

# An Investigation into the efficacy of Fungal Biomass as a Low Cost Bio-adsorbent for the removal of Lead from aqueous solutions

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**Abstract** - Some of the heavy metals such as lead ( $Pb^{2+}$ ) even in low concentration pose a threat to human wellbeing and other life forms. Various anthropogenic and industrial sources discharge this toxic metal into the biosphere. The present study explores the efficiency of untreated dead biomass of *Penicillium* sp. (a fungus) in the bio-sorption of  $Pb^{2+}$  ions from aqueous solutions. Different factors viz., initial  $Pb^{2+}$  ion concentration, adsorbent dose and contact time were studied. The maximum adsorption percentage (78.03%) of  $Pb^{2+}$  was found under the optimum conditions of 10 mg/l of  $Pb^{2+}$ , an adsorbent dose of 1g/L and contact time of 2 hours. Langmuir adsorption isotherm was best fitted for the present study ( $R^2=0.9984$ ). Bio-sorption reaction mechanism was explained through FTIR analysis of fungal biomass which revealed the presence of carbonyl, methylene, phosphate, carbonate and phenolic groups and their possible involvement in the  $Pb^{2+}$  ions bio-sorption process. SEM and EDX details provide the structural characterization and optical absorption peaks of dead fungal biomass and explain its surface morphology in the adsorption and removal of  $Pb^{2+}$  ions from aqueous solutions respectively. It can be concluded that untreated dead biomass of *Penicillium* sp. is a promising, efficient, low-cost bio-adsorbent for the removal of  $Pb^{2+}$  ions from the environment and wastewater effluents.

**Key Words:** Biosorption; low-cost bio-adsorbent; SEM; FTIR; Langmuir isotherm model

## 1. INTRODUCTION

Enhanced industrial and economic development has resulted in heavy metal pollution and their vast distribution in the environment which in turn poses a major challenge for their

effective treatment and management due to their toxic and persistent nature and accumulation in the food chain [1].

Many conventional technologies including filtration, ion-exchange, precipitation, coagulation, membrane separation, solvent extraction are available for mitigation of these dangerous pollutants but demands high energy and operation costs even lead to the generation of secondary pollutants/sludge. Due to which focus has been shifted towards the application of cost-effective, eco-friendly non-conventional methods for remediation of these heavy metals. Bioadsorption is one of the emerging process/methods which is considered to be beneficial for the removal of metal ions from aqueous solutions. Microbial biomass either living or dead as bioadsorbents has been found to be effective in the amelioration of heavy metal ions from wastewater/soil. Literature survey supports the use of fungi, algae, and bacteria as adsorbents for several heavy metals [2] [3].

Recently, lead removal from soil and aqueous samples have been reported by many fungal species like *Aspergillus niger* [4][6][11][14], *Trichoderma reesi* [4], *Mucor arcindloides* [4], *Saccharomyces cerevisiae* [4][9], *Penicillium austurianum* [4], *Penicillium verrucosum* [5], *Botrytis cinerea* [7], *Phanerochaete chrysosporium* [8], *Mucor rouxii* [10], *Aspergillus fumigatus* [11], *Penicillium simplicissimum* [11], *Trichoderma asperellum* [11], *Penicillium chrysogenum* [12] [13] [15], *Aspegillus nidulans* [15], *Aspergillus flavus* [15], *Rhizopus arrhizus* [15], *Trichoderma viride* [15].

The utility of fungal biomass as bioadsorbent is in the fact as are easy to separate, rarely sensitive to nutrient variation, pH etc, has less nucleic content in biomass, easily cultivated for large scale production, provides large surface area for adsorption reactions and are non-toxic [16][17].

The objective of the present study was to explore the lead removal potential of fungal biomass as biosorbent from aqueous solution in the batch process. The effect of parameters influencing biosorption processes such as initial lead concentration, adsorbent dose and contact time were also studied. The affirmation of lead biosorption on fungal biomass was done through Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy combined with X-ray energy dispersive spectrometer (SEM-EDX) analysis upon exposure to lead ions in the aqueous solutions.

