Eco. Env. & Cons. 28 (January Suppl. Issue) : 2022; pp. (S306-S310)
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ISSN 0971–765X

http://doi.org/10.53550/EEC.2022.v28i01s.043

Adsorptive removal of Zn (II) Ions from Wastewater using the Biosorbent of *Tectona grandis* Leaves: Equilibrium and Thermodynamic studies

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(Received 18 August, 2021; Accepted 15 September, 2021)

ABSTRACT

This study was conducted to explore the potential of *Tectona grandis* leaves as a biosorbent for removing the Zn (II) ions from wastewater solutions at the Department of Chemistry, S. S. Jeena Campus, Almora during April - September 2019-20. The batch experiments were employed by varying pH, contact time, biosorbent dose, metal ion concentration and temperature. Fourier transform infrared (FTIR) spectroscopic analysis showed that the hydroxyl (-OH), alkane (-CH_2), amine (-NH_2) etc. groups on the surface of *Tectona grandis* leaves biosorbent (TGLB) were responsible for the binding of Zn (II) ions. The Langmuir isotherm plot was demonstrated as the most relevant for biosorption data. The process was discovered as exothermic and spontaneous involving both physical and chemical bondings.

Key words: *Biosorbent, Contact time, Exothermic, Langmuir, Optimum, TGLB*

Introduction

It is a widespread environmental problem that heavy metals pollute water bodies. Toxic metal contamination in the environment is caused by industries such as metal plating, metallurgy, chemical processing units; electroplating; mining; paint and pigment industries, dumping industrial effluents, releasing toxic industrial wastes (Zwain *et al.*, 2014). As a result of their potential to accumulate in living organisms and the food chain, these heavy metals can cause long-term health problems. In the series of toxic heavy metals zinc stands at 75th position in the ATSDR 2019 substance priority list. The World Health Organization (WHO) has defined the permissible limit of zinc in drinking water as 5 mg/l. Zn (II) toxicity can cause vomiting, anemia, stomach cramps, skin irritations, nausea, coughing, dehydration, gastrointestinal, renal, neurological disturbances Hajahmadi *et al.*, 2015). The removal of Zn (II) is therefore mandatory before effluents are discharged into the principal water sources. There are various conventional wastewater treatment methods e.g., chemical precipitation, ion exchange, reverse osmosis, solvent extraction, etc. for the removal of metals from water, but they have various disadvantages such as high operational and capital cost, a large amount of sludge generation, slow process, high energy needs, incomplete removal of contaminants (Hajahmadi *et al.*, 2015). Due to its inexpensive cost, easy availability, adsorbent renewal capacity, no secondary sludge and considerable elimination of pollutants, biosorption is a potential substitute for conventional approaches (Zuo *et al.*, 2018). Biosorption involves an adsorbent prepared with biomaterial (leaves, barks, stems and agricul-

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tural wastes) and an adsorbate solution i.e., heavy metal ions.

The present study aims to evaluate the potential of *Tectona grandis* leaves as a biosorbent for Zn (II) ions removal from wastewater.

Materials and Methods

Preparation of biosorbent

Tectona grandis (teak) leaves were collected from the immediate vicinity of Board Office Colony, Ramnagar, Uttarakhand, India (29°23′37″N 79°07′08″ E). To eliminate dust and soluble contaminants, these leaves were washed thoroughly with double distilled water and dried for 48 hours in a hot air oven (Popular Traders S.N.-1680) at 333 K. Then, they were crushed and ground in a domestic grinder to get the powdered form. The powdered biomass was soaked in 0.1N HNO_3 for activation up to 24 hours at room temperature, then filtered and rinsed with double distilled water. The activated biomass was placed in a hot air oven for drying at 333K for 48 hours. Then it was passed through 63-micron sieves (240 BSS). Then, the sieved biomass was stored in an airtight bottle.

Preparation of adsorbate

The stock solution of Zn (II) ions of 1000 mg/l concentration was prepared by dissolving 4.376g of $ZnSO_4.7H_2O$ in 1000mL of double-distilled water. The pH of the working solutions was adjusted using 0.1 N HCl and 0.1N NaOH. A digital pH meter (Model: Systronic 361) was used to monitor the pH value of the solution.

