© 2016 IJSRST | Volume 2 | Issue 6 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology

Aminated *Desmostachya bipinnata* - Potential Biopolymer for the Removal of Lead Metal Ions from Wastewater

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ABSTRACT

The biopolymer from Desmostachya bipinnata (DB) is investigated as a potential bio-adsorbent for the removal of Pb (II). It is a holy herb of the South Asian region with medicinal value. DB was functionalized with two types of aminating agents, which created suitable metal chelating medium encountered in aqueous solution. The biopolymer was characterized with SEM, DRFTIR, elemental analysis, zeta potential, and TG/DTA, which indicate functionalization with amine groups. The effect of pH, initial concentration and contact time of the metal solution were monitored by batch method. The maximum adsorption capacities were found to be 130.40 mg/g and 87.20mg/g, respectively. Langmuir isotherm model fitted well and the rate of adsorption followed the pseudo second order kinetic model. Desorption experiments result in regeneration of about 92 % Pb (II). The regenerated biopolymers were used for six successive cycles without any significant decrease in adsorption and desorption. Thus, the biopolymer derived from DB can be used as a cost effective, efficient and environment friendly green material for the removal of Pb (II) from the waste water.

Keywords : Desmostachya Bipinnata, Heavy Metal, Batch Experiment, Pseudo- Second Order Kinetic Model, Functionalization, Regeneration.

I. INTRODUCTION

Environmental pollution with metal ions represents a potential threat to humans, animals and plants. Since the content of metal ions present in potable water and wastewater often exceed the permissible sanitary standards, it has become a serious issue (1). Although several adverse health effects of heavy metal ions have been known for long, exposure to heavy metals continues, and is even increasing in lesser developed countries. To avoid health hazards, toxic heavy metals should be removed from wastewater before disposal. Metal ions are non-biodegradable and many of them dissolve in aqueous solutions, therefore they become more available for living systems and accumulate in the environment (2 - 4). Lead is one of the non-essential toxic heavy metals (5, 6) found in dyes, pottery, insecticides, tobacco smoke, textiles, automobile exhaust, car batteries, canned fruit juices, hair coloring and smelting of lead. It causes abdominal pain, aching muscles and bones, headaches, high blood pressure, loss of appetite' nervousness and weight loss. High level accumulation of lead in body causes anemia, gout, damage the kidney, liver, reproductive system and central nervous system disorder (7-10).

Most of the wastewater treated on industrial-scales involves physical, chemical and biological treatment techniques (11). These methods are limited by technical and economic barriers (12, 13) when the concentration of metal ions in waste water is low. Awareness of these facts has generated research and development in the field of wastewater management, detoxification; and quality improvement has become imperative in eco-technologies. This has caused a paradigm shift to biosorption, where treatment of waste occurs through the use of biowaste (14) which is available locally, highly efficient, economic and renewable (15-17).

Agricultural biopolymers with high cellulosic content are potential biosorbents which bind a variety of heavy metals to different levels (18). This study is focused on the preparation of low cost raw and functionalized biopolymer from *Desmostachya bipinnata*. It contains cellulose, hemicelluloses and lignin as major constituents, which create active sites for metal adsorption. The experiments on adsorption of Pb (II) from waste water are carried out and effectiveness is evaluated between raw and functionalized biopolymer (19) and the possibility of reuse of biopolymer is also explored.

II. METHODS AND MATERIAL

Chemicals and Instrumentation

All the working solutions of different concentrations were prepared by diluting standard stock solution of lead nitrate with 0.1M nitric acid and 0.1M HEPES (2-[4-(2-Hydroxymethyl)-1-piperazinyl] ethanesulphonic acid) was used as the buffering agent (20). The pH of the working solutions was adjusted by adding dilute nitric acid and sodium hydroxide solutions. Aminating reagents like hydrazine monohydrate and dimethylamine were used. All the reagents and chemicals used in this study were of Fisher scientific analytical grade.

