

Potential Use of Leaf Biomass – *Wrightia tinctoria* for Removal of Pb^{+2}

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Abstract: The present investigation attempted to analyze the biosorption behaviour of novel biosorbent, *Wrightia tinctoria* biomass, for removal of Pb^{+2} from solution against the function of initial metal ion concentration, pH, temperature, sorbent dosage and biomass particle size. The maximum biosorption was found to be 98.51% at pH 4.7 and biosorption capacity (q_e) of Pb^{+2} is 11.04 mg/g. The Langmuir, Tempkin and Freundlich equilibrium adsorption isotherms were studied and observed that Langmuir model is best fit than the other model with correlation co-efficient of 1.0. Kinetic studies indicated that the biosorption process of Pb^{+2} followed well pseudo second order model with $R^2=1.0$. The process is exothermic and, spontaneous. The chemical functional groups –OH, CH_2 stretching vibrations, C=O of alcohol, C=O of amide, P=O stretching vibrations, -CH, were involved in the process. The XRD pattern of the *Wrightia tinctoria* was found to be mostly amorphous in nature. The SEM studies showed Pb^{+2} biosorption on selective grains of the biosorbent. It was concluded that *Wrightia tinctoria* leaf powder can be used as an effective, low cost, and environmentally friendly biosorbent for the removal of Pb^{+2} from aqueous solution.

Keywords: *Wrightia tinctoria*, Freundlich, Langmuir, Tempkin, FTIR, XRD and SEM.

1. Introduction

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment^[1]. Primarily some anthropogenic activities such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals^{[2][3]}. Numerous metals such as manganese (Mn), mercury (Hg), lead (Pb), Cadmium (Cd), arsenic (As), copper (Cu) are known to be significantly toxic due to their non-biodegradability and toxicity^{[4][5]}. Among these heavy metals, lead is considered as one of the most toxic one. The potential source of lead in industrial effluents includes – mining, smelting and refining of lead and other metals have in former times caused large emissions, etc.

The excessive intake of lead may cause plumbosis, learning disabilities resulting in a decreased intelligence (decreased IQ), attention deficit disorder, behaviour issues, nervous system damage, speech and language impairment, decreased muscle growth, Decreased bone growth and kidney damage. World Health Organization (WHO) has recommended that maximum acceptable limit for Pb(II) concentration in drinking water should be NMT 1.5 mg/l^[6]. Consequently, it is essential that the portable water should be given some treatment before domestic supply.

Several methods are used to remove lead from the industrial wastewater. These include reduction followed by chemical precipitation^[7], ion exchange^[8], reduction^[9], electrochemical precipitation^[10], solvent extraction^[11], membrane separation^[12], evaporation^[13] and foam-separation^[14]. Above cited conventional lead elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily

available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. These materials are identified as biosorbents and the binding of metals by biomass is referred to as biosorption.

In the present investigation, the use of *Wrightia tinctoria* leaf powder as an effective and inexpensive material for the removal of lead from aqueous solution was described. The paper is organized as follows: next section deals with the material and methods used for the estimation of lead.

2. Experimentation

2.1 Chemicals

Lead Nitrate $Pb(NO_3)_2$ and Nitric acid (HNO_3) were purchased from Merck. Stock solution of Lead (II) nitrate having concentration of about 1000 mg/L was prepared by using double distilled water. Various concentrations of test solution of Pb(II) ranging from 20-100 mg/L were prepared by subsequent dilution of the stock solution while the initial pH was obtained by adding 0.1N HNO_3 and calculating the pH, using a pH meter. Fresh dilution of the stock solution was done for each sorption study. All reagents used here were of AR grade chemicals.

2.2 Preparation of the adsorbent

The sorbents used were crushed *Wrightia tinctoria* Leaves. The *Wrightia tinctoria* leaves were taken and to be washed

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and air dried for some days until their weight remains constant. After drying, it is grinded in a grinder. The material obtained through grinding is screened through BSS meshes. Finally the adsorbent obtained is stored in air tight glass containers for further use. All the materials were used as such and no pre-treatment was given to the materials. The average particle size is maintained in the range of 63µm to 125µm while screening.