Biosorption experiments

Batch experiments have been used to analyze the impact of numerous parameters on metal ion removal, like pH, contact time, biosorbent dose, metal ion concentration, and temperature. By altering the parameter under study while keeping the others constant, the optimum condition of each parameter was identified. The experiments were conducted with 100mL of standard solution using conical flasks of 250mL. The solution was filtered with Whatman no. 42 filter paper and filtrate was digested with conc. HNO_3. The digested solution was analyzed by atomic absorption spectrophotometer (Optima 4300DV ICP, Perkin- Elmer, Boston, MA). The removal efficiency for each experiment was calculated by using equation (1) as follows:

$$\text{Removal }\% = \frac{C_i - C_e}{C_i} \times 100 \quad ..(1)$$

Where C_i is the initial metal ion concentration (mg/l) and C_e is the equilibrium metal ion concentration (mg/l).

Adsorption isotherm models

Langmuir adsorption model

This model is premised on a presumption that solutes are adsorbed in a monolayer onto the adsorbent's surface with a definite number of identical binding sites and uniform adsorption energy (Langmuir, 1917). Langmuir adsorption model is expressed as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad ..(2)$$

Where C_e is the metal ion concentration at equilibrium (mg/l), Q_e is the amount of metal ions removed (mg/g), K_L is Langmuir isotherm constant (l/mg) and Q_{max} is the maximum adsorption capacity (mg/g). The interaction between metal ions and the adsorbent surface is further calculated by dimensionless constant i.e., separation factor (R_L). R_L is expressed as follows:

$$R_L = \frac{1}{1 + K_L C_o} \quad ..(3)$$

Where C_o is the initial amount of adsorbate (mg/l) and K_L is the Langmuir constant (l/mg). The isotherm is favorable if $0 < R_L < 1$, unfavorable if $R_L > 1$ irreversible if R_L=0 and linear if R_L=1.

Freundlich adsorption model

This isotherm model consists of an empirical equation that proposes multilayer adsorption on the heterogeneous surface (Freundlich, 1907). It is expressed mathematically as follows:

$$\log Q_e = \frac{1}{n}\log C_e + \log K_F \quad ..(4)$$

Where, K_F is the Freundlich isotherm constant related to the adsorption capacity of the adsorbent and n is an empirical constant. If the value of 1/n is between 0 and 1, then it implies that the adsorption process is favorable.

Temkin adsorption model

The basis of Temkin isotherm relates with an assumption that due to adsorbent-adsorbate interactions, adsorption energy reduces linearly with surface coverage (Temkin, 1940). It can be represented in linear form as follows:

$$Q_e = B_T \ln A + B_T \ln C_e \quad .. (5)$$

Where, b_T is the Temkin constant related to the heat of adsorption (b_T= RT/b, where R=8.314J/mol/K, T is the absolute temperature and b is the heat of adsorption in J/mol), A is the equilibrium binding constant (L/g).

Thermodynamic study of adsorption

Thermodynamic parameters such as a change in Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were calculated using the following equations:

$$\Delta G^o = -RT \ln KC \quad .. (6)$$

$$K_c = \frac{Q_e}{C_e} \quad .. (7)$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad .. (8)$$

Where, R is the universal gas constant (8.314 J/mol/K), T is the temperature (K), Q_e is the concentration of adsorbed metal ions (mg/l), C_e is the metal ion concentration in solution (mg/l) and K_c is equilibrium constant.

Statistical Analysis

Data values are displayed as the mean ± standard error based on at least three independent experiments. The single-factor analysis of the experimental data was done for the level of significance at 5% to compare the treatment means.

Results and Discussions

FT-IR Characterization

The presence and shift of functional groups on TGLB before and after adsorption of Zn (II) ions was analyzed Fourier transform infra-red (FT-IR) spectrometer (Perkin Elmer, USA, Model: Spectrum 400) within the range 400-4000cm^{-1}, which are shown in figure1. The peak at 3433.652cm^{-1} represents the hydroxyl (-OH) group, at 2921.477cm^{-1} represents the asymmetric $-CH_2$ and –CH stretching vibrations, 1059.917cm^{-1} represents C-O stretching and at 619.151cm^{-1} represents the presence of aromatic amino acids ($-NH_2$ group) before the adsorption of Zn (II) ions (Rafatullah *et al.,* 2012). These peaks shift

