

EFFECTIVE REMOVAL AND RECOVERY OF LEAD FROM INDUSTRIAL WASTEWATERS USING NATURAL BIOMASS

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Abstract. *Rapid industrialization, urbanization and technological advancement in this century have drastically changed the biogeochemical cycles and balance of some of the heavy metals, thereby leading to environmental pollution in alarming proportions. Lead (i.e., Pb²⁺) is toxic to most organisms for concentrations higher than 0.05 mg/L, moreover, it is carcinogenic to animals. In the present study, batch biosorption of Pb²⁺ from wastewaters was studied using the nonliving biomass of *Aspergillus sp.* and *Fusarium sp.* isolated from soil. The specific metal removal increased with increase in initial lead ion concentration upto 500 mg/L observed with both the biomasses. A complete removal of the metal was observed at an initial metal ion concentration 50 mg/L and at pH 5.0. A maximum removal of 42.5 mg/g with *Fusarium sp.* and 37.3 mg/g with *Aspergillus sp.* was observed at pH 5.0 at 500 mg/L initial lead ion concentration. The adsorption equilibrium was obtained within 1h for all the concentration used. The adsorption equilibrium constants were obtained using both Freundlich and Langmuir adsorption isotherms. The desorption studies disclose the effective recovery of lead from the metal concentrated biomass using 0.1N Nitric acid solution within 0.5 h of time period increasing its effectiveness of reuse.*

Keywords: *Biomass; heavy metals; adsorption isotherms; adsorption constant; desorption.*

1. INTRODUCTION

Rapid industrialization, urbanization and technological advancement in this century have drastically changed the biogeochemical cycles and balance of some of the heavy metals, thereby leading to environmental pollution in alarming proportions [1-4]. Heavy metals contamination in water is a dangerous problem due to their toxicity and bioaccumulation in food chains [5-7]. Heavy metal pollution is a serious environmental problem because of the toxic effects of heavy metal ions on living organisms [8, 9]. Pb²⁺ is one of the major pollutants of the environment. Due to its extreme toxicity, the removal of lead from wastewaters, such as those of textile, electroplating, and petroleum industries, is essential for aquatic life and humans [10]. High level of lead exposure causes cognitive and other neurologic problems [11]. Adsorption and/or filtration on various substrates can be used to remove heavy metals from aqueous solutions. The ability to remove lead using low-cost substrates is thus particularly important [12]. There are many conventional techniques to reduce environmental problems associated with industrial effluents. Pb²⁺ levels in aqueous streams come from a variety of places, including smelting and mining, battery manufacturing, pigment printing, photography material, fuels, and explosive manufacturing [13]. Pb²⁺ in drinking water has a safe standard of 0.01 mg/L set by the World Health Organization (WHO) [14]. Chemical oxidation and reduction, chemical precipitation and filtration, reverse osmosis,

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electrochemical treatment, solvent extraction, membrane filtration, and adsorption are some of the methods reported to remove lead [15].

Due to its high competence in detoxifying dilute effluents, low disposable chemical/biological sludge volume, and low operating cost, current research has focused on biosorption technique that is effective for metal removal and recovery processes [16]. Among the various biosorbents reported, such as bacteria, fungi, algae, industrial and agricultural wastes, natural residues, chitosan and cellulose-driven materials, fungi are an appealing choice in wastewater treatment processes due to their massive and easy growth with inexpensive substrate [17]. Sludge is produced as a waste in heaps by other biomaterials, which raises the cost of effluent treatment plants [18]. Fungi significantly reduce the cost of effluent treatment plants by converting valuable fungal protein (a source of animal feed) and more effectively metabolizing complex carbohydrates into a wide range of enzymes and biochemicals [19]. Biosorption has recently gained popularity as a new method for removing toxic metals from wastewaters. The biosorption process, which uses biosorbents (made from microorganisms), has been recognized as a viable alternative to existing conventional methods for industrial wastewater detoxification since it consumes little energy and produces no chemical sludge [20]. Furthermore, when metals are present in very low concentrations, it is effective in removing them from wastewaters [4, 21].