2.3 Batch mode adsorption studies

Batch mode adsorption studies were carried out to investigate the effect of different parameters such as agitation time, adsorbent dosage, adsorbate concentration, pH and temperature. The range of different parameters studied in the present work is given in Table 1. Solution containing adsorbate and adsorbent was taken in 250 ml capacity conical flasks and agitated at 220 RPM in a mechanical shaker for a predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

Table 1

Parameters	Minimum	Maximum
Total Metal Concentration (PPM)	20	100
Dosage (gm.)	0.3	3.0
pH	3.0	6.0
Temperature (°C)	20	50

Tab. 1: Range of different parameters investigated in the present study

2.4 Metal analysis

Final residual metal concentration after adsorption was measured by Atomic Absorption Spectrophotometer (AAS). To estimate the percentage removal of lead i.e., Pb(II) from aqueous solution, the following equation was used.

$$\% \text{ Removal of Metal} = ((C_i - C_e) / C_i) \times 100$$

Where, C_i is Initial Concentration
 C_f is Final Concentration

Metal uptake (q_e) is calculated from the following equation
 $q_e = ((C_i - C_f) \times V) / (1000 \times W)$

Where, V is Volume of the solution
 W is Weight of the biosorbent

2.5 Adsorption Isotherms

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbents. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium. In the present study Langmuir, Tempkin and Freundlich isotherms are used to study the behavior of adsorbent. The models and parameters to be studied are as given in the Table 2.

Table 2

Isotherm	Model	Parameters
Langmuir	$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_a q_{max}} + \frac{1}{q_{max}} C_{eq}$	$1/(K_a q_{max})$ $1/q_{max} R_L$
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	K_f & $(1/n)$
Tempkin	$q_e = a + b \ln C_e$	a & b

Tab. 2: Isotherms and parameters to be studied.

In Langmuir model, q_{eq} is the adsorbate loading (mg/g) at equilibrium, C_{eq} is the equilibrium concentration in the fluid (mg/l), q_{max} is the adsorption capacity (mg/g) and K_a is Langmuir sorption equilibrium constant (l/mg). q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with heavy metal ions. The essential characteristic R_L , dimensionless separation parameter, is indicative of the isotherm shape that predicts whether an adsorption system is favorable or unfavorable and R_L is defined as

$$R_L = \frac{1}{1 + K_a C_0}$$

Where, C_0 is the initial metal ion concentration and

- If $0 < R_L < 1$, Adsorption is favorable.
- $R_L = 0$, Adsorption is irreversible.
- $R_L = 1$, Adsorption is linear.
- $R_L > 1$, Adsorption is unfavorable.

In Freundlich and Tempkin models, q_e is the amount adsorbed (mg/gm), C_e is the equilibrium concentration of the adsorbate (mg/l), K_f is the Freundlich constant related to the adsorption capacity, $(1/n)$ is the Freundlich constant related to the adsorption intensity. If $n > 1$, adsorption is favorable, a and b are constants related to energy and capacity of adsorption.

2.6 Kinetic Models

Kinetics and equilibrium of adsorption are the two major parameters to evaluate adsorption dynamics. It is important that a kinetic model is basically a mass balance which involves different variables describing mass transfer mechanisms within the adsorbent particle. It should not be regarded as a mathematical equation formulating the intra-particle diffusion rate. This is a very important point that is generally overlooked. In fact several kinetic models, currently in use, prove inadequate because of the applied simplifications alter the mass balance within the particle. The different kinetic models are like pseudo first order, pseudo second order e.t.c. The models and parameters to be studied are as given in the Table 3.

