# Sorption of Pp. (II), Ni (II) and Fe (III) from Aqueous Solution Using Encapsulated Root of (Farin Sansamii) *Lonchocarpus laxiflorus* Plant: Adsorption and Characterisation Studies

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## ABSTRACT

*The efficiency of Encapsulated Root of (Farin Sansamii) Lonchocarpus laxiflorus Plant as alternative low-cost sorbents for the removal of Pb(II), Ni(II) and Fe(III) ions from aqueous solutions was investigated. Batch adsorption studies were carried out to evaluate the effects of solution pH and initial metal concentration on adsorption capacity. The optimum sorption condition was found at pH 4, 3 and 6 respectively with 1 g biomass dosage of iron and 0.5 g of lead and nickel at 2 h equilibrium time. The adsorption data were fitted to the Freundlich and Langmuir isotherm models. The adsorption capacity and affinity of the root was evaluated. The Freundlich constant (n) and separation factor $(R_L)$ values suggest that the metal ions were favourably adsorbed onto the sorbent. The maximum adsorption capacities (Q) estimated from the*

*Langmuir isotherm model for Pb(II), Ni(II) and Fe(III) were 101, 151 and 52 mg/g for root. The characterisation studies were performed using Scanning Electron Microscope (SEM), X-ray Diffraction Spectrometer (XRD) and Fourier Transform Infrared Spectrometer (FTIR). The encapsulation process produced surfaces that act as sites for the adsorption and subsequent removal of ions. The amorphous nature of the adsorbent suggests that metal ions can easily penetrate the surface which is desirable for an effective removal and the presence of hydroxyl, amide and carboxylate groups as the main functional groups that may be involved in the complexation of metal ions for sorption processes.The metal ions bound to the active sites of the sorbent through electrostatic attraction.*

**Keywords:** Adsorption; Characterisation; Metal Ions; *Lonchocarpus laxiflorus* root; immobilization;

INTRODUCTION

Excessive levels of toxic metals in the environment have been a worldwide issue for many years (Pellera *et al*., 2011). Heavy metals are introduced into water by several industries such as mining, electroplating, petroleum refining and etc. They may pose toxicity to human especially at high concentration (Ibrahim *et al*., 2010). However, due to their high industrial value their application in industries is irreplaceable. Therefore, it is very important to remove heavy metals from the environment.

Various techniques have been applied for the removal of heavy metals from water. This includes membrane filtration, ion exchange and chemical precipitation, Flocculation and adsorption (Jimoh et al., 2011). These techniques are costly. Adsorption has been proposed as a cost-effective method for water decontamination. Activated carbon is widely used as an adsorbent for water treatment. It is effective to sequester metal ions from water aqueous solutions. However, activated carbon is expensive and sometimes ineffective, especially when metals are present in solution at very low concentrations (within the range of 1-100mg/cm$^3$ ) (Jimoh *et al.,* 2012).

In recent years, a number of alternative adsorbents have been studied for water clean-up. They are inexpensive, efficient and practical to be utilized. Agricultural and industrial wastes, as well as natural minerals are widely used as alternative biosorbents for many years. Examples of materials reported as adsorbents for heavy metals are; tea waste (Mahvi et al., 2005), palm pressed fibers and coconut husk (Tan, *et al.,* 1993), water fern *Azolla filiculoidis* (Zhao and Duncan, 1997), peat moss, duck weed *Wolffia globosa* (Upatham, *et al.,* 2002), *Rhizopus migricans,* cork and yohimbe bark wastes (Singanan, *et al.,* 2008) and leaves of indigenous biomaterials, *Tridax procumbens* (Singanan, *et al.,* 2006), Neem leaves(Vijay *et al.,* 2013; Innocent *et al.,*2009), hazelnut hull (Ali *et al.,*2012), Acid modified and unmodified gmelina Arborea leaves (Jimoh *et al.,* 2011). Apart from the plant based

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material, wood wastes such as sawdust (Kumar and Dara,1982), agricultural byproducts such as maize cab and husk, sun flower stalk, sago waste (Igwe and Abia,2003 and so on.

