

Short communication

Biosorption of Lead(II) and Zinc(II) from Aqueous Solutions by Nordmann Fir (*Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*) Cones

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Abstract

In the present study we reported the feasibility of cone biomass Nordmann fir (*Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*) as an alternative biosorbent to remove Pb(II) and Zn(II) metal ions from aqueous solutions. The effects of pH, initial metal concentration, biosorbent dosage and contact time were studied in batch experiments. It was found that the optimum pH for Pb(II) and Zn(II) ions removal by cone biomass was pH 6.0. At the optimal conditions metal ions biosorption was decreased as the initial metal concentration increased. The maximum biosorption efficiency of Nordmann fir was 82% and 56.2% at 5 mg/L initial metal concentration for Pb(II) and Zn(II), respectively. The experimental equilibrium data were evaluated by Freundlich and Langmuir isotherm models.

Keywords: Biosorption; *Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*; Lead(II); Zinc(II); Isotherm

1. Introduction

Lead and Zinc contamination of aquatic environment is great concern due to its accumulating properties on humans and other living organisms. Unlike organic pollutants, these toxic metals are non-biodegradable and therefore, the removal of them is extremely important in terms of healthy of livings specimens.¹ Lead is extensively used in many important industrial applications, such as storage battery, manufacturing, printing pigments, fuels, photographic materials, explosive manufacturing, coating, aeronautical and steel industries.^{2–3–4} Similarly zinc is one of the most important metals often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plant.⁵ It is reported that these toxic metal may cause health problems such as behavioral anomaly, learning disabilities and seizures.⁶ World Health Organization recommended the maximum acceptable concentration of lead and zinc in drinking water as 10 µg/L and 5.0 mg/L respectively.⁷

There are several methods for treating metal contaminant effluent such as ion exchange, adsorption, lime coagulation, membranes and evaporation chemical precipitation, oxidation, reduction, and reverse osmosis.^{8–9–10} But, technical and economical factors limit sometimes the feasibility of such process.^{11–12} Most of these, furthermore, are based on physical displacement or chemical replacement, generating yet another problem in the form of toxic sludge,¹³ the disposal of which adds further burden on the techno-economic feasibility of the treatment process.¹⁴ Biosorption, an alternative process, is the uptake of heavy metals from aqueous solutions by biological materials. Biosorption uses cheaper materials such as naturally abundant plant residues or byproducts of fermentation industries as biosorbents¹⁵ and biosorptive process is generally rapid and is suitable for the extraction of metal ions from large volumes of water.¹¹

In the last decade, algae,¹⁶ microorganism,¹⁷ sunflower stalks,¹⁸ lichen¹⁹, fungus¹⁵, palm and coconut fibers,^{20–21} leaves,²² fibrous network of papaya wood,²³ olive stones,²⁴ rice bran,²⁵ carrot residues²⁶ olive pomace²⁷

wheat bran,²⁸ and cone biomass²⁹ have been used successfully as biosorbent for toxic heavy metals removal.

Nordmann fir spread naturally in the Caucasus, Georgia, the East Black Sea and the northern parts of Armenia. It occurs at altitudes of 900–2200 m on mountains. Nordmann fir is one of the most important species grown for Christmas trees in the northeast Europe countries.³⁰ In addition to this; it is also a popular ornamental tree in parks and large gardens. The needle-shaped leaves of this species are used as a biosorbent in literature.³¹ The cones are 10–20 cm long and 4–5 cm broad, with about 150–200 scales and cylindrical and keep on plentiful resin.³⁰ Cone biomass was a waste itself and a readily available biosorbent.²⁹ The ovulate cone is the well known cone of the *Abies*, *Pinus*, *Picea* and other conifers.

The objective of the present work is to investigate the biosorption potential of Nordmann fir (*Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*) cone biomass in the removal of Pb(II) and Zn(II) ions from aqueous solution. The effects of pH, biomass dosage, contact time and initial metal concentration on the biosorption capacity of cone biomass were studied. The Langmuir, Freundlich models were used to describe equilibrium isotherms.