In the current study, lead adsorption was assessed using batch data at various initial lead concentrations and pH values. The Freundlich and Langmuir adsorption isotherms were used to test the equilibrium adsorption data, and the nature of biosorption was discussed. The studies also looked into the possibility of recovering lead from metal-concentrated biomass, which is crucial from a resource recovery standpoint because metals are non-renewable [22].

2. MATERIALS AND METHODS

2.1. MATERIALS

2.1.1. Microorganisms and growth conditions

The fungus *Fusarium sp.* (isolated from soil) used in the present study was grown in 250 mL Erlenmeyer flasks in a shaking incubator at 30°C and 180 rpm using 100 mL liquid media of the following composition (g/L): Glucose, (10.0); K₂HPO₄, (0.5); NaCl, (1.0); MgSO₄, (0.1); NH₄NO₃, (0.5) and Yeast extract, (5.0). The pH of the media was 6.0. An inoculum of 10 % (v/v) of a 36 h old culture was used for the growth of the organism.

2.1.2. Preparation of biomass

The cells grown in 36 hours (after the sugar was completely utilized) were centrifuged at 5000 rpm for 5 minutes at 30°C and then washed thrice with distilled water and dried at 80°C for 24 h. The dried biomass was then used for subsequent batch biosorption.

2.1.3. Lead ion solution

Synthetic metal containing solutions of different concentrations (50-500 mg/L) were prepared by diluting a stock solution prepared by dissolving the required quantities of Pb(NO₃)₂ in distilled water.

2.2. METHODS

2.2.1. Batch biosorption

Batch experiments were carried out with a weighed amount of the nonliving cells (4.5 g/L) in the Erlenmeyer flask (250 mL) containing 100 mL of metal (lead nitrate) solution of a known concentration. The pH of the solution containing metal ions was adjusted to the required value with 1N H₂SO₄ solution before mixing the biomass. The biosorption suspension was shaken at 150 rpm for 1 hour at 30°C. Periodically samples were withdrawn and centrifuged at 5000 rpm for 5 minutes. The separated supernatant liquid was analyzed for the residual metal concentration. All the batch experiments were carried out similarly to study effect of pH (2.0 – 6.0) and initial metal ion concentration (0-500 mg/L).

2.2.2. Desorption investigation

After equilibrium sorption experiments at pH 5, Pb²⁺ loaded biomass was dried at 70°C for 24 hours to assess desorption efficiency. To allow lead to be released from the dried biomass, it was exposed to 0.1N HNO₃ for 24 hours [23]. After that, the lead that had been desorbed was examined, and the desorption efficiency was calculated as follows:

$$\text{Desorption efficiency (\%)} = \frac{\text{released lead (mg)}}{\text{initially sorbed lead (mg)}} \times 100$$

2.2.3. Assay techniques

The residual lead ion concentration in the aqueous solution was measured by Atomic Absorption Spectrophotometer (AAS) with an air-acetylene flame [24].