Researchers have recognized that immobilizing biomass in a ganular or polymeric matrix may improve biomass performance and facilitate separation of biomass from the solution (Chandra *et al*., 2004) The American Bureau of Mines has investigated the use of biomass immobilized in porous poly-sulfonate beads (BIOFIX) for extracting toxic and heavy metals from dilute waste streams (Chandra et al., 2004). Gardea-Torresdey *et al*., 1998a, have removed copper ions from aqueous solutions by silica immobilized Medicago sativa (alfalfa). Immobilized biomass appears to have a greater potential than raw biomass for better capabilities of regeneration, reuse and recovery without destruction of biomass beads (Shan *et al* ., 2002).

This plant is a species of legume in the fabacae family. *Lonchocarpus laxiflorus* tree (Farin Sansamii) is distributed across Africa, Nigeria, east Senegal to Sudan, Ethiopia and Kenya. It is also found in savanna woodland, dry forested areas near water sources. (FromWikipedia, the free encyclopedia). There are many medicinal uses of the leaves and pounded bark and roots: to cure jaundice and liver disorders, to dress wounds, for stomach aches. The objective of this paper is to present the adsorptive potential of *Lonchocarpus laxiflorus* root as alternative low-cost sorbents for removal of Fe (III), Cd (II) and Pb (II) ions in aqueous solution .The adsorption studies were carried out as a function of solution pH and initial metal concentration. The equilibrium data were described by the Freundlich and Langmuir isotherm models. SEM, XRD and FTIR analyses were performed to elucidate the adsorption mechanism(s).

## Material and Methods

### Plant Collection and Treatment

The roots of *Lanchocarpus laxiflorus* plant were collected from a tree behind Modibbo Adama Federal University of Technology Yola, Nigeria. The root was washed thoroughly under running water to remove dust and any adhering particle and

then rise with distilled water. The sample was air dry for 2 weeks and the dry roots was grinded in analytical mill and sieve to obtain sorbent of known particle size range. The biomass powder was kept in an air tight bottle for further study (Igwe and Abia, 2006).

### Characterization of plant Material

### Fourier transforms infrared analysis

The functional groups of the sorbent, as well as binding mechanism(s) were confirmed using Shimadzu FTIR 8400S, SOP) Fourier Transform Infrared Spectrometer and the spectrum was obtained at the range of 4000-400cm$^{-3}$

### X-ray diffraction analysis

The x-ray diffraction pattern of *Lanchocarpus laxiflorus* root was observed using XRD-PANalytical Empyrean instrument with Cu Kα radiation source (λ=0.154nm). The applied voltage and current was at 40kV and 30mA respectively. APW 11840 diffractometer and PW 1729 X-ray generator (Philips, Holland) were used for this study producing CuK$_o$ radiation

### Scanning eletron microsopy analysis (SEM)

Scanning electron microscopy for raw and encapsulated roots of *Lanchocarpus Laxiflorus* was subjected to SEM study, the sample were gold coated and a magnification of 10- 100 times was used. A cam Scan series-2 (Cambridge Scanning Company, UK ) was used for SEM analysis

### Metal stock solutions

Pb(II), Ni(II) and Fe(III)) of 1000 mg/L were prepared by dissolving an appropriate amount of $Pb(NO_3)_2$, $Ni(SO_4).6H_2O$ and $(FeNO_3)_3.9H_2O$ salts in 250cm$^3$ of distilled water and make up to 1000cm$^3$L in a volumetric flask. The above stock solution was used to prepare working solution of various concentrations.

### Preparation of Sodium Alginate and Calcium Chloride Stock Solution

Sodium alginate was prepared by weighing 4.00 g and making it up to 100 cm$^3$ mark with distilled water in a volumetric flask and left overnight for complete dissolution. 0.12 M of calcium chloride was prepared by weighing 26.28g in to 1000cm$^3$ volumetric flask and making up to mark with distilled water according to

a standard procedure described by (Osemeahon *et al.*, 2012).

## Immobilization of the roots of Lonchocarpus laxiflorus plant

Sodium alginate was used for immobilization of the roots of *Lonchocarpus Laxiflorus* plant. 50 cm$^3$ of sample solution prepared by dissolving 4g of each test sample in 100 cm$^3$ of distilled water and mix with 50 cm$^3$ of 4% stock solution of sodium alginate and stir vigorously in 250 cm$^3$ beaker, to obtain a homogenous mixture. After mixing, the solution the solution was drawn through hyperdemic needles and was added drop wise to a stirred solution of 1M CaCl$_2$. A retention time of 1 h was allowed for the reaction to obtain complete precipitation of the immobilized roots powder of *lonchocarpus laxiflorus* plant. The beads thus formed i.e sodium alginates were kept in fresh CaCl$_2$ solution. Before sorption studies, the beads were removed and allowed to dry at room temperature. The dried solid mass was stored in a polythene bag for further use. (Mishra, 2013).