## 2. MATERIAL AND METHODS

### 2.1 Preparation of stock and standard solutions of lead nitrate [Pb (NO<sub>3</sub>)<sub>2</sub>]

In a clean beaker containing 100ml distilled water, 1.59g of Pb(NO<sub>3</sub>)<sub>2</sub> was dissolved with constant stirring to get a 10000ppm stock solution and afterward 10μL, 20μL and 30μL were pipetted out from it to make standard solutions of 5ppm, 10ppm and 15ppm in 20ml distilled water respectively. The standard solutions were prepared fresh and pH was measured each time before the experiment was conducted.

### 2.2 Preparation and characterization of bio-adsorbent

Dead and dried fungal biomass of *Penicillium sp.* was used for removal of Pb<sup>2+</sup> ions from aqueous solutions. It was procured from microbiology department of Lucknow University in dried and dead form only. The characterization of fungal adsorbent was done with the help of technique scanning electron microscopy-energy dispersive X-Ray (SEM-EDX) and Fourier-transform infrared spectroscopy (FTIR).

#### 2.2.1 Fourier transformed infrared (FTIR) spectral analysis

For FTIR studies, 4-5 mg of biosorbent (the lead-treated and the untreated fungal biomass) was covered in 400 mg of KBr. Round discs were obtained by pressing the ground material with the aid of a bench press and further readings were measured on Nicolet™ 6700 model (Thermo Scientific, USA) FTIR spectrometer.

#### 2.2.2 Scanning electron microscopy combined with X-ray energy dispersive spectrometer (SEM-EDX) analysis

The surface morphology and lead binding pattern in the lead-treated and the untreated fungal biomass samples were recorded using scanning electron microscopy combined with

X-ray energy dispersive spectrometer (SEM-EDX, JEOL, JSM 6490 LV, Japan).

### 2.3 Batch adsorption experiments

Batch equilibrium experiments were performed with 20ml of a standard solution of concentration 5mg/l, 10mg/l and 15mg/l and a desired adsorbent dose of 0.1g to 1g. The parameters studied include initial metal ion concentration, contact time and adsorbent dose. The mixture was transferred to 50ml Erlenmeyer flasks and stirred for 2h to 6h, filtered using Whatman filter No. 42 and analyzed for residual metal concentration through inductively coupled plasma- mass spectrometry (ICP-MS). All the experiments were performed at room temperature conditions.

The amount of lead adsorbed onto fungal biomass was calculated by using the following expression Eq. (1)

$$q_e = \frac{C_0 - C_f}{M} * V \quad (1)$$

Where q<sub>e</sub> is the quantity of lead biosorbed onto fungal biomass as mg/g; V is the volume of lead solution in liters; C<sub>0</sub> and C<sub>f</sub> are initial and final concentrations (mg/l) of lead in the solution and M is the weight of biomass taken for the batch experiment in g.

### 2.4 Adsorption isotherm Models

The mathematical relationship between the concentration of adsorbate before and remained after the sorption experiment is explained by using adsorption isotherm models. Langmuir and Freundlich adsorption isotherm models are used in this study. These are commonly used to assess the sorption capacity of bio-adsorbent in the adsorption system.

#### 2.4.1 Langmuir Isotherm

It is generally based on monolayer adsorption process i.e., once all the sites available on adsorbent are filled, no more adsorption process can take place or say it reaches the saturation point.

The general and the linearized form of this isotherm are represented in equations (2) and (3) respectively as follows:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \quad (3)$$

Where q<sub>e</sub> is the amount of sorbed metal at equilibrium (mg/g), q<sub>max</sub> is the monolayer sorption capacity (mg/g), b is the Langmuir constant, C<sub>e</sub> is concentration of metal ions in solution at equilibrium.

