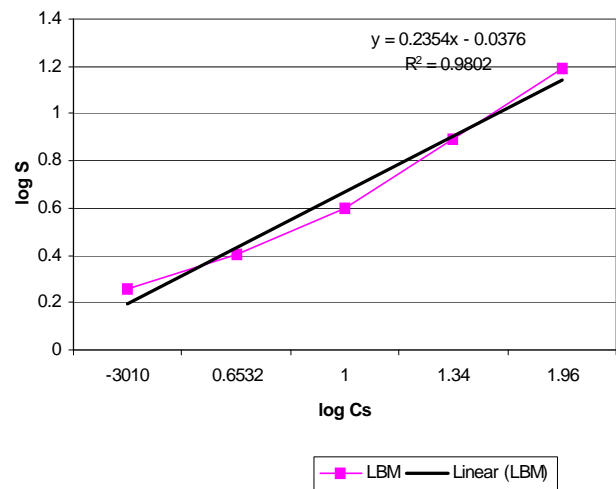


Figure 10: Freundlich Adsorption Isotherm For Batch Study using LBM

For Langmuir Isotherm using the equation, sorption data $C_s/C_e/m$ Vs C_s was plotted to produce a line with a slope of $1/A_m$ and an intercept of $1/(K_L A_m)$ using both FBM and LBM are shown in Figure 11 and 12 respectively.

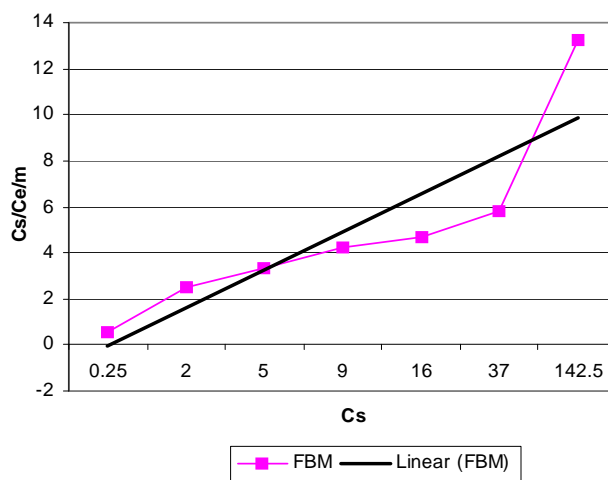


Figure 11: Langmuir adsorption Isotherm for Batch study using FBM

Freundlich constant and Langmuir constant are shown in Table 1 and 2 respectively. Results show that the R^2 values for fresh as well as leached biomass are greater than 0.9 for Freundlich Isotherm, so the adsorption was multi layered and physio-sorption type.

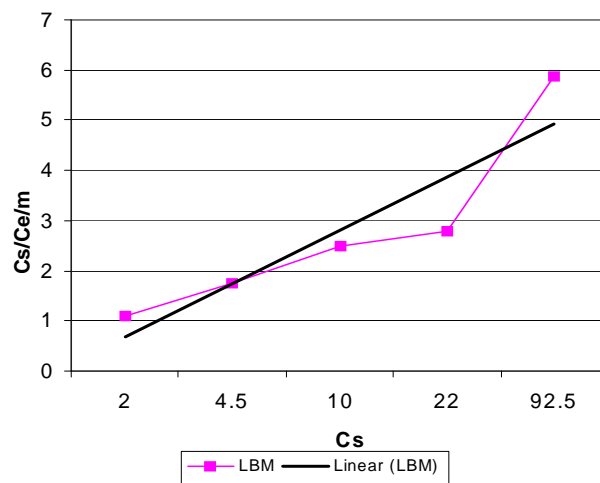


Figure 12: Langmuir Adsorption Isotherm For Batch Study using LBM

Table 1: Freundlich Adsorption constant

Biomass	Adsorption Mode	R^2	$1/N$	K_F
FBM	Batch	0.9561	0.2042	0.6174
LBM	Batch	0.9802	0.2354	0.9630