## Batch Adsorption Studies

The experiments were carried out in the batch mode for the measurement of adsorption capacities. From 100 ppm of lead, nickel and iron metal ions solution, 50 ml was taken into a 250 ml conical flask and 0.5 g of the LLR was added corked with a rubber bung and shaken with a flask shaker for 2 h at room temperature (30°C) at 180 rpm. The optimum solution pH was determined in the pH range of 3.0 - 7.0. The solution pH was adjusted using 0.5 mol/L

HCl or 0.5 mol/L NaOH.. The effect of initial metal concentration was studied in the range of 10 - 80 mg/L.The separation of the adsorbent and solutions was carried out by filtration with whatman filter paper No 42. The residual metal ions concentrations were determined using atomic absorption spectrophotometer (AAS). Pyeunicam Model SP. The percentage adsorption was calculated using the following equation:

$$\%\text{Adsorption} = [(C_i-C_f/C_i)] \times 100$$

[1]

## Results and Discussion

### Adsorption Studies

### Effect of Solution pH

The pH of the solution significantly affects the amount of metal ion adsorbed onto sorbents as it influences the properties of the sorbents, as well as the speciation of metal ions in aqueous solution.The effect of solution pH on metal ion adsorption is shown in Figure 1. From Figure 1, It can be seen that Ni and Pb still has the highest selectivity with sorption capacity percent of 99.89% in each case. For Fe the sorption capacity was low at about 53% at pH maximum value of 6, while the percent sorption capacity decreases with increase in pH. Generally it was observed that sorption capacity percent of Ni and Pb solutions decreases as pH values from 3- 4 and reach a minimum, then increases from pH 4- pH 7. This indicated that the initial pH values of the solution affect the adsorption between metal ion solution and the sorbent. The percent removal for Fe increases with

increased pH values up to maximum pH values of 7, At higher pH values (5-7) the metals biosorption increased due to the ionization of functional groups on the cell surface that serve as the binding sites related to isoelectric point for protein of the cell wall.This may be due to the repulsive effect between biomass of LLR and metal ions in solution got stronger (Guo-Xiu Xing *et al.,*

2006). At low pH values, more $H_3O^+$ ions will be available to compete with Pb(II), Ni(II) and Fe(III) ions for the adsorption sites of the biosorbents. In addition, at low pH most of the functional groups are protonated .This will reduce the number of binding sites available for the adsorption of metal ions
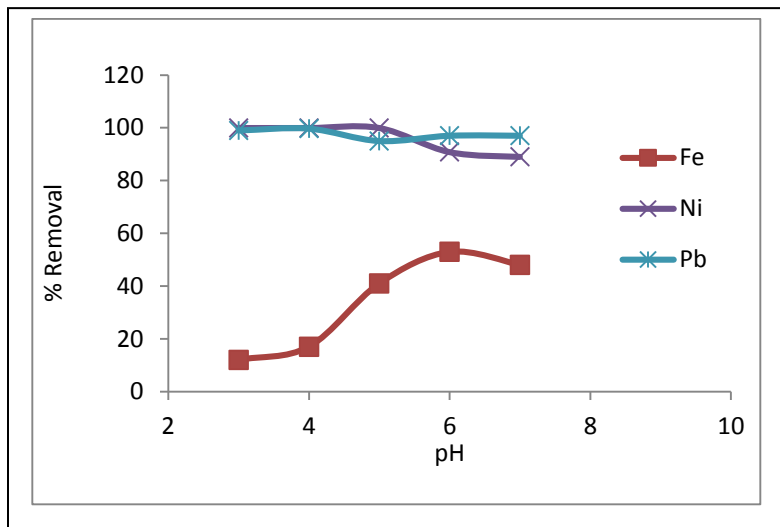