When a plot of  $(C_e/q_e)$  versus  $C_e$  is plotted, a straight line with a slope of  $(1/q_{max})$  and an intercept of  $(1/bq_{max})$  must be obtained.

### 2.4.2 Freundlich isotherm

Heterogenous surfaces involving adsorption processes are explained by using Freundlich isotherm. It is empirical and does not assume monolayer adsorption but is quite useful to explain adsorption data and fraction of actives sites available for sorption study.

The general and the linearized form of this isotherm are represented in equations (4) and (5) respectively as follows:

$$q_e = K_f C^{1/n} \quad (4)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

Where  $C_e$  is the equilibrium concentration (mg/g),  $q_e$  is the adsorbed amount at equilibrium (mg/g),  $K_f$  is the adsorption capacity (L/mg) and  $1/n$  is adsorption intensity, it also indicates the relative energy distribution and the heterogeneity of the adsorbate sites.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of initial metal ion concentration

The effect of initial metal ion concentration was determined at operational conditions of 0.1g adsorbent dose and contact time of 2h at pH 5.5 for initial metal ion concentration from 5 mg/l to 15 mg/l. Sorption capacity ( $q_e$ ) was found to be increased from 0.42 mg/g to 1.136 mg/g indicating an increase in adsorption rate with increase in initial metal ion concentration (Fig. 1) and reduced amount of metal ions in the aqueous solution. These findings could be explained as there is an acting huge force for rapid mass transfer, more the concentration of initial metal ions more will be adsorption rate. [18][19]

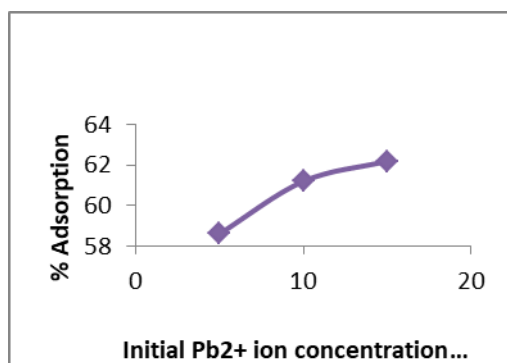


Fig.1. Initial metal ion concentration Vs % Adsorption

### 3.2 Effect of contact time

An investigation into the adsorption process in relation to contact time is an important parameter as it can help us to assess the efficiency of adsorption and to determine the saturation point with constant adsorbent dose and fixed initial metal concentration. Because at the beginning of the sorption process, more of the actives sites on the adsorbent is available and unoccupied and with the increase in time actives sites begins to get saturated by the metal ions present in the solution thereby decreasing the adsorption rate. [20] In the present study, the effect of contact time was determined at 10ppm/20ml with 0.1g adsorbent dose at pH 5.5 with contact time range from 2h to 6h and results showed decrease in concentration of metal ions in the solution and increased adsorption rate as up to 6 hours which can be explained due to unsaturation of actives sites and were still available for adsorption process (Fig. 2).

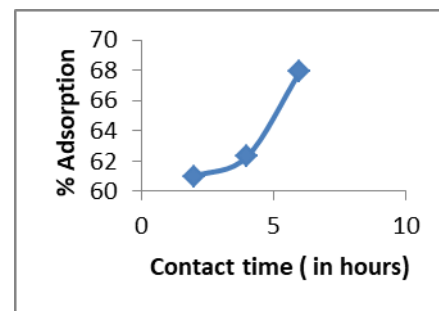


Fig.2. Contact time Vs % Adsorption

### 3.3 Effect of adsorbent dose

There is a direct relationship between adsorbent dose and percent adsorption. As we increase the dose of adsorbent and keep the initial metal ion concentration constant, more active sites are available for the metal ion to get adsorbed at the surface of adsorbent [21]. In the present study, the effect of adsorbent dose was determined at fixed 10ppm/20ml initial metal ion concentration and a contact time of 6hour at pH 5.5 and adsorbent dose ranges from 0.1g to 1g and results indicates increased adsorption rate as more actives sites are available with increased adsorbent dose at fixed concentration of metal ion (Fig. 3).