Table 3

Kinetics	Model	Parameters
Pseudo first order	$\ln(q_e - q_t) = \ln q_e - K_{1,ad} t$	q_e & K_{ad}
Pseudo second order	$\frac{t}{q_t} = \frac{1}{K_{2,ad} q_e^2} + \frac{t}{q_e}$	$1/q_e$ & $1/(K_{2,ad} q_e^2)$

Tab. 3: Kinetic models and parameters to be studied.

In the above given kinetic models, q_e (mg/g) is the mass of metal adsorbed at equilibrium, q_t (mg/g) is the mass of metal adsorbed at time t , $K_{1,ad}$ (l/min) is the pseudo first order reaction rate constant and $K_{2,ad}$ (g/mg. min) is the pseudo second order reaction rate constant.

2.7 Characterization of Biomass

2.7.1 Fourier Transform Infra-Red Spectroscopy (FTIR) Studies

The powdered biomass *Wrightia tinctoria*, prior and after adsorption was air dried, and de moisturized at 60°C in humidity control oven. The powder was analyzed by Fourier Transform Infra-Red spectrophotometer by Potassium Bromide (KBr) pellet method in the wave number range of 400.00 Cm^{-1} to 4000.00 Cm^{-1} .

2.7.2 Scanning Electron Microscopy (SEM)

The dried biomass powder *Wrightia tinctoria* and the corresponding metal ion loaded powder was coated with ultra-thin film of gold by an ion sputter (JFC-1100), exposed under electron microscope (JEOL, JX-8100) at working height of 15 mm with voltage ranging between 10 kV to 25 kV.

2.7.3 X-Ray Diffraction (XRD)

The X-ray Diffract gram (XRD) of the biomass, *Wrightia tinctoria* powder sample was obtained (XRD-6000 Shimadzu), the intensities were recorded as a function of 2θ at a scan speed of 1.2 $^\circ/\text{min}$ and XRD patterns were recorded from 10° to 70° .

3. Results and Discussions

3.1 Effect of Equilibrium Time

As the time increases the concentration decreases up to 30 mins and from 30 mins onwards as the time increases the concentration remains constant with the value of 29.211 mg/L for 0.5 gm. dosage, 18.667 mg/L for 1.0 gm. dosage and 8.294 mg/L for 1.5 gm. dosage. It is represented in figure 1. This shows that the equilibrium is reached at 30 mins. So, the equilibrium time for the biosorption of Pb^{2+} using *Wrightia tinctoria* is 30 mins at room temperature.

3.2 Effect of Biosorbent Dosage

Figure 2 represents the effect of biosorbent dosage on the lead metal solution. As the dosage of the biosorbent increases the metal uptake also increases but again decreases from 0.5 gm. which gives the Optimum Dosage at room temperature.