Figure 1: Effect of pH on Sorption of Metal Ions on LLR

## Effect of Initial Metal Concentration

In Figure 2, the percent sorption by LLR increase when initial concentration increases the percent sorption or uptake of Pb, Ni and Fe with percent removal up to 99%. The uptake rate of the metal ion will

increase with increase in the initial concentration (Sun *et al*., 2008). At lower initial solute concentrations, the ratio of the initial moles of solute to the available surface area is low; the fractional sorption thus becomes independent of the initial concentration. In general, the rapid increase

in the uptake of all the metal ions can be attributed to the interaction between the metal ions and the active sites of the adsorbent. This is because the higher the concentration of metal ions, the higher the amount of Pb, Ni and Fe present in the solution, thus the more adsorption of the metal ions occur on the adsorption site of the absorbent. These findings indicate that the sorbents is effective in dilute metal solutions and also the ratio of sportive surface of the biomass to metal availability is high and can remove metal concentration up to 10mg/L. This can remove or reduce the problem associated with most sorbent with low efficiency. Similar results were reported on immobilized biomass of Rhizopus arrhizus for chromium (vi) and Nickel biosorption (Prakasham *et al*., 1999 ; Kumar *et al*., 2012).
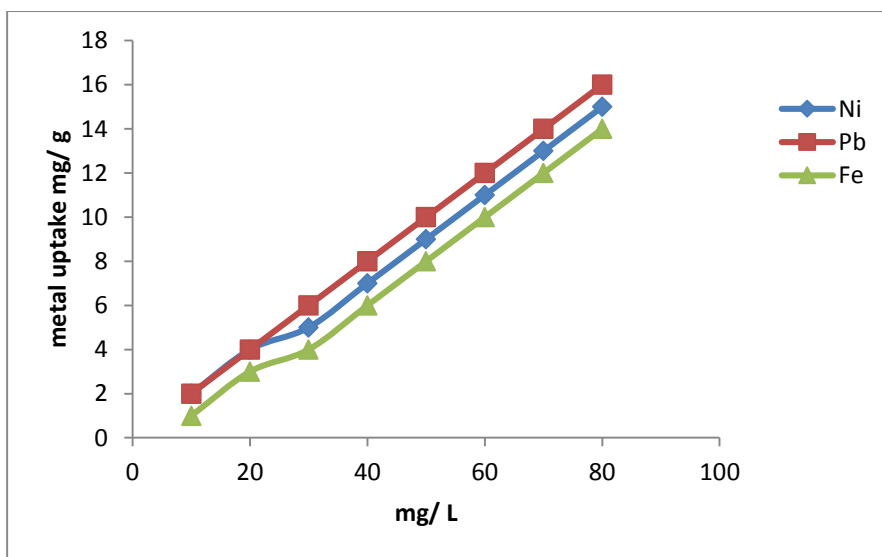


Figure 2: Heavy Metal Uptake of Nickel, Lead and iron by LLR sorbent at Different Metal Ion Concentrations

## Isotherm Models

Adsorption isotherm models have been used to describe the distribution of metal ions between the solid phase (adsorbent) and liquid phase (solution) when equilibrium was reached. The Freundlich and Langmuir isotherm models have been widely used to describe the interaction between metal ions in solution and adsorbents. Freundlich isotherm model is an empirical equation based on adsorption on a multilayer heterogeneous surface. The linear form of

the Freundlich equation is expressed as Equation (2) Freundlich, H.M.F. (1906)

$$Log q_e = log\ K_f + \frac{1}{n} \log C_e$$

[2]

Where $C_e$ is the equilibrium concentration of metal ion (mg/L), $q_e$ the amount of metal ion adsorbed per unit weight of adsorbed at equilibrium (mg/g), n is the Freundlich constant and $K_F$ is the adsorption capacity (mg/g). $K_F$ and n can be determined from a linear plot of log $q_e$ against log $C_e$. Langmuir isotherm model deals with adsorption at monolayer surface with a finite number of identical sites. The linear form of the Langmuir equation is rendered as Equation (3) Langmuir, I. (1916)

$$q_e\ =\ Q^o\ b\ C_{e\ /\ 1+}\ bc_e$$

[3]