3. RESULTS AND DISCUSSION

3.1. RESULTS

3.1.1. Effect of various parameters

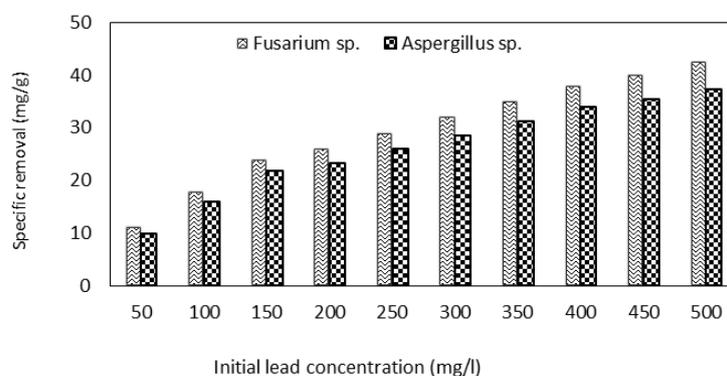
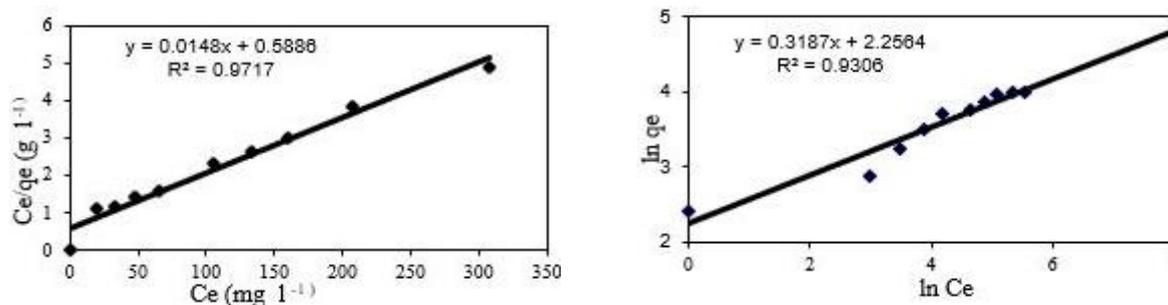
Table 1 shows the effect of pH on percent metal (Pb) adsorption and specific lead removal (mg/g), respectively, by the nonliving dry biomass (as an adsorbent) of the *Fusarium* sp. and *Aspergillus* sp. at 50 mg/L initial lead ion concentration. The above Table indicates an increase in percent metal adsorption with an increase in pH value from 2.0 to 5.0 for both the biomass, beyond which no significant change was observed in the adsorption with further increase in pH up to 6.0.

The Pb adsorption with *Fusarium* sp. was found to be only 12% at pH 2.0, whereas a complete adsorption (100 %) of the metal was observed at pH 5.0. In a similar manner, with *Aspergillus* sp. the adsorption was 10% at pH 2.0, and 88% at pH 5.0, was observed. An increase in metal removal with increasing pH of the solution was also observed by Dursun [25]. At very low pH values with a high proton concentration fungal cells are surrounded by the hydronium ions, which restrict the approach of metal cations as a result of repulsive force [26].

Table 1. Effect of pH on lead adsorption at 50 mg/L initial concentration.

Biomass	Initial lead conc [mg/L]		pH				
			2	3	4	5	6
<i>Fusarium</i> sp.	50	Adsorption [%]	12	20	42	100	99
		Specific lead removal [mg/g]	3.55	5.33	9.33	11.12	11.01
<i>Aspergillus</i> sp.	50	Adsorption [%]	10	17	34	88	86
		Specific lead removal [mg/g]	3.13	4.72	7.72	9.79	9.55

The specific removal (mg/g) at different initial lead concentration ranging from 50 to 500 mg/L at pH 5.0 is shown in Fig. 1. The biomass concentration used for all the experiments was 4.50 g/L. It can be seen in the graph that the specific metal removal at different initial lead concentration ranging from 50 to 500 mg/L at pH 5.0. However, mg of lead adsorption/g of biomass increased with an increase in initial lead concentration and a maximum adsorption (42.50 mg/g) and (37.30 mg/g) was observed at 500 mg/L with the biomass *Fusarium* sp. and *Aspergillus* sp., respectively.

**Figure 1. Effect of initial Lead concentration on specific removal [mg/g] of lead.****Figure 2. (a) Langmuir adsorption isotherm (b) Freundlich adsorption isotherms of lead by *Fusarium* sp.**

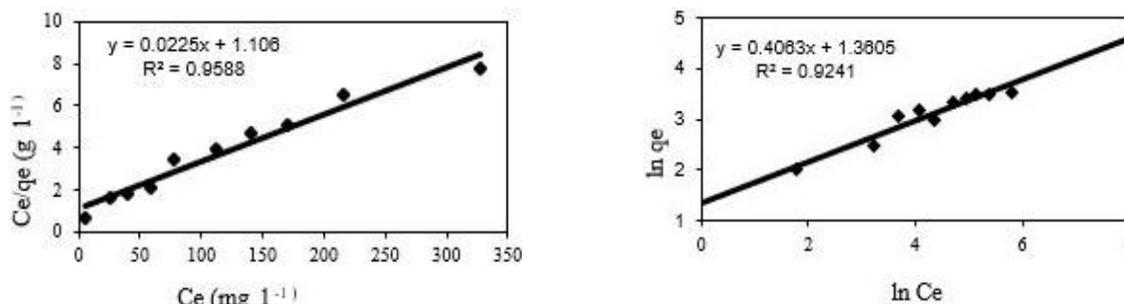
The adsorption data obtained at different initial metal ion concentrations (0-500 mg/L), pH 5.0 and at 30°C, respectively. The values of adsorption isotherm constants (Tables 2a and 2b) were calculated from the slopes and the intercepts of the straight lines shown in Fig. 2a (Langmuir isotherm) and Fig. 2b (Freundlich isotherm) along with the regression coefficients.