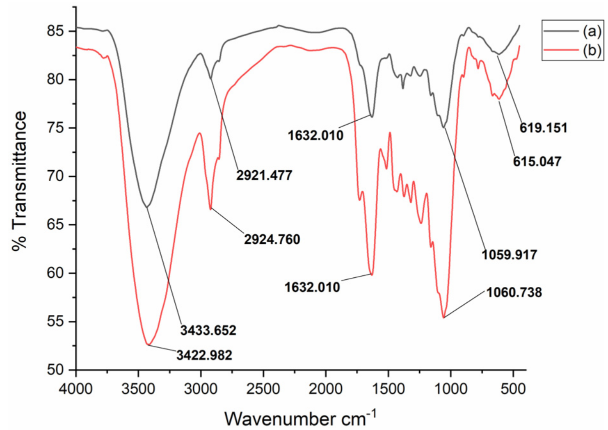

Fig. 1. FT-IR spectra of TGLB before (a) and after (b) adsorption of Zn (II) ions

to 3422.982, 2924.760, 1060.738, 615.047cm^{-1}after biosorption indicating the involvement of the corresponding functional groups in binding Zn (II) ions to TGLB surface.

SEM Analysis

The surface morphology of the biosorbent surface was captured and analyzed by Scanning Electron Microscope (SEM) (JEOL, Japan, Model: JSM 6100). The SEM images of TGLB surface before and after adsorption of Zn(II) ions are shown in figure 2. The difference between the before and after adsorption images is clearly visible.

Effect of pH

The effect of pH on % removal of Zn (II) ions by TGLB was analyzed by changing the pH from 2 to 7. It was ascertained that the % removal efficiency of Zn (II) elevated from pH 2-5 and then dropped from pH 5 to pH 7. It is attributed to the dense concentration of H^+ ions at smaller pH values that have higher mobility than the heavy metal ions and get attached with the biosorbent active sites before the metal ions. However, at higher pH, the possibility of generating the metal hydroxide complexes also increases, which consequently decreases the number of free-moving metal ions (Kumar *et al.,* 2020).

Effect of contact time

On increasing the contact time from 20 min to 80 min, there was a steep increase in the %removal (54.3% to 78.1%), from 80 min to 120 min, it was slower. This indicated that the active sites were filled very rapidly in the initial phase, while there were fewer active sites available on the biosorbent

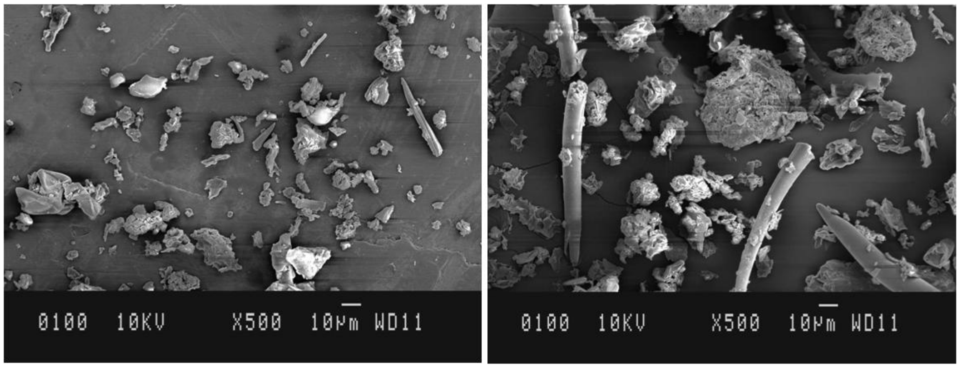

Fig. 2. SEM images of TGLB surface before and after adsorption of Zn (II) ions respectively

surface for further adsorption (Vishwakarma *et al.*, 2018).

Effect of biosorbent dose

The percentage of adsorbed Zn (II) ions increased from 71.96% to 87.7 % when the biosorbent dose was increased from 1 g to 5 g. This initial rise is obvious because raising the biosorbent dose increases the number of functioning sites for metal ions to chelate with. However, the later small changes can be attributed to accretion in the number of active functioning sites while the metal ions concentration was fixed at 10 mg/l (Kumar *et al.*, 2020).

Effect of initial metal ion concentration

The percent removal decreased from 70.16% to 56.89% on increasing the metal ion concentration from 10 mg/l to 50 mg/l. As the metal ion concentration increases, all the active sites get filled gradually and there is no room for the rest of the metal ions to fill at higher metal ion concentrations, resulting decrease in overall % removal.

Effect of temperature on % removal efficiency

The effect of temperature on % removal was examined at temperatures 298, 308, 318, 328, 338K. It increased from 75.8% to 78.46% on increasing the temperature from 298K to 308K and then gradually decreased up to 50.7% at 338K.

