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Removal of Zn (II) ions from aqueous solution and industrial waste water using leaves of *Araucaria cookii*

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ABSTRACT

Removal of Zn (II) ions was investigated from aqueous solution using the leaves of *Araucaria cookii*. The factors influencing Zn (II) ion adsorption were pH, contact time, and adsorbent mass and metal ion concentration. Maximum adsorption of Zn (II) ions was at pH 9, contact time of 70 min, adsorbent mass of 2g, and ion concentration of 200 ppm with agitation speed of 200 rpm. Maximum uptake of bio sorbent was 97.9%. Using contact time pseudo first order and pseudo second order reactions were studied. Isotherm investigations were studied using Langmuir and Freundlich equations.

Key words: Biosorption, *Araucaria cookii* (A.C.), Zinc, Langmuir, Freundlich.

INTRODUCTION

Zinc is a very common heavy metal that occurs naturally in the environment and its spread through the environment is a natural phenomenon. Zinc is occurring in the earth's crust at an average concentration of 70 mg/kg and it is classified as a border line metal. Under aerobic conditions, Zinc is the predominant species at acidic pH, but it is replaced by Zn (OH)₂ at pH 8-10 [1]. Zinc is put at 74th rank with a score of 932.89 points in the series of toxic heavy metals, as per Comprehensive Environmental Response Compensation and Liability Act (CERCLA) 2007[2].

Zinc is naturally released into the environment, although industrial activities are mostly responsible for zinc pollution. Elevated levels of zinc may come from a variety of sources like mining and foundry activities, zinc, lead and cadmium refining, electroplating, steel production, carbon combustion, and solid waste incineration. Various zinc salts are used as in wood preservative, catalyst, photographic paper, and accelerators for rubber vulcanization, ceramic, textiles, fertilizers, pigments, and batteries [3]. Due to its mobility in natural water ecosystems and its toxicity to higher life forms it causes bio transformation and biomagnifications in the food chain [4].

United States Environmental Protection Agency (USEPA) and World Health Organisation (WHO) have demarcated the permissible limit of Zinc in waste water and potable water as 5 mgL⁻¹ and 3mgL⁻¹, respectively [5, 6]. The excessive intake of metal by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney [7].

The traditional approaches for the removal or recovering metals such as precipitation, oxidation/reduction, ion exchange, filtration, electrochemical processes, membrane separations and evaporation, exhibit several disadvantages such as high cost, incomplete removal, low selectivity, high energy consumption, and generation of toxic slurries that are difficult to eliminate [8].

Biosorption of heavy metals by biomass has been much explored in recent years. Activated carbon is a common adsorbent but due to its high cost, and cheaper, more accessible, eco friendly and highly efficient adsorbent materials like [9] rice husk [10], saw dust [11], pine bark and canola meal [12, 13], sea weed [14] pine bark, pine needles and leaves [15], cashew nut shell [16], Potato peel waste [17].

The present work is aimed to develop a cost effective Zn adsorbent from *Araucaria cookii* (Commonly called X-mas tree) leaves powder. It is a coniferous tree included in the family Araucariaceae. They are magnificent evergreen trees with apparently whorled branches and stiff, flattened pointed leaves. In the present study dried foliage leaves of *A. cookii* were examined for their sorption properties towards Zn (II) ions. The effects of various parameters such as pH, contact time, initial Zn (II) concentration, particle size and it does have been studied. Adsorption kinetics and isotherm models were used in to evaluate experimental data and to find out the possible biosorption mechanism.

MATERIALS AND METHODS

Biomass preparation

Leaves of *A. cookii* used as the biosorbent were obtained in dry form from Mysore city, Karnataka state, India. The leaves were washed with deionised water, cut into small pieces, sun dried for seven days followed by drying in an oven at 70°C for 24 h. Subsequently, the material was ground and sieved through laboratory sieves to get fraction of 100 µm, 200 µm and 300 µm. The sieved biosorbent was washed several times to remove the dust particles in the dried form and stored in a dry place until the usage.

Preparation of adsorbate

Metal ion solution of Zn²⁺ was prepared from Zinc sulphate 7- hydrate purified Merck- A.R. grade stock standard of concentration 1000 mg/L. The synthetic waste water was prepared by diluting the stock standard. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH. The final concentrations of metal ions were analysed by AAS.