The surface morphologies of raw and functionalized biopolymer were studied by a scanning electron microscope (SEM S-3000 N Scanning Electron Microscope of HITACHI, Japan). Presence of certain functional groups was identified using Diffused Reflectance Fourier Transform Infrared Spectroscopy (DRFTIR Harrick scientific corporation). The degradation and thermal stability was compared using thermo-gravimetric analysis (TGA) and differential thermo gravimetric analysis (DTA) in a nitrogen atmosphere, using a thermal analysis (TG /DTA6200, Japan), with increase in temperature of 10^0/min.

The percentage compositions of elements present in the biopolymers were analyzed using Elementar Vario Macro elemental analysis instrument. The equilibrium concentrations of metal ions were measured with inductively coupled plasma atomic emission spectrophotometer (ICP-AES, SPECTRO, Analytical Instrument, Kleve, German). The pH measurements were carried out with pH meter (Hanna instrument).

1) Preparation of Biopolymer

Powdered raw biopolymer was prepared from the herb, *Desmostachya bipinnata* (DB). About 200 g powdered raw biopolymer was treated with concentrated sulphuric acid, which created a suitable environment for its ring opening (21). Then the biopolymer was washed with deionized water to remove excess acid and any other soluble low molecular weight substance, until neutrality.

The acid treated biopolymers were functionalized with hydrazine monohydrate (FDB-H) and dimethylamine (FDB-Dm).

The procedures for the preparation of functionalized biopolymers were published in earlier papers (19, 22).These biopolymers were used for adsorption experiments.

Batch Experiments

All the batch experiments were carried out using 25 mg of biopolymers with 20 ml Pb (II) solution in 50 ml Erlenmeyer flasks. The flasks were shaken at 150 rpm in a shaker for 24 h to attain equilibrium.

Effects of pH

The pH affects the surface charge and degree of ionization of metal solutions. Batch adsorption tests for Pb (II) were performed by keeping the concentration of metal ions constant (50 mg/L), as the function of pH (pH=1-7). The pH of metal ions was maintained by adding dilute nitric acid and sodium hydroxide solutions in each flask, and was shaken. Solutions were then filtered and their equilibrium concentrations were measured. The adsorbed amount of metal ions was calculated from the decrease in the metal-ions concentration, from which percentage adsorption (23) was calculated.

2) Zeta potential measurement

The pH_{pzc} measurement was carried out at different pH ranging from 1- 12. A volume of 20 ml deionized water was taken in separate flasks, and pH was adjusted with the help of 0.1 M nitric acid and sodium hydroxide, respectively. 25 mg of biopolymers (RDB, FDB-H and FDB-Dm) was added to each flask and shaken to equilibrate for 2 h. Then the mixtures were filtered, and the optimum pH as well as the zeta potential of the solutions was measured.

3) Effect of Initial metal ion concentration

The metal uptake capacities of FDB-H and FDB-Dm for Pb (II), at different concentration (25 - 800 mg/L,) were carried out in separate flasks at optimum pH value. The solutions were filtered and equilibrium concentrations of the metal ions were measured. The sorption capacity of metal ions is the concentration of the metal ions onto the biopolymer, which can be calculated from the mass balance principle as shown in equation (1).

$$q = \frac{C_i - C_e}{W} \times V \qquad (1)$$

where, q = amount of adsorbed metal ions per gram of adsorbent, (mg/g), C_i = initial concentration of metal ions (mg/L) before adsorption, C_e = equilibrium concentration of metal ions (mg/L) after adsorption, W = weight of biopolymer (mg) and V = volume of metal ion solution (L)