2. Materials and Methods

2.1. Biosorbent Preparation

Nordmann fir (*Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*) ovulate cones were used in this investigation. They were washed with deionized water and dried at 80 °C for 24 h. The dried biomass was ground in a mortar to a very fine powder and sieved through a 400-mesh copper sieve.

2.2. Solution Preparation

The metal stock solutions of Pb(II) and Zn(II) were obtained by dissolving Pb(NO₃)₂ (Sigma, St. Louis, MO, USA) and Zn(NO₃)₂·6H₂O (Sigma) salts in double distilled water. The test solutions containing single Pb(II) or Zn(II) ions were prepared by diluting 1.0 g/L stock metal ion solution.

2.3. Batch Biosorption Studies

The range of concentrations of prepared Pb(II) and Zn(II) solutions varied from 5–100 mg/L. Biosorption experiments were carried out in 250 ml Erlenmeyer flasks using 100 ml metal bearing solution with a known quantity of the dried biosorbent (4 g/L). Before mixing with the cone biomass for effect of pH, the pH of each solution was adjusted to desired values with HNO₃. Biosorption at pH above 6.0 was not carried out to avoid any possible interference from metal precipitation. The biosorption medium was placed in a mechanical platform shaker (Ther-

molyne ROSI 1000) and stirred for 3 h at 25 °C and at a fixed agitation speed of 200 rpm. The samples were taken at definite time and were filtered immediately to remove biomass by filter paper (Whatman GF/A) and heavy metals in the remaining solution were analyzed. The metal biosorption equilibrium was modeled by using the Freundlich and Langmuir models at the optimum pH value of solution.

2.4. Analysis of Pb(II) and Zn(II) ions

The concentration of unadsorbed Pb(II) and Zn(II) ions in the effluent were determined using an atomic absorption spectrophotometer (Perkin Elmer Analyst 360).

3. Results and Discussion

3.1. Effect of pH

The pH value one of the most important parameters that influence the adsorption behavior of metal ions from aqueous solutions. The influence of pH on the adsorption of Pb(II) and Zn(II) ions were studied within the range of pH 2.0–6.0 and the results were presented in Fig. 1. The uptake of metals increases with an increase in solution pH. Similar results were also reported in literature for different biomass.^{14–24} A sharp increase in the biosorption occurred in the pH range 3.5 to 5.0. The maximum biosorption was found to be 75% for Pb(II) and 41.3% for Zn ions at pH 6.0. Therefore, all the biosorption experiments were carried out at pH 6.0. At pH values higher than pH 6.0, metal ions precipitated and biosorption studies at these pH values could not be performed.³² At low values of pH the decrease in the removal efficiency could be referred to the fact that the mobility of the hydrogen ions is higher than that of the metal ions and it reacts with active sites before adsorbing the metal ions.³³ The result demonstrated that lead and zinc biosorption by cone biomass were affected by the initial pH of solution.

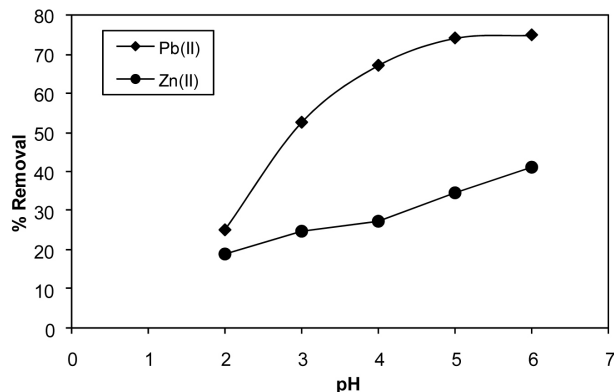


Fig. 1: Effect of pH on Pb(II) and Zn(II) biosorption efficiency (initial metal concentration (C_0) = 50 mg/L, biosorbent dose (m) = 4.0 g/L).