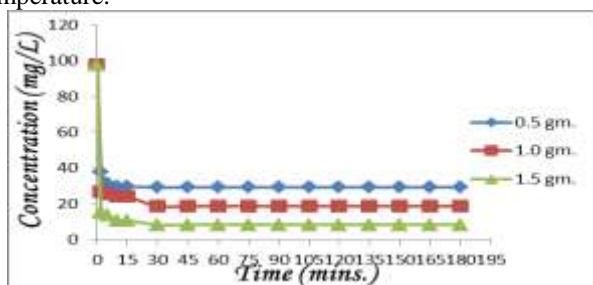


Figure 1: Effect of Equilibrium Time

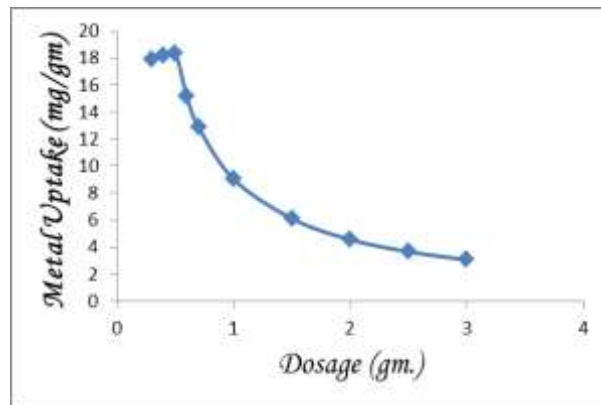


Figure 2: Effect of Biosorbent Dosage

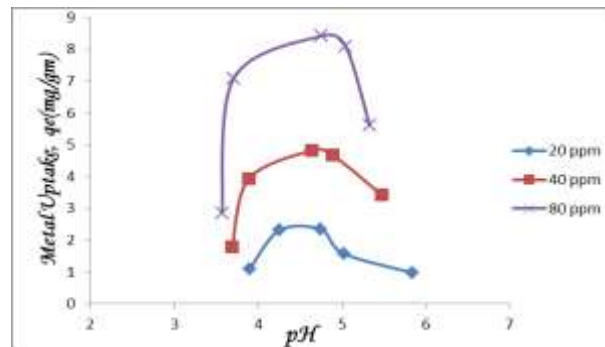


Figure 3: Effect of pH

3.3 Effect of pH of the Solution

Initially as the pH increases the metal uptake increases and then decreases. At a pH 4.0435 of 80 ppm concentration we obtain a maximum metal uptake of 8.4162 mg/gm. So, the optimum pH is taken as 4.7 at room temperature. The effect of pH is as shown in the figure 3.

3.4 Effect of Concentration of the Solution

As represented in figure 4 the percentage removal varies with concentrations for various pH. We can observe that at 60 ppm of 0.5 ml acid, maximum percentage removal of metal of 98.86% is obtained. So, the optimum concentration of the metal removal is 60 ppm at room temperature.

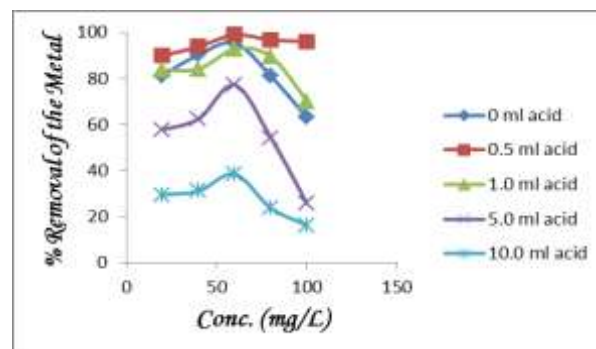


Figure 4: Effect of Concentration

3.5 Adsorption Isotherms

The data fits well for the Langmuir model compared to other. The different models for data are represented in fig.5, fig.6 and fig.7.

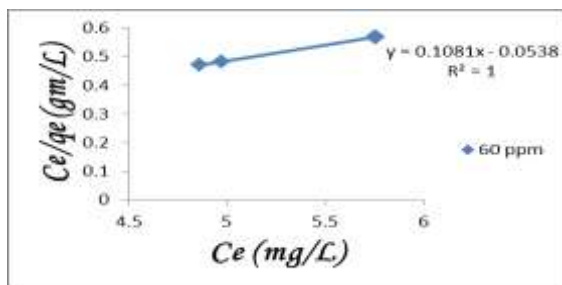


Figure 5: Langmuir Isotherm at 60 ppm

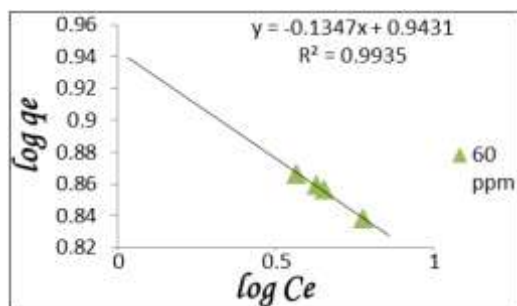


Figure 6: Freundlich Isotherm at 60 ppm

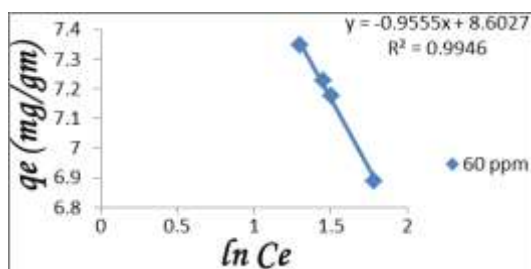


Figure 7: Tempkin Isotherm at 60 ppm

3.6 Kinetic Models

The kinetic studies indicate and the rate data follows pseudo second order kinetics. The models are represented in fig.8 and fig.9.