All the results were analyzed by single-factor analysis as shown in Table 1.

Biosorption thermodynamics

The findings of thermodynamic parameters are shown in Table 2. The negative values of ΔG^o and ΔH^o indicated that the biosorption process of Zn (II) ions on TGLB is spontaneous and exothermic. The negative value of ΔS^o(-68.997 KJ/mol) demonstrated a decrease in standard entropy on the biosorbent surface after the biosorption process indicating that the process is associative.

Also, the ΔG^o values appeared to rise for 308K and then continuously drop with an increase in temperature, implying that the biosorption process became less spontaneous at higher temperatures and involved physisorpton. Similar results were found in the case of biosorption of Cd (II) using meranti

Table 1. Effect of varying biosorbent dose, metal ion concentration and temperature on removal of Zn (II)

pH		Contact time		Biosorbent dose		Metal ion concentration		Temperature	
pH	C_e(mg/l)	T (min)	C_e(mg/l)	Dose (g)	C_e(mg/l)	C_i(mg/l)	C_e(mg/l)	T(K)	C_e(mg/l)
2	7.21±0.095	20	4.57±0.046	1	2.80±0.96	10	2.98±0.066	298	2.42±0.040
3	5.87±0.064	40	3.35±0.09	2	2.41±0.023	20	6.57±0.161	308	2.15±0.035
4	4.64±0.080	60	2.65±0.049	3	1.92±0.102	30	10.95±0.156	318	2.87±0.055
5	2.35±0.051	80	2.19±0.038	4	1.55±0.067	40	15.91±0.107	328	3.52±0.038
6	3.01±0.038	100	2.06±0.029	5	1.23±0.055	50	21.55±0.098	338	4.93±0.070
7	3.47±0.064	120	2.06±0.029	-	-	-	-	-	-
CD	0.212	0.159		0.238		0.394		0.157	
SE(m)	0.068	0.051		0.074		0.123		0.049	

±Standard Error, SE (m) Standard Error Mean, CD Critical Difference

Table 2. Thermodynamic parameters value for adsorption of Zn (II) ions on TGLB

Metal ion	T(K)	ln Kc	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS°(J/mol/K)
Zn (II)	298	1.1417	-2.8287	-23.994	-68.997
	308	1.2950	-3.3162		
	318	0.9099	-2.4059		
	328	0.6102	-1.6641		
	338	0.0280	-0.0786		

Table 3. Parameters of the Langmuir, Freundlich and Temkin isotherm models for Zn (II) biosorption on TGLB

Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
K_L(L/mg)	Q_{max}(mg/g)	R^2	K_F(mg/g)	1/n	R^2	b_T(J/mol)	A (L/g)	R^2
0.0893	4.3103	0.999	0.4742	0.606	0.981	0.957	0.864	0.996

wood biosorbent (Rafatullah *et al*., 2012).

Biosorption Isotherms

Langmuir isotherm model showed the best fit (R^2=0.999) that implied the monolayer adsorption on the homogeneous surface of TGLB. The value of Freundlich constant 1/n was 0.606 and the R_L values corresponding to the Langmuir isotherm were 0.528, 0.459, 0.271, 0.218, 0.182 for initial metal ion concentrations of 10, 20, 30, 40, 50 mg/l respectively i.e., between 0 and 1, which implied favorable adsorption of Zn (II) ions. The various parameters of Langmuir, Freundlich and Temkin isotherm models are shown in Table 3.

Conclusion

The batch experiments conducted in current study demonstrated TGLB as a significant and cost-effective biosorbent for Zn (II) ions removal from contaminated wastewater. The optimum value of pH was 5. The maximum capacity for monolayer adsorption was 4.31 mg/g. Langmuir isotherm model was the best-fitted model with experimental findings. The process of biosorption was asserted to be spontaneous (ΔG°=(-)ve), exothermic (ΔH°=-23.994KJ/mol) and followed an associative mechanism. Physical interactions and chemical bonds were included in the biosorption mechanism. Using *Tectona grandis* leaves as biosorbent for decontaminating the water is a cost-effective and eco-friendly way and can also serve a good example of waste management.

Acknowledgment

The authors are thankful to the College of Veterinary and Animal Sciences (G. B. Pant University of Agriculture and Technology), Pantnagar; Sophisticated Analytical Instrumentation Facility (SAIF) and Central Instrumentation Laboratory (CIL) (Punjab University), Chandigarh for providing lab facilities for AAS, SEM and FT-IR tests respectively.

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