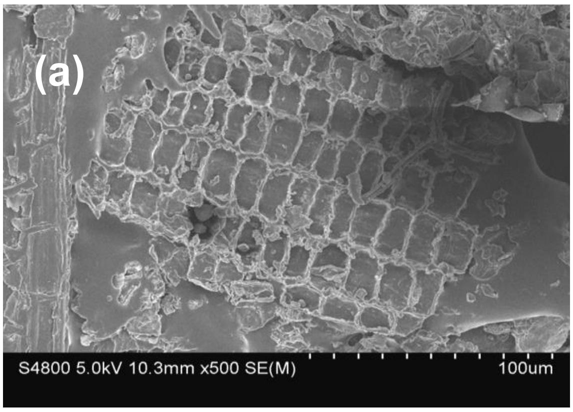
4) Effect of contact time

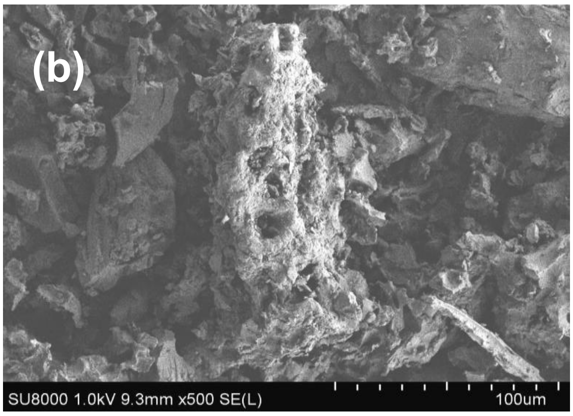
Kinetic studies of sorption are helpful to find the removal rate of metal ions from aqueous solutions. The effects of contact time on to sorption of Pb (II) were studied from 5- 360 min. Metal solutions of 50 mg/L at optimum pH were taken in 14 different flasks. All the flasks were shaken for the desired time interval and their concentrations were measured. The amount of metal adsorbed at time (t) was calculated from the mass balance between initial concentration and concentration at particular time (t) to analyze the rate of sorption metal ions onto the biopolymer.

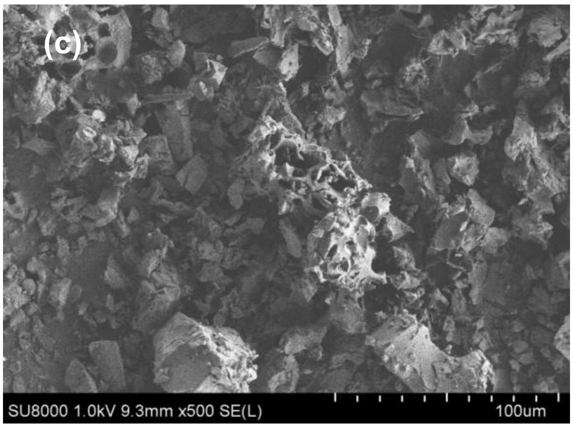
III. RESULTS AND DISCUSSION

Morphological (SEM) Analysis

The SEM image of raw biopolymer (RDB) revealed smooth and even surface as shown in Figure1(a), which changed to rough and uneven porous structure after functionalization as in Figure1(b), and 1(c) for FDB-H and FDB-Dm, respectively. This change is due to the introduction of the amine functional group onto the surface of the biopolymers which enhances the metal ion sorption. After performing batch experiments, the surface morphologies of lead loaded functionalized biopolymers were also studied and compared with the functionalized biopolymers. The rough, uneven and porous surface of the functionalized biopolymers were changed to even and smooth surface with bright images indicating the adsorption of metal ions onto functionalized biopolymers, as in Figure 1(d) and 1(e), for Pb FDB-H and Pb FDB-Dm respectively.