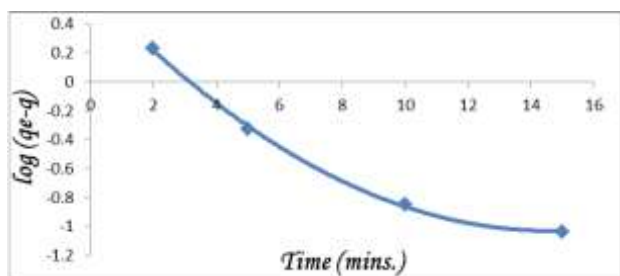


Figure 8: Pseudo First Order Kinetics

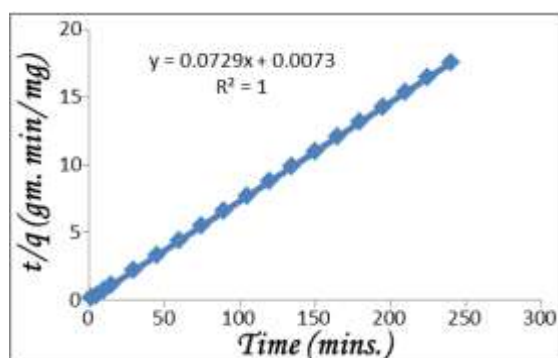


Figure 9: Pseudo Second Order Kinetics

3.6 Characterization of Biomass

3.6.1 FTIR Studies

The FTIR differences of spectra in pure plant biomass adsorbent were compared to the spectra obtained in metal ion loaded (Table 4) plant biomass to determine whether the observed differences are due to interaction of the metals ions with functional groups (Fig.10 a). The broad absorption peak at 3420.21 cm^{-1} indicates the presence of amino groups (Rajesh et al., 2010; Venkata et al., 2010) and it is shifted to 3325.33 cm^{-1} , which might be, due to the strong interaction with Pb^{+2} metal ion. These results indicated the involvement of these functional groups in biosorption process.

The CH_2 stretching vibrations showed characteristic absorption peaks at about 2935.31 cm^{-1} for unloaded biomass and shifted to 2934.58 cm^{-1} . This may be due to the weak interaction with Pb^{+2} metal ion (Fig.10 b). The stretching vibration band (Suleman et al., 2009) 1618.67 cm^{-1} is due to olefinic C=C and carbonyl C=O stretching and shifted to the 1619.30 cm^{-1} . The band at 1376.07 cm^{-1} is due to the $-\text{CH}_2$ bending vibrations and the peak shifted to 1375.94 cm^{-1} for Pb^{+2} loaded biomass. These results indicated the involvement of these functional groups in biosorption process. The absorption peaks around 1060.91 cm^{-1} are indicative of P=O stretching and shifted to 1032.90 cm^{-1} .

The appearance of new peak at 1439.92 cm^{-1} was probably due to the modification of the surface functional groups with the interaction of Pb^{+2} ions. These band positions revealed that the functional groups C=O carboxylic acid of amide, C=O carboxylic acid of alcohol and CH_2 stretching respectively. The analysis of the FTIR spectra showed the presence of functional groups (carboxyl, hydroxyl and amino) able to interact with Pb^{+2} ions.