Simulation studies

Industrial waste water samples were collected from electroplating industries located in Mysore city, Karnataka, India. The water samples were shaken in a rotary shaker at 200 rpm for 10 min. The slurry after mixing with the biosorbent was centrifuged at 5000 rpm for 30 min. The clean filtrate after decantation was subjected to analysis for various parameters following standard methods (APHA 1998) [18]. The concentrations of heavy metals were analysed by AAS. The results are given in the Table 1.

Table 1: Physico-chemical characteristics of industrial waste water

Parameter	Characteristics
Colour	Brown
pH	5.8
Total dissolved solids (mg/L)	15,000
Suspended solids	1,600
Chloride (mg/L)	510
Sulphate (mg/L)	380
Calcium (mg/L)	1890
Magnesium (mg/L)	610
Iron (mg/L)	2
Zinc (mg/L)	24
Nickel (mg/L)	6

Biosorption Experiments / Batch Experiments

The effects of various parameters on the removal of Zn²⁺ using *Araucaria cookii* were studied. Batch adsorption studies were conducted at room temperature by taking, 20 ml of 1000 mg/l of Zn²⁺ in a pre cleaned capped tubes and adjusting to required pH. 2 g/L adsorbent was shaken at a constant stirring speed of 200 rpm in a rotary shaker. Samples were withdrawn at appropriate time intervals (10- 90 min) and the adsorbent was separated by centrifugation at 6000 rpm for 10 min. The supernatant was analysed for residual metal ion concentration. Each experiment was conducted in triplicate and the mean values were considered. The per cent removal of Zn (II) was calculated for each run using the following formula.

$$R = (C_0 - C_f) \times 100 / C_0 \quad (1)$$

Where, C₀ and C_f were the initial and residual concentration of Zn (II) respectively in solution in mg/L.

The amount of metal uptake by plant biomass was calculated as the difference between the initial and final concentrations of metal after adsorption in the aqueous solution. The metal uptake capacity was determined using the following formula:

$$q = V (C_0 - C_f) / m \quad (2)$$

Where, q is the Zn (II) uptake (mg/g), C_0 and C_f are the initial and final Zn (II) concentration respectively in the solution (mg/l). V is the solution volume (L) and m is the mass of adsorbent (g)

Effect of pH on Biosorption studies

In order to find out the influence of pH on adsorption of Zn^{2+} using the dried leaves of *A.cookii*. were studied at pH range of 1-10 by the following procedure as reported earlier [19]. Twenty ml of 1000 mg/l of Zn^{2+} ions were taken in pre-cleaned capped tubes. The pH of the solution was adjusted as required by using 0.1M HCl or 0.1M NaOH.

Effect of size variation on biosorption

The effect of size variation (100-400 μ m) on adsorption capacity was studied by taking 20 ml of 1000 mg/l of Zn (II) ions in pre cleaned capped tube at pH 9, with contact time of 70 min. The resulting mixture was stirred in a rotary shaker. After 30 min it was filtered and Zn content was measured.

Effect of dosage

The adsorption capacity of Zn (II) in biosorbent, was determined by taking varying dosage from 0.2 to 4g of biosorbent in a pre cleaned separate capped tube containing 20 ml of 1000mg/l of Zn (II) solution and adjusting pH to 9. The mixture was agitated for 30 min in mechanical rotary shaker. The unadsorbed Zn (II) was measured by AAS.

Effect of contact time on Bio sorption

The effect of contact time on adsorption of Zn (II) on *A.cookii*. was studied by taking 20 ml of (1000mg/l) Zn(II) in a pre cleaned capped tube containing 2g of adsorbent and adjusting pH to 9. The mixture was shaken for different time intervals varying from 10 to 90 min. The resulting solution was filtered and measured for residual Zn (II) by AAS.

Effect of metal ion concentration

The initial metal ion concentration was varied from 25 to 250 mg/l. Zn (II) solution was taken in a pre cleaned capped tube and the study was done by taking biosorbent dose of 2g/l, at pH 9 with contact time of 70 min biosorbent volume of 100 μ m at room temperature. The mixture was shaken (200 rpm) for 30 min. The supernatant solution was used to measure unadsorbed Zn (II) ions by AAS.