Table 2a. Langmuir constants by *Fusarium* sp.

Metal ion	Langmuir constants		
	Q° (mg/gm)	b (l/mg)	R²
Lead (II)	67.56	0.03	0.971

Table 2b. Freundlich constants by *Fusarium sp.*

Metal ion	Freundlich constants		
Lead (II)	K_F	n	R^2
	9.56	3.13	0.9306

**Figure 3. (a) Langmuir adsorption isotherm (b) Freundlich adsorption isotherms of lead by *Aspergillus sp.***

Figs. 3a and 3b show, both Langmuir and Freundlich adsorption isotherms of Pb to express the metal adsorption potential of *Aspergillus sp.* The adsorption data obtained at different initial metal ion concentrations (0-500 mg/L), pH 5.0 and at 30° C, respectively. The values of adsorption isotherm constants (Tables 3a and 3b) were calculated from the slopes and the intercepts of the straight lines shown in Fig. 3a (Langmuir isotherm) and Fig. 3b (Freundlich isotherm) along with the regression coefficients.

According to 'Q⁰' calculated with *Aspergillus sp.* the maximum amount of lead (Fig. 3a) adsorbed per gram of adsorbent to form a complete monolayer on the surface was 44.45 mg, and the adsorption affinity 'b' for binding lead on the adsorbent sites was 0.02 (L/mg).

Table 3a. Langmuir constants by *Aspergillus sp.*

Metal ion	Langmuir constants		
Lead (II)	Q^0 [mg/gm]	b [L/mg]	R^2
	44.45	0.02	0.958

Table 3b. Freundlich constants by *Aspergillus sp.*

Metal ion	Freundlich constants		
Lead (II)	K_F	n	R^2
	3.9	2.4	0.924

Table 4. Adsorption and desorption cycles

Metal ion/Sorbent	Adsorption [%]	Desorption [%]	Cycle
Lead (II)/ <i>Fusarium sp.</i>	80	71	I
	76	57	II
Lead (II)/ <i>Aspergillus sp.</i>	71	60	I
	66	49	II

3.2. DISCUSSION

The increase in adsorption with increase in pH is due to the decreased availability of hydrogen ions for the protonation of the cell wall functional groups, thus increasing the strong relation of biosorption to the number of available surface negative binding charges [27].

The relation between the amount of metal adsorbed by the adsorbent and unadsorbed component in solution at a constant temperature can be represented by both Langmuir and Freundlich adsorption isotherms, which provide the equilibrium data required for the designing of the adsorption system. The Langmuir adsorption isotherm, which is applicable to monolayer sorption onto a surface having homogeneously distributed identical binding sites over the surface sorbent, is given by equation (1) or (1a), (1b):

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (1)$$

or

$$\frac{1}{q_e} = \frac{1 + b C_e}{Q^0 b C_e} \quad (1a)$$

or

$$\frac{C_e}{q_e} = \frac{1 + b C_e}{Q^0 b} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (1b)$$

where q_e is the amount of metal adsorbed per gram of dried biomass at equilibrium (mg metal adsorbed per gm of dried biomass; biomass is often reported as a mass per unit area: g m^{-2} or Mg ha^{-1}) and C_e is the residual (equilibrium) metal concentration remaining in the solution after sorption (mg metal per litre). The Langmuir constants, Q^0 and b , indicate the maximum amount of metal ion bound per g of adsorbent to form a monolayer (mg/g) and the adsorption affinity (L/mg) for binding of the metal on the adsorbent sites, respectively.