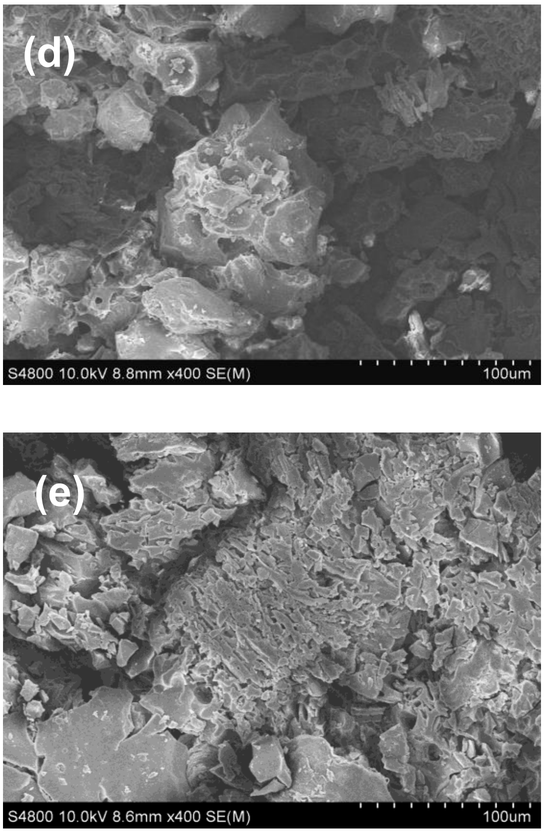


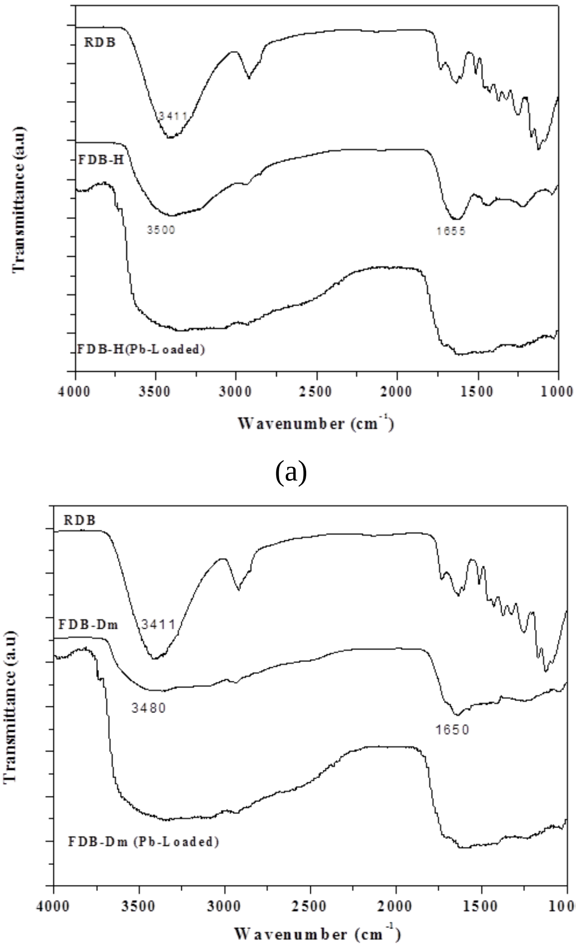
Figure 1 : SEM of *D.bipinnata* (a) RDB(b) FDB-H(c) FDB-Dm(d) Pb FDB-H(e) Pb FDB-Dm

Diffused Reflectance Fourier Transform Infrared Spectroscopy (DRFTIR) Analysis

DRFTIR spectra are useful tools in identifying the presence of various types of functional groups in a molecule (24, 25). The intense sharp adsorption peak around 3411 cm^{-1} in Figure 2(a), (b) for RDB can be assigned to the *O–H* stretching vibration, due to hydrogen bonding of polymeric compounds like alcohols, carboxylic acids and phenols, (as in cellulose, hemicelluloses and lignin), indicating the presence of free hydroxyl groups on the surface of biopolymer. The peak around 2926 cm^{-1} corresponds to *C–H* stretching in CH_2 and CH_3 groups. The weak peak at 931 cm^{-1} corresponds to the glycoside bonds present in the polysaccharide structure (26, 27).

Sharp differences in spectra were noticed after the functionalization of biopolymers, as shown in Figure 2(a) and (b). The intense sharp peak at around 3411 cm^{-1} and 2926 cm^{-1} in RDB has been changed and at around 3500 cm^{-1} and 3480 cm^{-1} , a broad peak is seen in FDB-H and FDB-Dm, respectively, which may be due to the overlapping of the hydroxyl group with amine group. The peak at around 1650 cm^{-1} was observed in both types of functionalized biopolymers which may be due to *N-H* bending vibration of amines. This further indicates that large number of amine groups have been grafted into the surface of biopolymers.

DRFTIR spectra of lead loaded FDB-H and FDB-Dm were also studied and compared with the spectra of FDB-H and FDB-Dm. The peaks were broadened and shifted at the lower wave number, as well as reductions in transmittance were also observed as shown in Figure 2 (a) and (b). The decrease of wave number for the peak due to metal adsorption may be attributed to the attachment of the metal ions on the NH_2 or OH groups, which affected the stretching vibration of these functional groups. It also indicates that the amine functional groups are involved in the adsorption of lead metal ions (24, 28, 31).