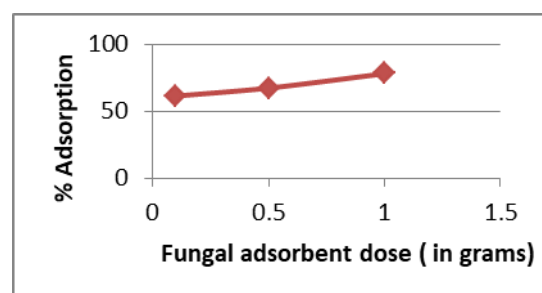


Fig. 3 Adsorbent dose Vs % Adsorption

### 3.4 SEM-EDX and FTIR analysis

SEM-EDX analysis tells us about the surface morphology and structural characterization of adsorbent along with their chemical composition and relative spectral energies. Results of lead untreated and treated adsorbent are shown in fig. 4, 5 and 6 respectively. An attempt was made to explore the surface of dry fungal adsorbent for any modification which could have been occurred due to adsorption of lead ions and fig. 4(b) indicates rough irregular morphology containing dead ruptured hyphae of fungal biomass loaded with lead ions in comparison to fig. 4(a) which is taken before adsorption of lead ions. EDX analysis as shown in fig. 5 (before adsorption) and fig. 6 (after adsorption) respectively revealed change in inorganic chemical constituents by weight percent and some reduction indicating ion-exchange could be considered as one of the dominant adsorption mechanism in lead ion biosorption onto fungal biomass. [22][23]

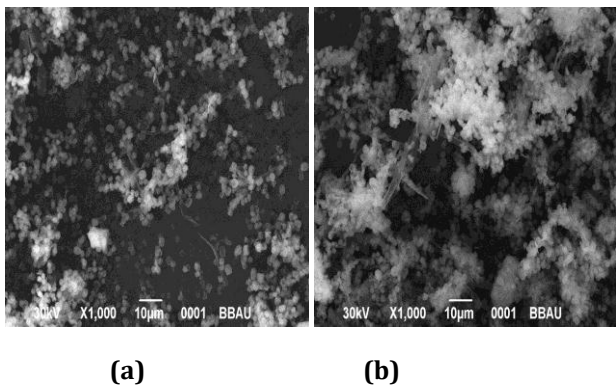


Fig. 4 SEM micrographs of fungal adsorbent before sorption (a) and after sorption (b) of Pb<sup>2+</sup> ions (15ppm) at 1000X magnification