RESULTS AND DISCUSSION

3.1 Effects of Initial pH of the Biosorption

The pH of the solution is the most important parameter in the biosorption of Zn^{2+} ions. The pH value affects the surface charge of the biosorbent [20]. The pH of the solution controls the biosorption process. A lower pH to the acidic range makes the biosorbent to be highly protonated hence the amount of metal ions sorption gets reduced to 55%. This is because the metal ions are prevented from binding to the functional groups on the biosorbent. Increase in pH enhances the sorption process up to 97.9 % at pH 9. These studies were not extended to higher pH, because of the precipitation of Zn (II) ions when it forms hydroxides. According to Sengil et.al. [21] at lower pH, H^+ ion competes strongly with Zinc ions for active sites. When the pH is increased, the competing effect of H^+ ions decreases and consequently the metal uptake gets increased Fig. 1.

3.2 Effect of Particle size

The average particle size was changed from 100 to 400 μ m keeping the other variables constant. The adsorption capacity of metal ions on *Araucaria cookii* increased by decreasing the particle size (Fig 2). This result can be attributed to the relationship between the effective specific area of the adsorbent particles and their sizes. This can be explained by the fact that for small particle a large external surface area results in a power driving force per unit surface area for mass transfer [22]. Similar results were obtained by Israel et al., [23].