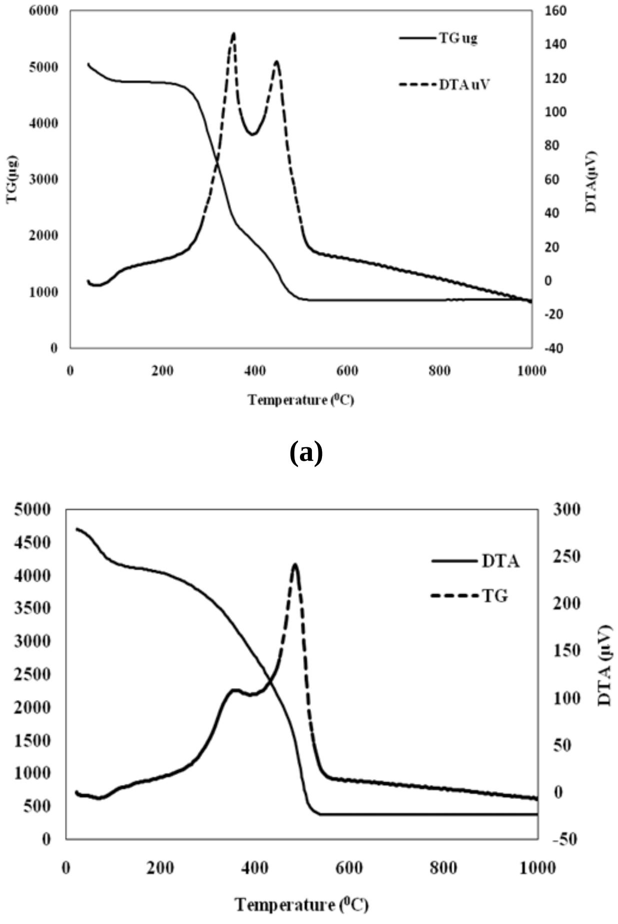
(a)

(b)

Figure 2: DRFTIR spectra of (a) RDB, FDB-H, Pb FDB-H (b) RDB, FDB-Dm, Pb FDB-Dm

Thermal Gravimetric Analysis (TG/ DTA)

Raw and functionalized biopolymers degraded mainly in two stages such as devolatization and solid decomposition. The first stage of decomposition started at around 240^0C and 270^0C and second at 440^0C and 490^0C, for RDB and FDB as shown in Figure 3(a) and (b). Finally the ash left was less than 1mg. The second degradation stage of FDB took place at temperatures higher than in RDB which was due to partial reduction of hemicelluloses and lignin present in the biopolymer during the functionalization process (30).The functionalized biopolymer was thermally more stable than raw biopolymer and did not degrade, which enhances sorption process.



(a)

(b)

Figure 3: TG and DTA curve for (a) RBD (b) FBD

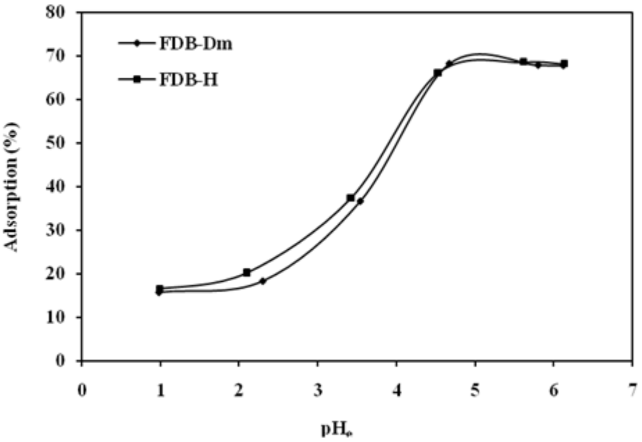


Figure 4: Effect of pH on adsorption of Pb (II) on to FDB

Elemental Analysis

The percentage composition of Nitrogen, Carbon and Sulphur were found to be1.13 %, 41.27 % and 0.56% in the raw *D. bipinnata.* After functionalization, the percentage composition of nitrogen increased to 7.56 (FDB-H) and 5.42 (FDB-Dm) respectively, which supports the introduction of amine functional group onto the *D. bipinnata.*