3.6.2 Scanning Electron Microscopy (SEM)

SEM is a useful technique in the study of both the natural sorbent morphology and its modification derived from sorbate interactions. SEM is an electron microscope which provides images of the sample surface by scanning it with a high energy beam of electrons. The electron interactions with the atoms of the sample produce signals that contain information about topography, morphology, and composition of the sample surface (Valeria et al., 2010).

In this investigation, possible mechanisms involved in the sorption of the toxic elements in the biomasses and differences due to the application of the amendments were investigated using scanning electron microscopy. The SEM images were taken by applying 10 kV voltage with different magnification times for the clarification of surface. The SEM micrographs of *Wrightia tinctoria* plant biomass before and after biosorption were depicted in (Fig.11 a). It is evident from analysis that the surface areas of plant biomass are uneven, heterogeneous.

SEM image of native biomass (Fig.11 a) shows the amorphous and granular surface areas. The change in morphology after biosorption indicates the accumulation of liquid phase concentration of charge moieties onto plant biomass surface areas (Fig.11 b). Further, the amorphous

and granular surfaces of biomass are found to be much compact and denser due to accumulation of Pb^{+2} ions.

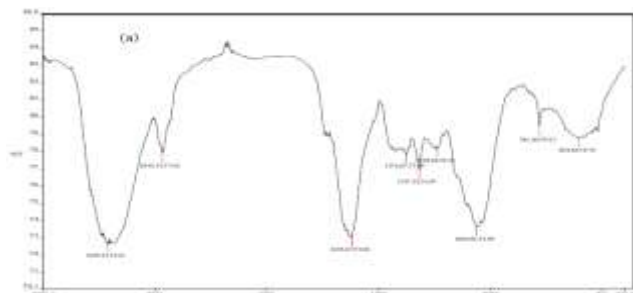


Figure 10 (a): Before Biomass Loaded

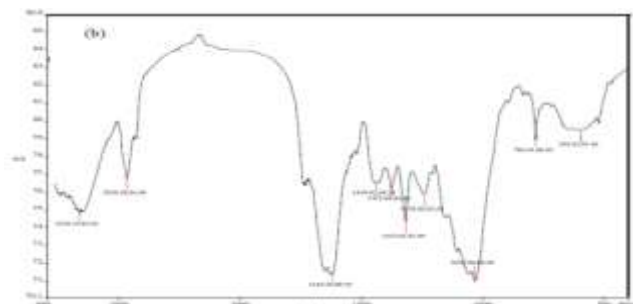


Figure 10 (b): Pb^{+2} loaded Biomass

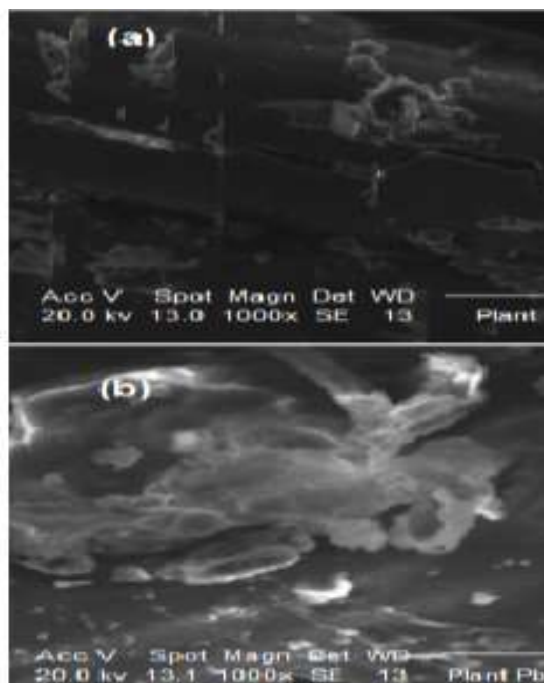


Figure 11: Scanning Electron Microscopy (SEM)
 (a) SEM before Biomass loading
 (b) SEM with Pb^{+2} loaded Biomass