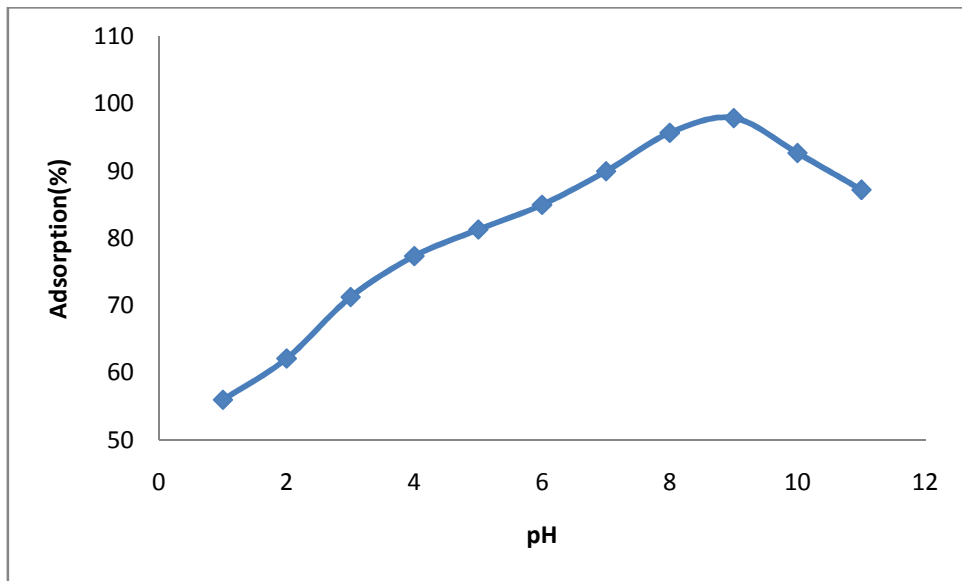


Fig.1. Effect of pH on adsorption of Zn (II) by A.cookii

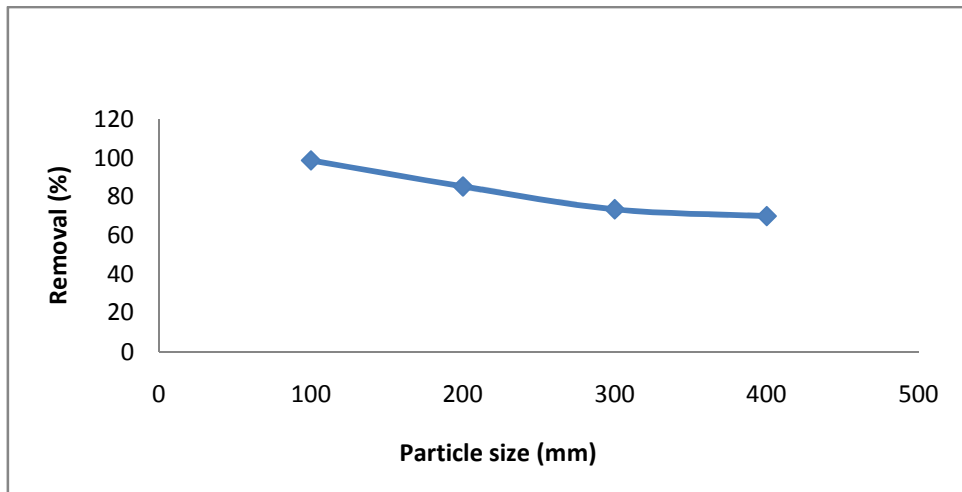


Fig.2. Effect of particle size on adsorption of Zn (II) by A.cookii

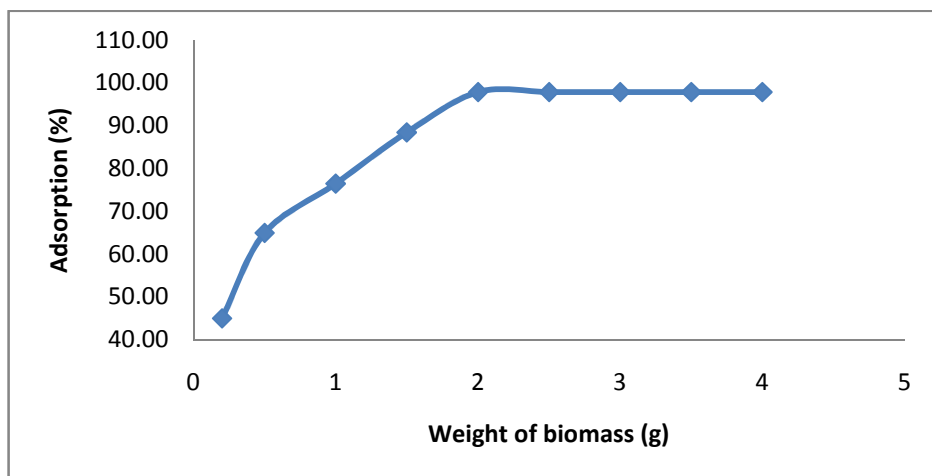


Fig.3. Effect of biomass variation on adsorption of Zn (II) by A.cookii

3.3 Effect of Biomass dosage

The biosorbent dose is an important parameter to study adsorption capacity of Zn (II) with fixed metal ion concentration (200 mg/L^{-1}). The percent removal of metal ion increases with increasing weight of the biosorbent from 0.2 g to 4 g/L^{-1} as shown in Fig 3. The percent removal of Zn (II) ion reaches maximum at 2 g/L^{-1} of biosorbent. The maximum biosorption efficiency of Zn (II) on *A.cookii* was 97.9% at 2 g/L^{-1} biomass dose. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in surface area and more adsorption sites available [24, 25]. Further increase in adsorbent dose beyond 2 g/L^{-1} keeps Zn (II) adsorption static which may be due to attainment of equilibrium between liquid and solid phases [26]. The adsorbed ions either block the access to the initial pores or cause particles to aggregate thereby reducing the active available site [27]. Similar results were reported by Kannan et al., [26] and Greene et al., [28].

3.4 Effect of contact time on biosorption

The effect of contact time on biosorption was studied on *A.cookii* (Fig 4). This was achieved by varying the contact time from 10 - 90 min in a separate runs. The rate of adsorption increased with increase in contact time. The biosorption of Zn (II) on *A.cookii* was rapid in the first 10 min and maximum (97.9 %) was reached at 70 min. After 70 min the rate of adsorption was static. This may be due to the decrease in available sites caused by blocking access to initial pores or aggregation of particles reducing active site availability [27]. Similar results were reported by Saeed et al [29].