3. 2. Effect of Contact time

Fig. 2 shows the effect of reaction time on the biosorption of Pb(II) and Zn(II) by biosorbent from aqueous solutions. It was observed that the biosorption uptake of Pb(II) and Zn(II) increases with rise in contact time up to 180 minute. The rate of metal biosorption by the cone biomass was very rapid, reaching almost 95% of the maximum biosorption capacity within 10 min of contact time. Such rapid biosorption process has been correlated with the characteristics of the biomass, and its physico-chemical interactions with the metal ion. After this time there was no considerable increase. Therefore the reaction time was selected as 180 min for further experiments.

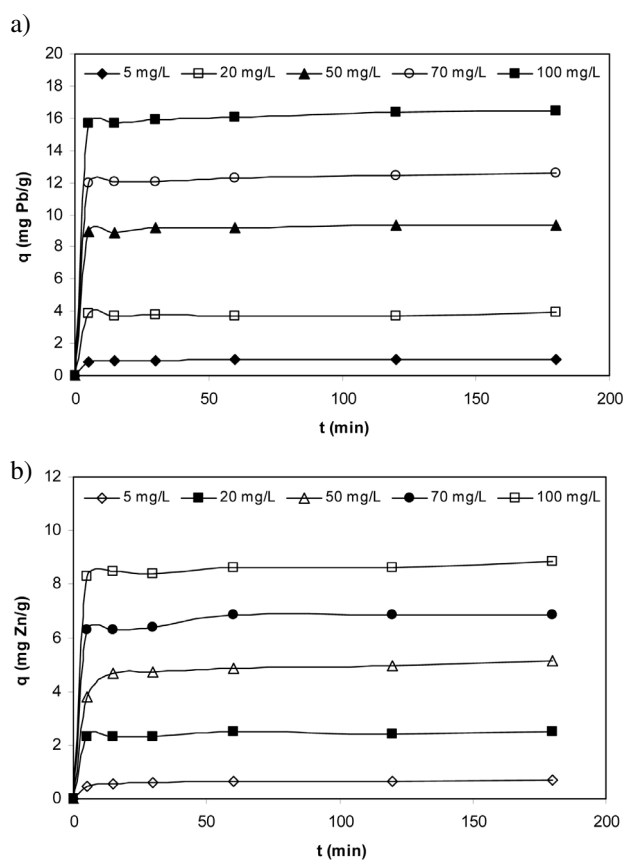


Fig. 2: Effect of contact time on biosorption for a) Pb(II) and b) Zn(II) at optimum pH values ($m = 4.0$ g/L).

3. 3. Effect of Initial Metal Concentration

The metal ion removal capacity of cone biomass is presented as a function of the initial concentration of Pb(II) and Zn(II) in the aqueous solution in Fig 3. The experiments were carried out using metal ion solutions ranging from 5 to 100 mg/L. From 5 mg/L metal ion solution, the biosorption of 82% lead and 56.2% zinc were achieved

with 4.0 g/L Nordmann fir. It was observed that the biosorption efficiency of metal ions to the cone biomass decreased as the initial concentration of metal ions was increased. The biosorption capacity increased first with increasing of the initial concentration of metal ions and reached a saturation value. At higher concentrations, more metal ions are left unadsorbed in solution due to the saturation of adsorption site. The biosorption of Zn(II) seemed to the same trends as indicated for Pb(II). When the initial concentration increased from 5 to 100 mg/L, biosorption increased from 0.7 to 8.85 mg/g for Zn(II) and 1 to 16.5 mg/g for Pb(II). It was also found that the biosorption capacities of biosorbent to Pb(II) were significantly higher than that of the Zn(II). The decrease of biosorption capacity of biomass with the increase of metal concentration