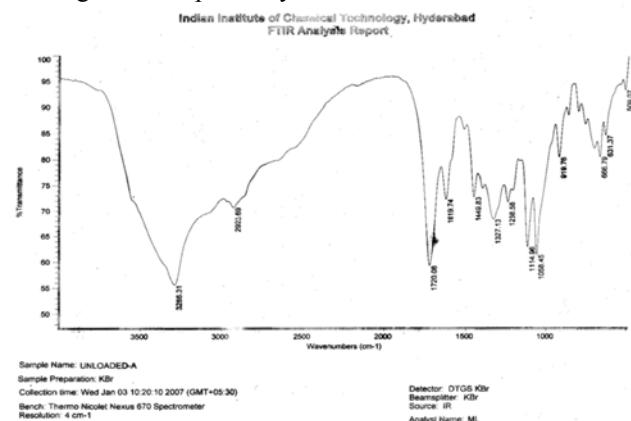
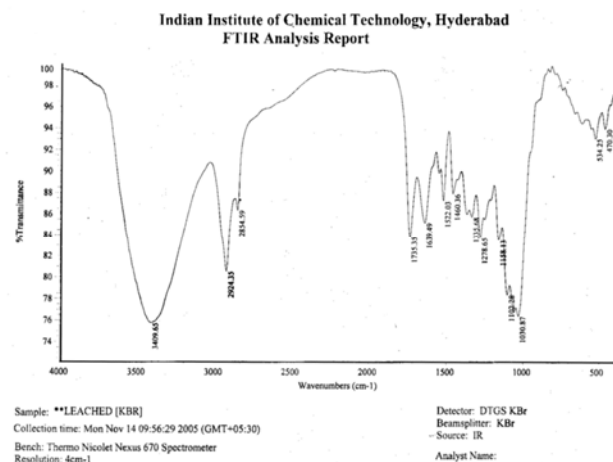
Table 2: Langmuir Adsorption constant

Biomass	Adsorption Mode	R^2	A_M	K_L
FBM	Batch	0.7728	0.606	-0.9712
LBM	Batch	0.83	0.9451	-0.3477

Identification of Ni (II) Binding Functional Group

On FT-IR study of fresh (FBM) and leached (LBM) biomass of *Calotropis procera* impregnated with nickel ions showed the presence of a broad peak in the region above 3000 cm^{-1} which reveals the presence of C=C which may be either due to alkene or aromatic groups. The presence of aromatic group was confirmed by the appearance of peaks in the region 1639.99 cm^{-1} and 1522.03 cm^{-1} . The region between $1660\text{--}1500\text{ cm}^{-1}$ indicates the presence of stretching in NO_2 group. Appearance of a peak at 3409 cm^{-1} showed the presence of -OH groups, as the bands around $2800\text{ to }3600\text{ cm}^{-1}$ are assigned to OH groups. Appearance of two weak bands at 859 and 766 cm^{-1} indicated C-H stretching in phenyl group, as the absorption band in the region between $870\text{--}675$ is assigned to phenyl group substitution. The presence of phenolic group in the cell wall of the biomass explains nickel adsorption by cation exchange property which is confirmed by an increase in pH of the solution after equilibrium contact time. The absorbance between $1640\text{--}1760\text{ cm}^{-1}$ was due to the C-O stretching in carboxylic acid, present in biomass. Biomass contains aromatic group. The peak observed in the region between $1660\text{--}1500\text{ cm}^{-1}$ confirms the stretching of nitro group. The peak between $1470\text{--}1350\text{ cm}^{-1}$ indicates a bending of C-H in alkane. The biomass contains various acidic groups, which were confirmed by the peak obtained in the region between $1260\text{--}1000\text{ cm}^{-1}$ (22-23).

Based on FT-IR study it can be concluded that the metal binding in biomass of *Calotropis procera* takes place by the substitution of amine, nitro and carboxylic groups by the Ni(II). The FT-IR of fresh biomass and chemically leached biomass are presented in Figure 13 and Figure 14 respectively.

**Figure 13:** FT-IR Spectra of FBM of *Calotropis procera***Figure 14:** FT-IR Spectra of LBM of *Calotropis procera*

Application of Biomass for Removal of Nickel from Industrial Effluents

The studies conducted using synthetic metal ion solution (multi-element standard) revealed the practicability of the leached biomass as a potential sorbent for removal of Ni(II) from industrial wastes and effluents. The metal ions and the range of concentrations chosen were representative of typical industrial waste and effluents. In a set of experiments with the leached biomass demonstrated that 250 mg l^{-1} of nickel present in the industrial waste could be removed to 70 % at pH 3. The removal of toxic metal at pH 2.5 reduced the percentage removal of nickel to 56% as shown in Table 3.

Table 3: Adsorption experiment on simulated water with Ni(II)contamination

Sample	pH	Percentage removal of nickel
Lab	3.0	85
Wastewater	2.5	56
Wastewater(adjusted pH)	3.0	70

Conclusion

In this study the ability of the biomass of *Calotropis procera* to remove Ni(II) in synthetic solution has been clearly demonstrated. The *Calotropis biomass* was successful in removing Ni(II) with 85% sorption efficiency from aqueous solution containing 250 mg/L Ni(II). Biosorption was rapid and equilibrium was achieved within 30 minutes. Chemically treated biomass (LBM) showed better Ni(II) removal capabilities compared to fresh biomass (FBM). It was observed that adsorption was pH dependent and maximum adsorption occurred at pH 3. Based on Lagergren equation the kinetic of Ni(II) biosorption can be taken as the first order kinetic

reaction. Column type of biosorption was more efficient as compared to batch mode adsorption study because of more close packing of adsorbent sites.