Table 4

S. No	Band Position Cm^{-1}		Description
	Before Biomass Loaded	Loaded with Pb^{+2}	
1	3420.21	3325.33	-OH stretching vibrations
2	2935.31	2934.58	CH_2 stretching vibrations
3	1618.67	1619.30	olefinic C=C and carbonyl C=O stretching
4	-----	1439.92	C=O carboxylic acid or amide
5	1376.07	1375.94	- CH_2 bending vibrations
6	1317.42	1317.01	- CH_2 bending vibrations
7	1238.04	1239.90	- SO_3 Group
8	1060.91	1032.90	P=O stretching vibrations
9	781.20	781.01	N containing bioligands
10	604.82	595.93	N containing bioligands

Tab.4: Band positions of with and without loaded biomass with Pb^{+2}

3.6.3 X-Ray Diffraction (XRD) Studies

The diffracted X-ray intensities were recorded as a function of 2θ by using Copper target, at a scan speed of $1.2^\circ/\text{min}$. XRD patterns were recorded from 10° to 70° for *Wrightia tinctoria* before and after biosorption and were depicted in figure (Fig.12 a and 12 b) They are indicating the poor crystallinity of pure biomass *Wrightia tinctoria*. Further the shifts in 2θ and d-spacing values were observed in Pb^{+2} loaded biomass (Zhu et al., 2009; Adan et al., 2011). These observations revealing that there was a change in crystallinity of biomass *Wrightia tinctoria* after the biosorption.

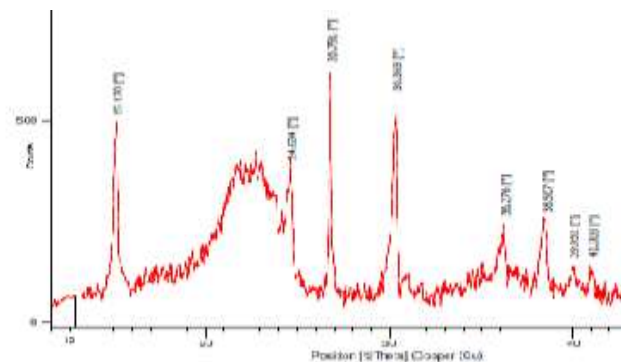


Figure 12(a): XRD before Biomass loading

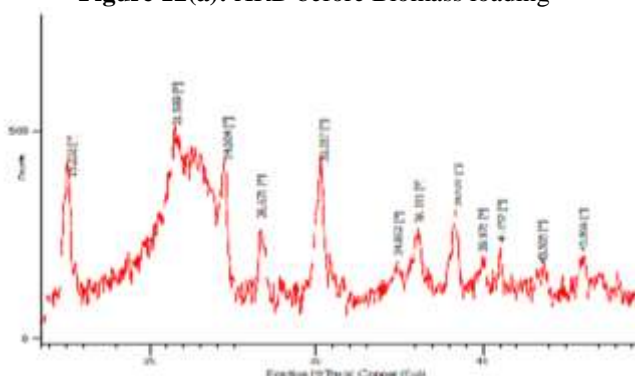


Figure 12(b): XRD with Pb^{+2} loaded Biomass
Figure 12(b)

4. Conclusions

From the above studies, the conclusions were drawn as follows

- 1) The time required to reach equilibrium is 30 mins.
- 2) Optimum dosage that we obtained is 0.5 gm.
- 3) The process is exothermic and spontaneous.
- 4) Optimum concentration that we obtained is 60 ppm.

- 5) The kinetic studies indicate and the rate data follows pseudo second order kinetics.
- 6) Optimum p^H is 4.7 with metal uptake of 11.04 mg/gm. and % of the metal removal is 98.86%.
- 7) Langmuir type of equation represents the equilibrium data well.
- 8) The nature of the biosorbent is poor in crystallinity.
- 9) The chemical functional groups –OH, CH₂ stretching vibrations, C=O of alcohol, C=O of amide, P=O stretching vibrations, –CH, were involved in the process.

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