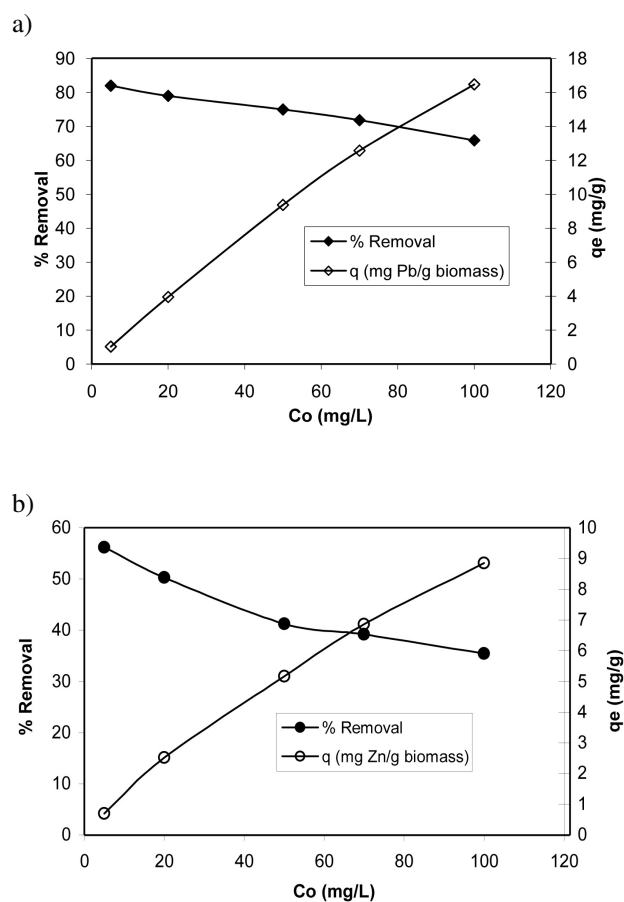


Fig. 3: Effect of initial metal concentration on biosorption capacity (q_e mg/g biosorbent) and the biosorption efficiency of Nordmann fir for a) Pb(II) and b) Zn(II) ($m = 4.0$ g/L).

could be attributed to higher probability of interaction between metal ions and biosorbents. Moreover, higher initial metal concentration provides an increased driving force to overcome all mass transfer resistance of metals between aqueous and solid phases and accelerate the probable collision between metal ion and sorbent.³⁴

3. 4. Adsorption Isotherm

Adsorption isotherms express the relation between the amount of adsorbed metal ions per unit mass of biosorbent (q_e) and the metal concentration in solution (C_e) at equilibrium. Two important isotherms are selected in this study, which are the Freundlich and Langmuir isotherms.

The empirical Freundlich isotherm model based on a heterogeneous surface is given below by Eq. (1)

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

Where q_e is the amount of metal sorbed by cone biomass (mg/g), C_e is the metal concentration in the solution at equilibrium (mg/L), K_f and n are Freundlich constants characteristic of the system. K_f and n are indicators of adsorption capacity and intensity, respectively.

The Langmuir biosorption isotherm assumes that biosorption takes place at specific homogeneous sites within the biosorbent and has found successful application in many biosorption process of monolayer biosorption. The linear form of the Langmuir isotherm equation represented by the following Eq. (2).

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

Where Q_{max} and b are Langmuir constants denoting maximum adsorption capacity and the affinity of the binding sites, respectively.

Both isotherms consider q_e as a function of the C_e , corresponding to the equilibrium distribution of ions between aqueous and solid phases as the C_e increases. The batch biosorption data were fitted to the above two models by non-linear regression analysis using the software package STATISTICA 6.0 for WINDOWS. The Freundlich and Langmuir equations for isotherm data were modelled using Simplex and Quasi-Newton algorithms. The curves in Fig. 4 were generated from Freundlich and Langmuir model equations, respectively. As seen from Fig. 4, both the Freundlich and Langmuir adsorption models were suitable for describing the short-term biosorption of lead and zinc by Nordmann fir Table 1 shows the model constants along with correlation coefficients for biosorption of lead and zinc on cone biomass.