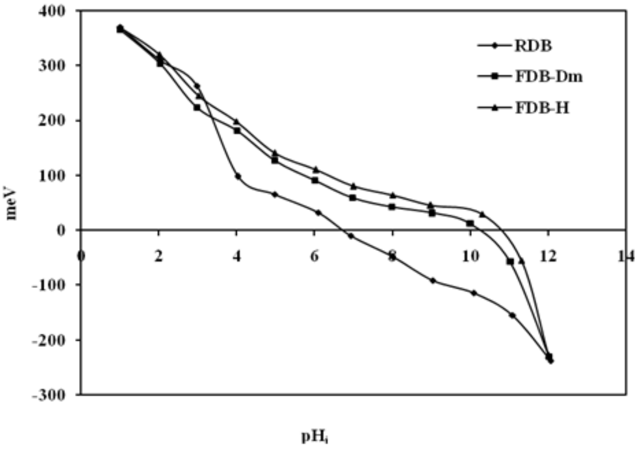


Figure 5: Zeta potential (pH_{pzc}) curve of RDB and FDB

Effect of pH

Variation in pH could change the characteristics as well as the availability of metal ions in solution. At low solution pH, a large quantity of protons (H+) in solution will compete with the metal ions for binding on the functional groups onto the biopolymer surface. Hence, there would be a decrease in sorption of metal ions. But the sorption of metal ions increases with the increase in pH, due to the decrease in competition between protons (H+) and metal species for the active sites on the biopolymer surface. However, a small decrease in sorption was observed after a certain pH owing to the increase in concentration of hydroxyl ions in the medium. The micro precipitation of Pb $(OH)_2$ was observed at pH 6.5 from blank tests due to the decrease in solubility of Pb $(OH)_2$ ions. The maximum sorption of Pb (II) was found at optimum pH value 4, as shown in Figure 4.

Zeta potential analysis

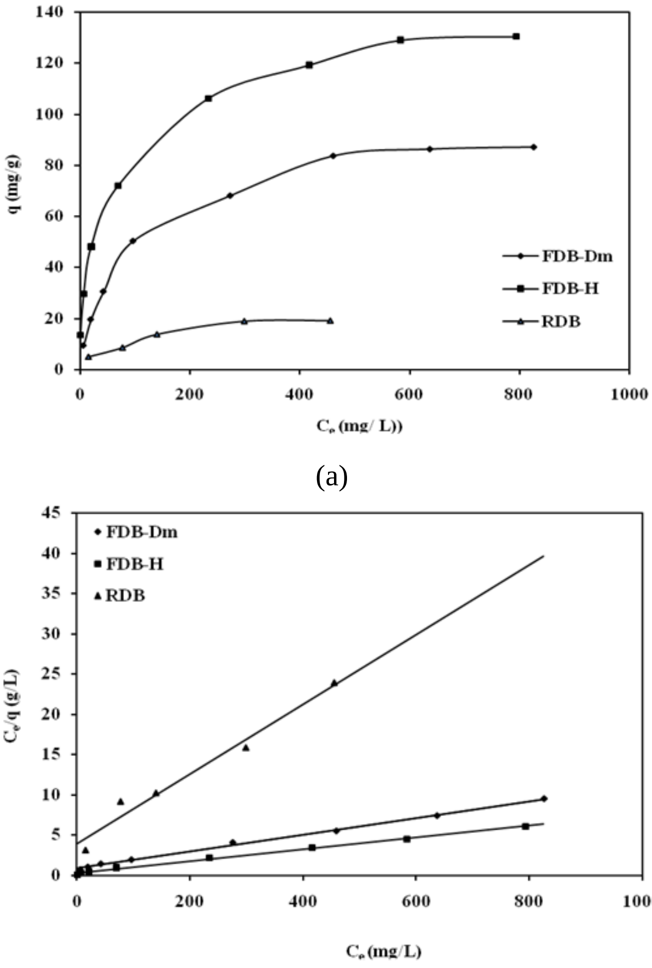
Zeta potential is commonly used to predict and control dispersion stability (31). pH_{pzc} is the pH at which the net charge on the surface of biopolymer becomes zero. The zeta potential of RDB and FDB in the solution at different pH values are shown in figure 5. It indicates that the surface of biopolymer becomes positive below pH 6 and negative above pH 6. The pH_{pzc} values had shifted towards higher pH ranges around 10(FDB-Dm) and 11(FDB-H) after functionalization, which suggest the introduction of amine functional groups onto the surface of biopolymer. The maximum adsorption was found at acidic pH range, which could be due to the complex formation with metal ions by the amine functional group on to the surface of the biopolymer