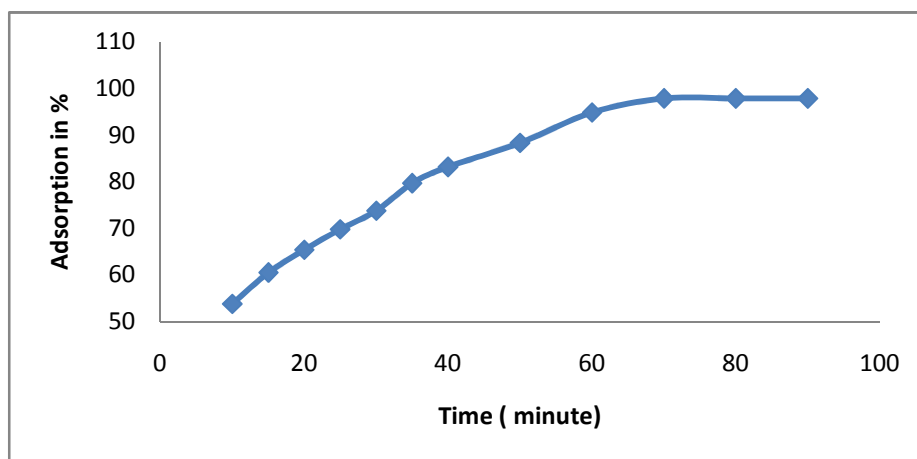


Fig.4. Effect of contact time on adsorption of Zn (II) by *A.cookii*

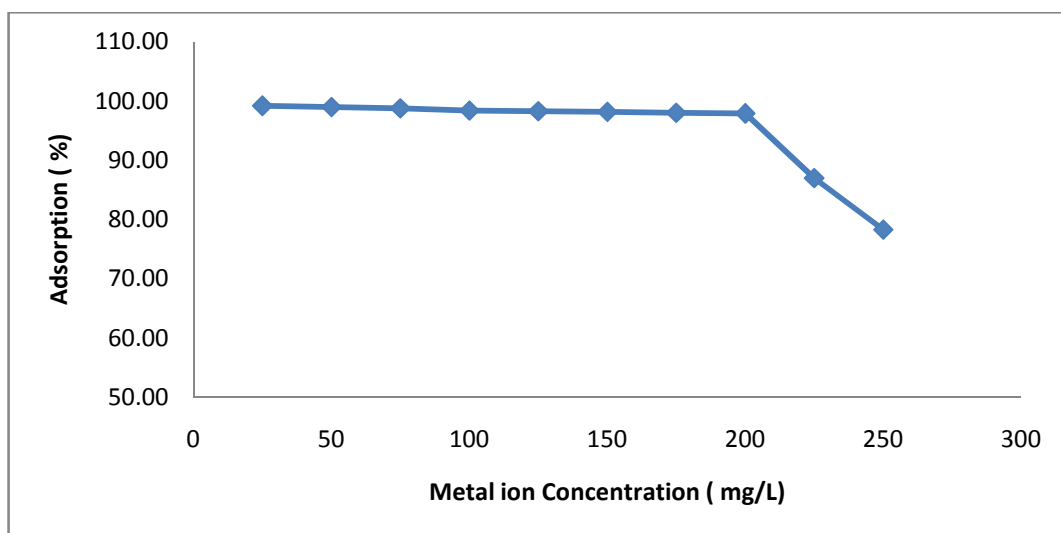


Fig.5. Effect of Zn (II) ion concentration on adsorption by *A.cookii*

3.5 Effect of initial metal ion concentration

The removal of Zn (II) as a function of metal ion concentration by *A.cookii* is depicted in Fig 5. The initial metal ion concentration was increased from 25 to 250 mg/L. The percentage removal of Zn (II) was higher at lower

concentration and decreased at higher concentration. Per cent removal decreased from 99.2 to 78.32% as initial metal concentration was increased from 25 to 250 mg/l. This may be due to the fact that at lower concentration the ratio of the initial moles of Zn (II) surface area available was low and subsequently fractional sorption became independent of the initial concentration [20]. Similar study was reported by Lehman [30] also.

3.6 Adsorption Kinetic study

The effect of contact time on biosorption has been used to examine the mechanism of biosorption processes such as mass transfer and chemical reaction, and a suitable kinetic model was used to analyze the data. Hence, pseudo- first order and pseudo- second order rate equations were applied.

Pseudo- first order model

The pseudo- first order rate expression based on solid capacity is generally expressed as follows [31].

$$\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \quad (3)$$

Where, q_e is the amount of metal adsorbed (mg/g), q_t is the amount of metal adsorbed at time t (mg/g), K_1 is the rate constant of pseudo first order adsorption (l/min). Values of adsorption rate constant (K_1) for the metal adsorption onto *Araucaria cookii* were determined from the straight line plot of $\log (q_e - q_t)$ against t . The data fitted with a poor correlation co-efficient (Fig 6) thereby indicating that rate of removal of Zinc onto *Araucaria cookii* did not follow the pseudo first order equation. The values of Pseudo first order equation parameters together with correlation co-efficient are given in the Table 2.