The b values obtained from the Langmuir model, suggest that the metal binding affinity was in the order

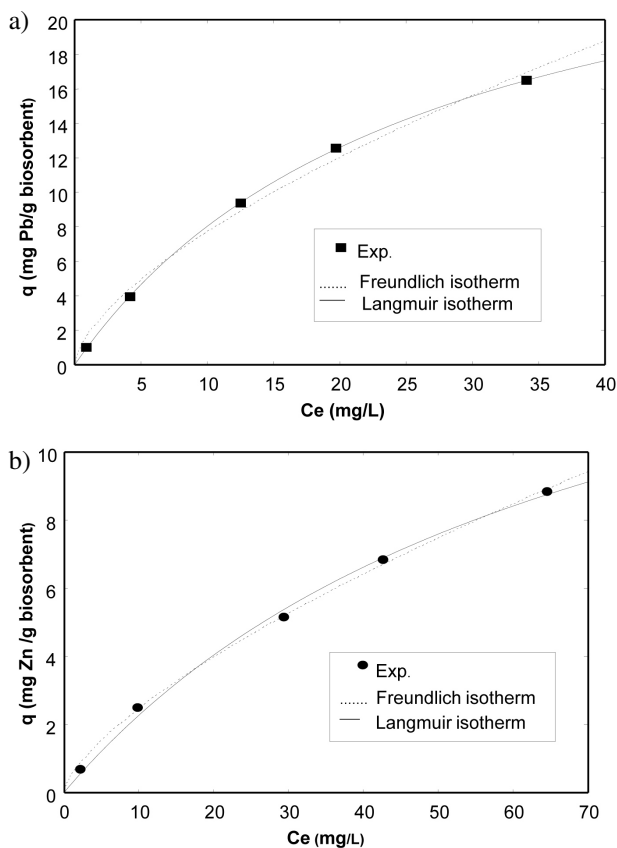


Fig. 4: Application of equilibrium adsorption models by Nordmann fir for a) Pb(II) and b) Zn(II).

Pb(II) > Zn(II). The organic functional groups in the biomass have a higher affinity for Pb(II). The experimental values of the maximal biosorption capacities (Q_{max}) of cone biomass were 29.35 and 18.41 mg/g for Pb(II) and

Table 2: Comparison of maximum biosorption capacity of Caucasian fir for Pb(II) and Zn(II) ions with those different plant biomasses.

| Adsorbent | q_{max} (mg/g) | | Reference |
|-----------------|------------------|--------|------------|
| | Pb(II) | Zn(II) | |
| Coir | 18.9 | 8.6 | 35 |
| Rice husk | 4.0 | | 36 |
| Hazel-nut shell | 1.78 | | 37 |
| Papaya wood | | 13.4 | 23 |
| Barley Straw | 15.2 | 5.3 | 38 |
| Nordmann fir | 29.3 | 18.4 | This study |

Table 1: Freundlich and Langmuir model parameters for biosorption of metal ions by cone biomass ($m = 4.0$ g/L; $T = 25$ °C).

| Metal ion | Freundlich isotherm | | | Langmuir isotherm | | |
|-----------|---------------------|------|------|-------------------|-----------|------|
| | K_f | n | R | Q_{max} (mg/g) | b (L/g) | R |
| Pb | 1.77 | 1.56 | 0.99 | 29.35 | 0.04 | 0.99 |
| Zn | 0.51 | 1.45 | 0.99 | 18.41 | 0.01 | 0.99 |