Effect of initial metal ion concentration

Adsorption capacities of raw and functionalized *D. bipinnata* were evaluated at pH 4, taking different concentration of Pb (II) solution, and the concentrations were measured after equilibrium was attained. The maximum adsorption capacity was found to be only 19 mg/g, indicating that raw biopolymer is less efficient for binding the heavy metals. Therefore, the raw biopolymer was functionalized with two different types of aminating reagents to enhance the adsorption of metal ions (32), and their adsorption capacities were evaluated at different metal ions concentrations as shown in Figure 6 (a) and (b) respectively. The maximum amount of metal ions adsorbed (q_m) are given in Table1.

Initially the adsorption capacity of the biopolymer was found to increase with an increase in the initial concentration of metal ions solution up to 600mg/L. In both cases, when the initial concentration exceeded from 400mg/L, the sorption capacity remained almost constant, since the active sites form a monolayer to block the biopolymer surface and cannot adsorb any more metal ions (33). As the active sites on the biopolymers were almost fully occupied by metal ions, hence a further increase in concentration of metal ions resulted in no more adsorption.

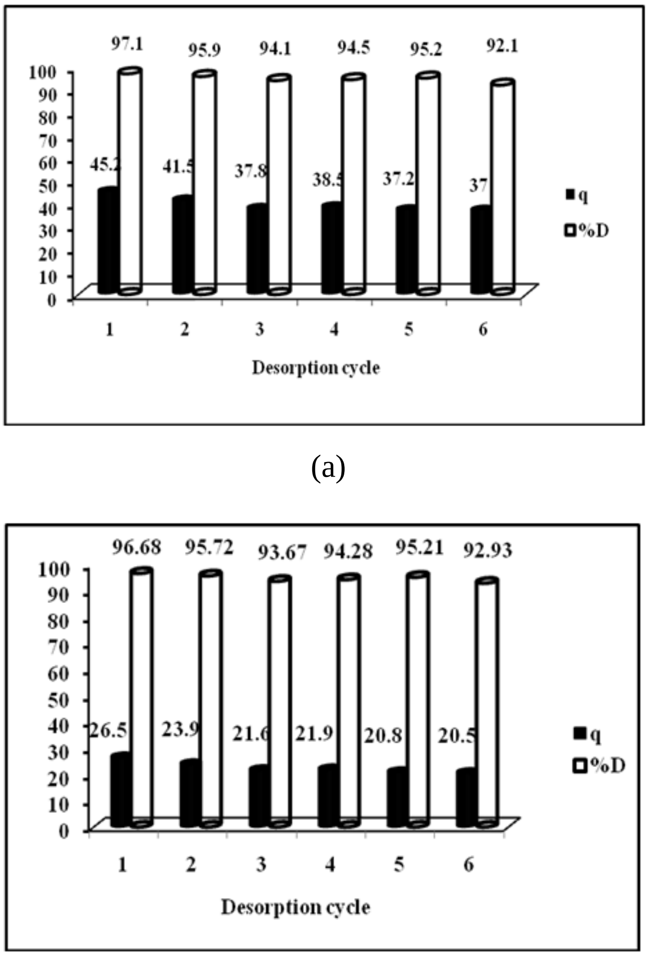
The high adsorption capacity of Pb (II) in functionalized biopolymers could be due to high electro negativity and small hydrated radius, which creates a greater affinity for negatively charged adsorption sites onto FDB. The correlation coefficient (R^2) value was found to be 0.99, indicating that the Langmuir isotherm model fitted well, as shown in Figure 6 (b).