Rearranging we have $\quad 1/qe = 1/ce(1/Q^o b)$

$+1/Q^o$

[4]

where $q_e$(mg/g), is the amount adsorbed at equilibrium, $C_e$ (mg/l), is the equilibrium concentration and $Q^o$ and b (L/mg) are the Langmuir constants related to the affinity of binding sites i.e. the affinity of sorbent for the sorbed species and $Q^o$ (mg/g), which represents the monolayer sorption capacity ( Ali *et al*., 2012). Generally for good sorbent, high valves of $Q^o$ and low valves of b are

required, equilibrium concentration $C_e$ and equilibrium capacity $q_e$ will be calculated for each initial concentration. $1/C_e$ will be plotted against $1/q_e$ and a straight line will fit in the data. $Q^o$ and b will be calculated from slope and intercept of lines. ( Hubbe *et al*., 2011).The Q values estimated from the Langmuir isotherm model were in the order of: Ni(II) > Pb(II) > Fe(III) for the root. The stronger affinity of biosorbents towards Ni(II) than Pb(II) and Fe(III) may be due to ion electronegativity and ionic radius. These characteristics increase the attraction force between metal ions and active sites of the biosorbents Wiwid *et al*., 2014 Therefore, the amount of metal ion bound to the biosorbents increased. From Table 1, the n values from application of the Freundlich isotherm model is less than 1 indicates that the metal ions are absorbed by the root parts of *Lonchocarpus laxiflorus* plant.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor L = 1/ 1+bCo where Co (mg/L) is the highest initial concentration of adsorbent and b (L/mg) is Langmuir constant. The parameter RL indicates the nature of shape of the isotherm accordingly

RL > 1 unfavourable adsorption

0<RL< 1 Favourable adsorption

RL = 0 Irreversible adsorption

RL = 1 linear adsorption

The value of RL in the present investigation has been found to be 0.07, 0.3 and 0.1 at 30 º C showing that the adsorption of nickel, lead and iron was favourable at temperature studied.

The maximum adsorption capacity (Q) of roots for Ni (II), Pb(II) and Fe(III) was compared with other low-cost adsorbent. As presented in Table 2, it is apparent that the adsorption capacity of biosorbents studied was comparable with other adsorbents. The difference in adsorption capacity can be related to the difference in physical and chemical characteristic of the adsorbents.

Table 1: Isotherm constants and correlation coefficient for sorption of metal ions   from aqueous solution using LLR biosorbent

| Parameters | Heavy metals | | |
| --- | --- | --- | --- |
| | Fe | Ni | Pb |
| Langmur | | | |
| $q_{max}$ (mg/g) | 52 | 151 | 101 |
| bL/mg | 1.3 | 0.31 | 9 |
| $R^2$ | 0. 60 | 0.92 | 0.93 |
| | | | |
| Freundlich | | | |
| n | 0.74 | 0.89 | 0.59 |
| $R^2$ | 0.8568 | 0.9484 | 0.8254 |
| $K_f$ (mg/g) | 2.05 | 0.72 | 0.93 |

Table 2: Comparison of adsorption capacity (Q) estimate from Langmuir isotherm models for various low-cost adsorbents

| Sorbents | Q (mg/g) Ni(II) | Q (mg/g) Pb(II) | Q(mg/g) Fe(III) | References |
| --- | --- | --- | --- | --- |
| **Immobilized Bombax costatum calyx** | - | 96.36 | 98.65 | Osemeahon *et al.,* 2013 |
| **Tea waste** | 48 | 65 | - | Mahvi *et al.,*2005 |

| Immobilized mycelia of polyporus squamosus | 131 | 153 | 17.94 | Wuyep et al., 2007 |
|---|---|---|---|---|
| Immobilized Microalgae | 59.58 | 121.29 | - | Mahvi et al., 2008 |
| TFW | 15.26 | 65 | | Mahvi et al.,2005 |
| Lonchocarpus laxiflorus root | 151 | 101 | 52 | This Study |