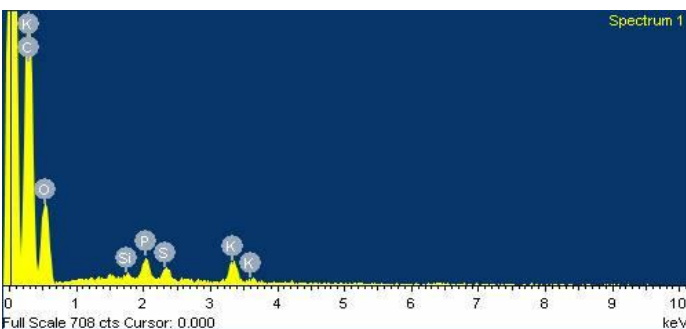


Fig. 5 EDX spectrum of Fungal adsorbent before adsorption

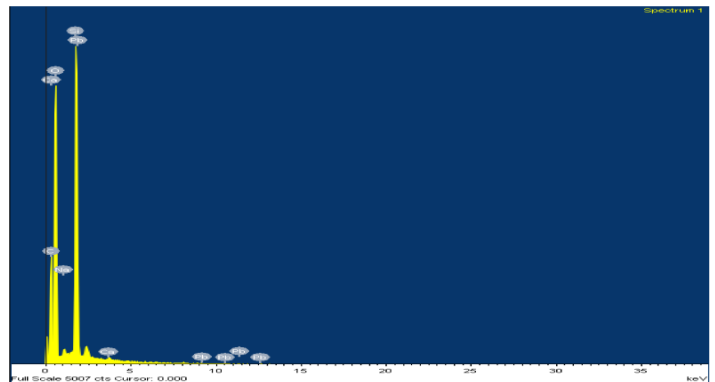
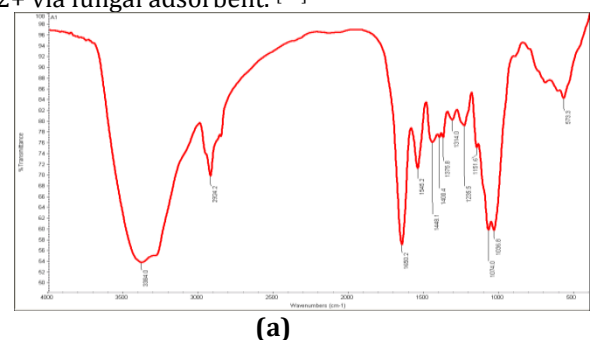
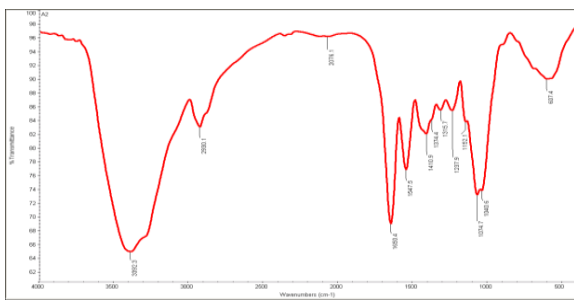


Fig. 6 EDX spectrum of Fungal adsorbent after adsorption

FTIR analysis is done to determine the types of functional groups present on the surface of the adsorbent. Results of IR spectra before and after adsorption are presented in fig. 7(a) and 7(b) respectively. The largest peak of wave number 3384 cm<sup>-1</sup> shown in Figure 7, corresponds to either free or H-bonded O-H groups that could be present in carboxylic acids on the surface of the fungal adsorbent. The peak at 2924.2 cm<sup>-1</sup> wave number corresponds to the C-H stretching that could exist in the alkanes. As for peaks of wave numbers in the range of 1650.2 to 1314.0 cm<sup>-1</sup>, are an indication of the olefinic and aromatic bond, and bands of wavenumber 1235.5 to 573.3 cm<sup>-1</sup> are an indication of C-O bond. C-O bond may be due to carboxylic acids, hydroxy groups or fiber carbonaceous that are present in the structure of fungal adsorbent that is composed of lignin and cellulose. Those groups probably act as proton donors that once get deprotonated, the hydroxyl group or the carboxyl group adsorb the heavy metal ions.

As shown in Fig. 7(b), the peak representing the O-H bond was only shifted from 3384 cm<sup>-1</sup> to 3392.3 cm<sup>-1</sup>, which is an insignificant change. Whereas the peak of the C=O bond was shifted from 573.3 to 607.0 cm<sup>-1</sup>, and the peak of the C-O bond was shifted from 1066.8 to 1107.8 cm<sup>-1</sup>. Those shifts can be attributed to the surface complexation created between Pb<sup>2+</sup> and the carboxylic acids functional groups; hence, it is an indication that chemical complexation between Pb<sup>2+</sup> and the carboxyl groups could be one of the mechanisms partially responsible for the biosorption of Pb<sup>2+</sup> via fungal adsorbent. [24]





(b)