(a)

(b)

Figure 6: (a) Adsorption Isotherm (b) Langmuir Isotherm for Pb (II) onto RDB and FDB



(a)

(b)

Figure 7: Desorption study on (a) FDB-H (b) FDB-Dm

Table 1: Langmuir adsorption isotherm model parameters and q_{max} of FDB

Biopolymer	q_{max}(mg/g)	q_{graph} (mg/g)	b(L/mg)	R^2	K_2
FDB-H	130.40	142.86	0.024	0.99	4.54 x10^{-3}
FDB-Dm	87.20	100.00	0.012	0.99	4.59 x 10^{-3}

Effect of Contact Time

Sorption kinetics gives information about the rate and time at which metal ion is adsorbed and reaching the adsorption equilibrium. Pseudo first- order and pseudo second-order rate equations (34) were used for kinetic modeling. The experimental data showed an increase in adsorption with the increase in time from 5 -120 min, then it almost reached a saturation (35). All kinetic data of the metal ions was tested with pseudo first order and pseudo second-order rate equations. The data were fitted poorly, (data and figure not given), and the Lagergren correlation coefficient (R^2) value was very low for the first-order rate equation Therefore, pseudo second-order kinetic model were used to evaluate the experimental kinetics sorption data given by Ho and McKay.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

Where, q_t= amount of the adsorption at time t (min), k_2 = rate constant of the pseudo second-order kinetic adsorption, (g/mg/min). The R^2 value for Pb (II) concentration was higher than 0.99, indicating the applicability of the model for the entire adsorption process and also confirmed the chemisorptions of the Pb (II) onto the FDB.

Mechanism of adsorption

The sorption mechanism of lignocellulosic materials is different from those of other conventional adsorbents. These mechanisms are complex because they implicate the presence of different interactions. Metal complexation by amine functionalized biopolymers may thus involve two different mechanisms: chelation and ion exchange, depending on the pH, which may affect the protonation on the surface of the biopolymers (36, 24). The functionalized polymers possess high percentage of nitrogen, in the form of amine groups, which are responsible for metal ion binding through chelation mechanism. Amine sites are the main reactive groups for metal ions rather than hydroxyl groups, which contribute to adsorption of metal ions (37). In this study, the maximum adsorption occured at acidic pH value, which is not only due to ion exchange, but mainly due to chelation mechanism.

Regeneration and Reuse of biopolymers

The efficiency and reusability of both the functionalized biopolymers were evaluated with adsorption desorption experiments. In this study, NaOH, HCl and HNO_3 were used as eluting agents. Among them 0.1M nitric acid was found to be most effective, releasing the metal ions adsorbed on to the FDB. Figures 7(a) and 7(b) show the loading capacity and the percentage desorption of the biopolymer for Pb (II). The result revealed that above 92 % of metal ions were desorbed from the biopolymer up to six cycles, indicating that the metal adsorbed biopolymer can be regenerated almost completely with 0.1M nitric acid; and the biopolymer can be repeatedly used for metal ions sorption, thereby minimizing the cost for preparation of biopolymer and the sorption process.

IV. CONCLUSION

This research work has explored a potentially excellent biopolymer *Desmostachya bipinnata (DB)*, which is equally compatible to commercially used synthetic adsorbent.

It was functionalized with hydrazine monohydrate and dimethylamine. Analyses indicated the introduction of amine functional groups on to the DB. The sorption performances were fitted well with Langmuir model with high R^2 of 0.99 and the rate of sorption followed the pseudo second order kinetics. The possible reaction mechanisms involved were mainly through complexation. About 92% metal ions were desorbed from both the biopolymers during the regeneration and reuse experiments.

The process indicates the efficiency, cost effectiveness and possible reuse of the biopolymer. It must have potential application in the removal of trace amounts of Pb (II) present in waste water.

V. ACKNOWLEDGEMENTS

Authors wish to thank Central Department of Chemistry- Tribhuvan University and Department of Agricultural Biotechnology- Padua University, Italy, for providing the laboratory facilities to carry out this research work.

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