### Characterisation Studies

### SEM Analysis

The surface morphology of the biosorbents raw and encapsulated form was observed using SEM analysis. It can be seen from these figure3 that the external surfaces of the raw powdered samples of LLR are characterized by rough irregular and large cavities with well developed porous structures. These irregular and porous surfaces which are requirements for any potential adsorbent are clearly seen in the SEM image of the powdered sample. The implication of this is that the porous structures could act as active sites for metal ion adsorption. But physical adsorption mechanism plays an important role in this regard (Folasegun et al., 2014). However, the availability of large cavities which is one of the factors for micro porous with large pore diameters means the raw powered microstructures will reduce their physical adsorption for metal ions. But encapsulation will reduce this negative effect by producing small coarse porous aggregates with micro pores of small diameters as observed in the encapsulate samples shown in Figures 3.Therefore, the encapsulation process produced surfaces with particles that were narrow in size, cylindrical and plate-like shapes that act as sites for the adsorption and subsequent removal of ions
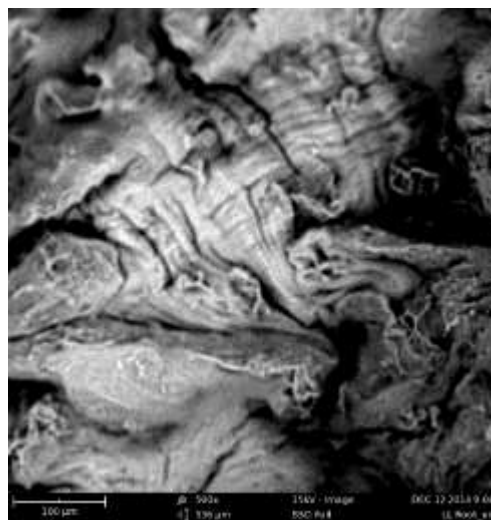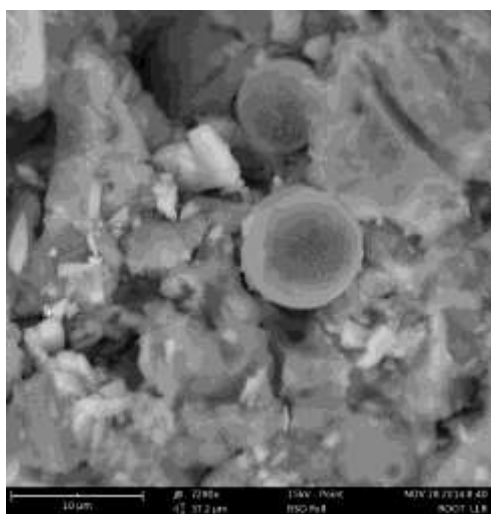
(e)                                   (f)

Figure 3: SEM of LLR Powdered in Raw (e) and Encapsulated form (f)
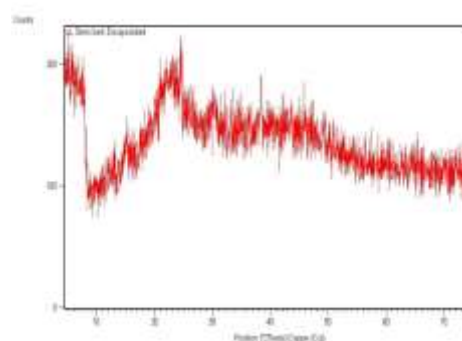
### XRD Analysis

The XRD patterns for LLR in raw and encapsulated form are shown in Figures 4. These give information about the changes in the crystalline and amorphous nature of the adsorbent. Sharp intensity XRD peaks have been observed at typical scanning angles of $2\theta = 20$ which slightly disappear in the XRD images of encapsulated sorbent. The presence of weak intensity peaks in the spectra may be due to amorphous nature of this adsorbent which is broader in the XRD pattern of encapsulated form. The amorphous nature of the adsorbent suggests that metal ions can easily penetrate the surface which is desirable for an effective removal. This could be the reason for high sorption capacity of the sorbent. These results are in good agreement with those reported by Kugbe *et al.,* 2009.
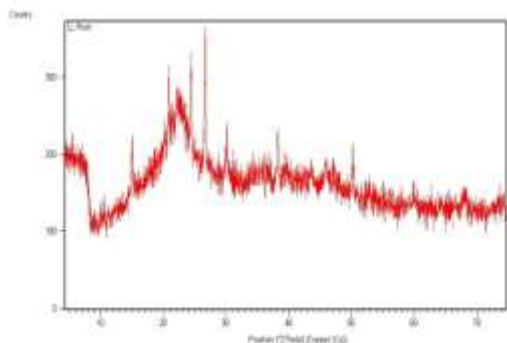
(e)                                   (f)