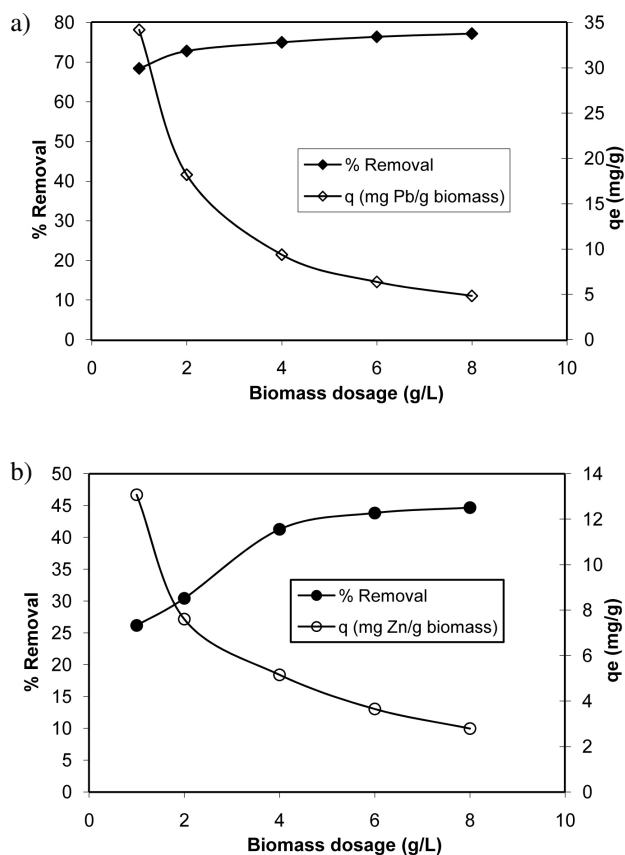


Fig. 5: Effect of initial biosorbent concentration on biosorption capacity and the biosorption efficiency of Nordmann fir for a) Pb(II) and b) Zn(II) ($C_0 = 50$ mg/L).

Zn(II), respectively. Table 2 presents the comparison of biosorption capacity of Caucasian fir for Pb(II) and Zn(II) with those of various biomasses in literature. The biosorption capacity of Caucasian fir for these metal ions is higher than that of the majority of other biomasses given in Table 2. But direct comparison is difficult due to the varying experimental conditions used in these studies.

3. 5. Effect of Biosorbent Concentration

The influence of initial biosorbent concentration on the sorption capacity of cone biomass was studied for metal concentration of 50 mg/L and a content of 1.0–8.0 g/L of biomass. The experimental results are presented in Fig. 5. The increase in biomass dose from 1.0 to 4.0 g/L resulted in a rapid increase in biosorption of metal ions. This is because of the availability of more binding sites for complexation of metal ions. The highest Pb(II) and Zn(II) uptake was observed at 8 g/L. Further, increment in cone biomass dose did not cause significant improvement in biosorption. Pb(II) and Zn(II) binding capacity values showed a reverse trend and therefore, its magnitude decrease with increment in biomass dosage. Its maximum values were, therefore, obtained for the lowest biosorbent dosage (1 g/L).

4. Conclusions

The results indicated that Nordmann fir (*Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*) cone biomass may be used as an inexpensive, and effective for the removal of lead and zinc from aqueous solutions. The lead and zinc biosorption of the cone biomass was influenced by the initial pH of solution, initial metal concentration, biosorbent dosage and contact time. Maximum uptake capacities of both metals were found to occur at pH 6.0. Lead and zinc biosorption equilibrium data were fitted by the Freundlich and Langmuir model.

5. References

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Povzetek

Raziskovali smo možnost uporabe biomase, dobljene iz storžev kavkaške jelke (*Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*), kot biosorbenta za adsorpcijo Pb(II) in Zn(II) iz vodnih raztopin. Proučevali smo vpliv pH, začetne koncentracije ionov, količino biosorbenta ter kontaktni čas na proces adsorpcije. Ugotovili smo, da proces za Pb(II) in Zn(II) poteka optimalno pri pH = 6.0 vendar je manj učinkovit pri višjih začetnih koncentracijah ionov. Pri začetni koncentraciji ionov 5 mg/L se adsorbira 82 % Pb(II) in 56.2 % Zn(II), v obeh primerih pa adsorpcijo lahko opišemo s Freundlichovo in Langmuirjevo izotermo.