It was found that the maximum Ni(II) uptake capacity was 15.75 mg/g for batch adsorption and 20.75 mg/g in column adsorption mode from the 250 mg/L of Ni(II) solution. Batch elution tests revealed that close to complete elution of Ni(II) could be achieved from the biomass using 0.1N HNO₃ solution. The results are very encouraging for the industrial application of the technique.

Reference

- Gangaiya, P.: Land based pollution sources in Kiribiti: A case study. SPREP series # 80. *South Pacific Regional Environmental Program, Apia Western Samoa* **1994**.
- Davey, E. W., Morgan, M. J.; Erickson S.J. A biological measurement of copper complexation capacity in seawater. *Limnol Oceanogr.* **1973**, *18*, 993-997.
- Nies, D. H.: Resistance to cadmium, cobalt, zinc and nickel in microbes. *Plasmid* **27**, 17-28. Parker P. *Encyclopaedia of environmental science* (2nd edn). 1980; *McGraw Hill, New York*. **1992**.
- Chen, C. Y.; Lin, T. H.: Nickel toxicity to human term placenta: in vitro study on lipid peroxidation, *J. Toxicol. Environ. Health Part A.* **1998**, *54*, 37-47[CrossRef].
- Parker, P.: *Encyclopaedia of environmental science* (2nd edn). *McGraw Hill, New York*. **1980**.
- Revathi, M.: Removal of nickel ions from Industrial Plating Effluents Using Activated Alumina as Adsorbent. *J. of Environmental & Engg.* **2005**, *47*, 1.
- Volesky, B.: Biosorption and biosorbents. In: *Biosorption of heavy metals*. Boston, USA, *CRC press*, **1990**, 3-5.
- Kapoor, A.; Viraraghavan, T.: Fungal biosorption- an alternative treatment option for heavy metal bearing wastewater: a review. *Bioresource Technology*, **1995**, *53*(3), 195-206.
- Viraraghavan, T. M.; Drohamraju, M.: Removal of copper, nickel and Zinc from wastewater by adsorption using peat. *Env Sci Health.* **1993**, *28A*, 1261-1276.
- Dimitrova, S. V.: Metal sorption on blast-furnace slag. *Water Research*, **1996**, *30*, 228-232.
- Maranon, E.; Sastre, H.: Heavy Metal Removal in Packed Beds Using Apple Wastes. *Biores. Technol.* **1991**, *38*(1), 39-43.
- Marshall, W. E.; Champagne, E. T.; Evans, W. J.: The use of rice milling by products to remove metal ions from solution. *J. Env Sci Health*, **1995**, *9A*, 1977-1992.
- Periasamy, K.; Namasivayam, C.: Removal of nickel(II) from aqueous solution and nickel electroplating industry wastewater using an agricultural waste: *Peanut hulls Waste Manage*, **1995**, *15*, 63-68.
- Larson, V. J.; Schiernp, H. P.: Phosphorous in soil advances in agronomy. *J. Env Qual.* **1981**, *10*, 188-193.
- Meena, A. K.: et al., Adsorption of Ni(II) and Zn(II) from aqueous solution by chemically treated activated carbon. *National conference on carbon (Indo- carbon) Kanpoor*. **2003**, pp131-141.
- Sharma, Y. C.; Prasad, G.; Rupainwar, D.C.: Removal of Ni(II) from aqueous solutions by sorption. *Interl J. of Env. Stud.* **1992**, *40*, 535.
- Shumate, E. S.; Strandberg, W. G.: Accumulation of metals by microbial cells. *Comprehensive Biotechnology.* **1985**, *13*, 235-247.
- Andres, M. Y. J. H.; Hubert, C. J.: Bacterial biosorption and retention of thorium and uranyl cations by mycobacterium smegmatis. *J. of Radio analyses Nuclear Letter*, **1992**, *166*, 431-440.
- Fourest, E.; Roux, C. J.: Heavy metal biosorption by fungal mycelial by-products: mechanisms and influence of pH. *Applied Microbiology and Biotechnology*, **1992**, *37*(3), 399-403.
- Hussein, H.; Krull, R.; Abouel-Ela, S. I.; Hempel D C.: Interaction of the different heavy metal ions with immobilized bacterial culture degrading xenobiotic wastewater compounds. In: *Conference Proceedings: International Water Association World Water Conference, ss(2^o, 15th - 19th October, 2001, Berlin, Germany)*, **2001**.
- Hussein, H.; Farag, S.; Moawad, H.; Isolation and characterisation of *Pseudomonas*. Resistant to heavy metals contaminants. *Arab Journal of Biotechnology*, **2003**, *7*, 3-22.
- Ashkenazy, R.; Gottlieb, L.; Yannai S.: Characterization of acetone washed yeast biomass functional groups involved in lead biosorption. *Biotechnol, Bioeng.* **1997**, *55*(1), 1-10.
- Padmarathy, V.; Vasudevan, P.; Dhingra, S. C.: Thermal end spectroscopic studies on sorption of Ni(II) ion on protonated baker's yeast. *Chemosphere.* **2003**, *52*(10), 1807-1817.