Figure 4: XRD image of *Lonchocapus laxiflorus* Root in Raw (e) and Encapsulated form (f)

### FTIR Analysis

The presence of functional groups on the surface of sorbent was confirmed using FTIR analysis. In addition, FTIR analysis provides information on possible mechanism(s) involved in metal ion adsorption. Figure 5 shows absorption of peaks at approximately 3400 were due to stretching vibrations of hydroxyl groups which are one of the main components of

cell wall polysaccharides of the plants (Suantak *et al* ,. 2011). The adsorption peaks at 2930 cm$^{-1}$ were likely due to the presence of C-H asymmetric stretching vibration in – COOH group (Kumar *et al* ., 2012 ) of methylene groups on the surface. The absorption bands at 1630 cm$^{-1}$ may be assigned to Amide I and amide II (protein) respectively (Pradhan *et al.*, 2007). While the peaks in the range of 1437cm$^{-1}$- 1328 could be attributed to carboxylate group (Pradhan *et al.*, 2007). The broad peaks at 1245 and 1240 could be due to (C- C) or

(C- H) or (C-O) stretching of the carboxyl groups (Singh *et al*., 2010). The peaks in the region (1051- 1061)) cm$^{-1}$ were due to the presence of C- C Stretching of the polysaccharides (Singh *et al*., 2010). In conclusion, the FTIR spectroscopic analysis of the root of *Lonchocarpus laxiflorus* plant indicated the presence of hydroxyl, amide and carboxylate groups as the main functional groups that may be involved in the complexation of metal ions for sorption processes.
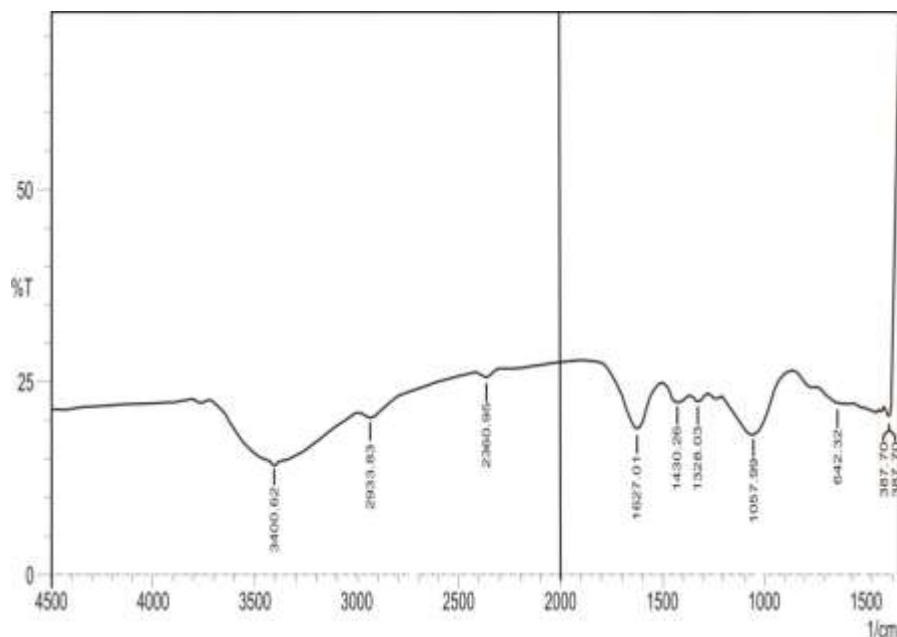


Figure 5: FTIR Spectrum of *Lonchocarpus laxiflorus* Root

## Conclusion and Recommendation

Results from this study revealed the feasibility of the root as alternative low-cost biosorbents for the removal of Pb(II), Ni(II) and Fe(III) ions from aqueous solution. Equilibrium data well with Langmuir isotherm model with monolayer adsorption and the value of the separation factor RL indicated that the adsorption of nickel, lead and iron was favourable at temperature studied .The presence of functional groups in the sorbents favours metal ion binding. Adsorption and characterisation studies however are preliminary evaluation of such utilisation for water treatment. It is also necessary to evaluate the effectiveness of the roots to treat real industrial effluents. *Lonchocarpus laxiflorus* root are abundantly available at low-cost.

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