Fig. 7 FTIR spectrum of fungal adsorbent before adsorption (a) and after adsorption (b)

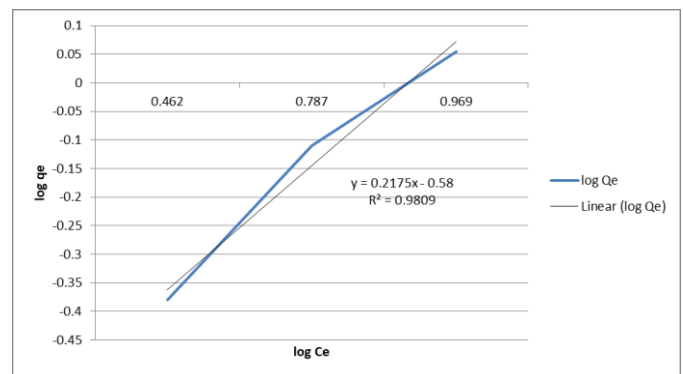


Figure 5: Freundlich isotherm

### 3.5 Adsorption isotherms

The values of Langmuir and Freundlich constants for lead ions uptake on dry fungal biomass are given in Table 1 and 2 respectively. The values of Langmuir constants  $q_{max}$  and  $b$  are calculated by plotting against  $1/q_e$  and  $1/C_e$  and Freundlich constants  $K_F$  and  $n$  were obtained by the plot of  $\log q_e$  vs  $\log C_e$ . The  $R^2$  value of Langmuir constant was 0.9984 was found to be higher than  $R^2$  value of Freundlich (0.9809), indicating that Langmuir data fitted well than Freundlich data in adsorption process (Figure 4 & 5). It is considered to be well-fitted model if  $R^2$  value is close to unity. [25]

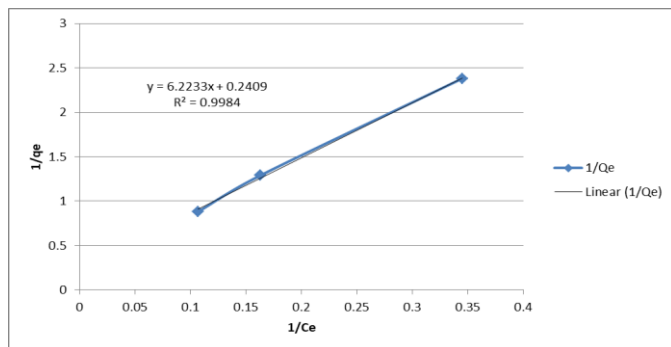


Figure 4: Langmuir isotherm

Table 1: Parameters of Langmuir isotherm

| $q_{max}$ (mg/g) | $b$ (l/mg) | $R^2$  |
|------------------|------------|--------|
| 0.16             | 25.94      | 0.9984 |

Table 2: Sorption Parameters of Freundlich isotherm

| $K_f$ | $n$  | $R^2$  |
|-------|------|--------|
| 3.80  | 4.59 | 0.9809 |

### 4. CONCLUSIONS

The present research was designed to investigate the efficiency of a dry fungal adsorbent for the removal of lead ions from their aqueous solutions. The effect of parameters such as initial metal ion concentration, contact time and the adsorbent dose was selected for adsorption study. The selected dead biomass of fungus showed a notable metal adsorption capacity over a limited range of parameters. The Langmuir adsorption isotherm was found to be best fitted with the present study.

The dead fungal biomass may be employed in the future for heavy metal remediation from real wastewater and comparative study can be assessed between dead and living fungal biomass. Further, column studies could be done to compare metal uptake and sorption capacity with different metal ion concentrations, adsorbent dose and contact time. Column bed height could be varied to compare adsorption efficiency.

### 5. ACKNOWLEDGMENT

Authors are thankful to the Head and Coordinator, Department of Microbiology, University of Lucknow, Lucknow for biomass availability and support.

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