The values of Q^0 and b can be calculated from the slope and intercept of the plot C_e/q_e against the residual concentration, C_e [28]. The Freundlich adsorption isotherm is applicable to adsorption of the metal ion on a heterogeneous surface and is expressed as equations (2) and (2a):

$$q_e = K_F C_e^{1/n} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} C_e \quad (2a)$$

where K_F and n are the Freundlich constants and are related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. Equation (2) can be linearized in logarithmic form and Freundlich constants n and K_F can be determined from the slope and intercept which are equal to $1/n$ and K_F , respectively [28].

In the present study, both Langmuir and Freundlich adsorption isotherms were tested with the experimental data describing the adsorption equilibrium of Lead to express the metal adsorption potential of *Fusarium sp.*

Table 2a shows the Langmuir adsorption constant ' Q^0 ' calculated in the present study indicates that the maximum amount of lead (Fig. 2a) adsorbed per gram of adsorbent (*Fusarium sp.*) to form a complete monolayer on the surface was 67.56 mg and the adsorption affinity 'b' for binding of lead on the adsorbent sites was 0.03 (L/mg). The adsorption capacity (K_F) and adsorption intensity (n) obtained from the intercept and slope of the Freundlich adsorption isotherm were 9.56 and 3.13 for the metal. With respect to the values of linear regression coefficient (R^2), both Langmuir and Freundlich models agreed well with the experimental data. However, Langmuir model exhibited a better fit of the adsorption data due to a higher value of R^2 . Both the models can be applied for a monolayer adsorption. However, the Langmuir model which is applicable to monolayer sorption onto a surface

having homogeneously distributed identical binding sites over the surface sorbent provides a more realistic description of adsorption by the adsorbent [29, 30].

The metal's adsorption capacity (K_F) and adsorption intensity (n) were 3.9 and 2.4, respectively, based on the intercept and slope of the Freundlich adsorption isotherm [20]. Both the Langmuir and Freundlich models agreed well with the experimental data when it came to the values of the linear regression coefficient (R^2). The Langmuir model had a better fit of the adsorption data due to a higher R^2 value. As a result, both biomasses indicated monolayer adsorption. However, when compared to *Aspergillus* sp., the Langmuir model, which is applicable to monolayer sorption onto a surface with homogeneously distributed identical binding sites over the surface sorbent, provides a more effective adsorption by *Fusarium* sp.

After first and second desorption with 0.1N HNO_3 , desorption studies with *Fusarium* sp. show a good potential for desorbing metals from saturated adsorbent with about 80% and 71%, respectively. HNO_3 is thought to be capable of dissolving lead and forming soluble salts of $Pb(NO_3)_2$. Furthermore, metal cations are easily displaced by H^+ ions due to the intense competition for adsorption sites between H^+ ions and metal cations in acid conditions [31]. As a result, these acids are proton exchanging agents with a high desorption potential under the conditions of this study. Meanwhile, after the first cycle, the desorption capacity of *Aspergillus* sp. was 71%, but after the second cycle, it was only 60%. The subsequent adsorption cycle must be considered when selecting the desorption agent. Even if they have a high desorption capacity, some desorption agents are considered inefficient because they damage the adsorbent's binding sites [31]. As a result, the reusability of both biomass was investigated using a two-cycle adsorption-desorption study.

4. CONCLUSION

The biomass of both *Fusarium* sp. and *Aspergillus* sp., non-living fungal biomass were able to adsorb significant amounts of lead from an aqueous solution. pH and initial metal concentrations influenced the adsorption process. At 500 mg/L initial lead concentration and pH 5.0, the maximum adsorption (42.5 mg/g and 37.3 mg/g) was obtained with *Fusarium* sp. and *Aspergillus* sp. The adsorption isotherm constants calculated from both the Langmuir and Freundlich adsorption isotherms indicated that both the biomass and lead removal had a favourable adsorption capacity. The potent desorbing reagent was identified as 0.1N HNO_3 solution for effective lead recovery (80%) from *Fusarium* sp. and (71%) from *Aspergillus* sp. from metal-loaded biomass. As a result, these findings serve as the foundation for the development of a viable operational strategy for the treatment of lead-contaminated waste waters.

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