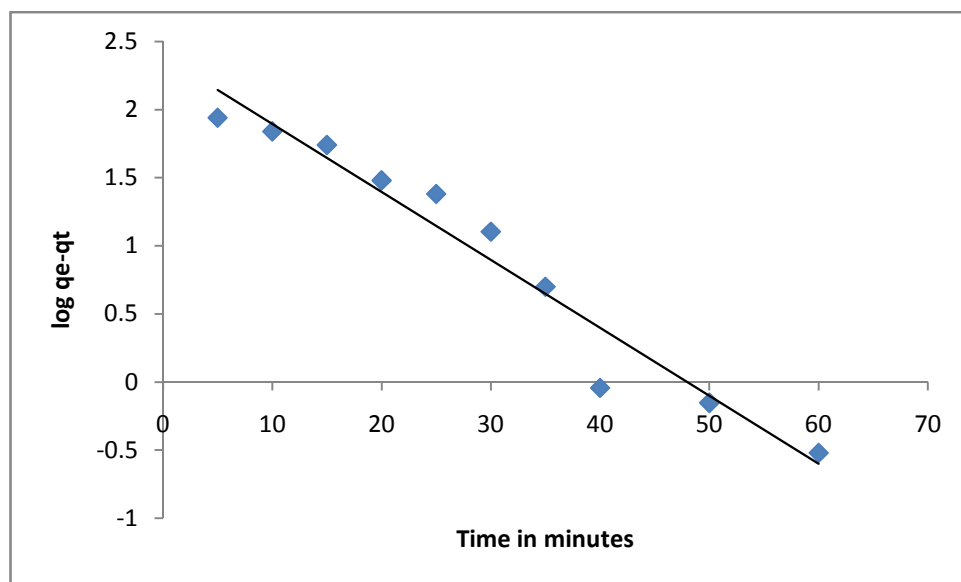


Fig.6. Pseudo first – order sorption Kinetics for Zn (II) by A.cookii

Pseudo second order model

Table 2: Pseudo first- order and Pseudo second –Order constants for Zn (II) biosorption by A. cookii

Metal	Pseudo first order			Pseudo second order			
	q _e (mg/g ¹)	K ₁ (min ⁻¹)	R ²	q _e (mg/g ⁻¹)	K ₂ (g mg ⁻¹ min)	R ²	h
Zn (II)	1.2070	0.00427	0.9816	1.738	0.1297	0.999	0.3917

The pseudo second order equation is also based on the sorption capacity of the solid phase. It predicts the behavior over the whole range of data. It is also in agreement with chemisorptions being the rate controlling step and is expressed as [32].

$$d_q/dt = K_2 (q_e - q_t)^2 \quad (4)$$

Where, q_t and q_e are the amount of metal adsorbed at time t and at equilibrium (mg.g⁻¹) and K_2 (g.mg⁻¹ min⁻¹) is the pseudo second order rate constant for adsorption process. The integrated form of equation (4) can be expressed as

$$t/q = 1/K_2q_e^2 + 1/q_e t \quad (5)$$

The initial sorption rate, h (mg/g. min), at $t = 0$ is defined as

$$h = K_2 q_e^2 \quad (6)$$

Where, K_2 and h values were determined from the slope and intercept of the plots t/q against t (Fig 7). The straight lines in the plot of linear pseudo- second order equation show good agreement of experimental data with the pseudo second order kinetic model for different initial metal ion concentrations. The values of pseudo second order equation parameters together with correlation coefficients are shown in Table 2 and Fig.7. The correlation co-efficient for the equation was $R^2 = 0.998$ and this was true for all concentrations. The calculated q_e values also agree very well with the experimental data. This strongly suggests that the biosorption of Zn^{2+} metal on to *A.cookii* is most appropriately represented by Pseudo second order adsorption process [21, 25]. Thus pseudo second order models suitably describe the adsorption of kinetic data in the present study. This model assumes two reactions non chemical equilibrium and non physical equilibrium [33, 34]. The first reaction is fast and second reaction is slower that can continue for a longer period. The sorption rate h has been widely used for evaluation of sorption rates [35]. In the present study, the value of h is 0.3917 and K_2 is 0.1297 (g/mg/min). This confirms that there is more than one mechanism involved in the adsorption process [36]. Similar performances have been observed in the bio sorption of Cu^{2+} on green algae [25] Sugar beet pulp [37] and activated wood saw dust [7].

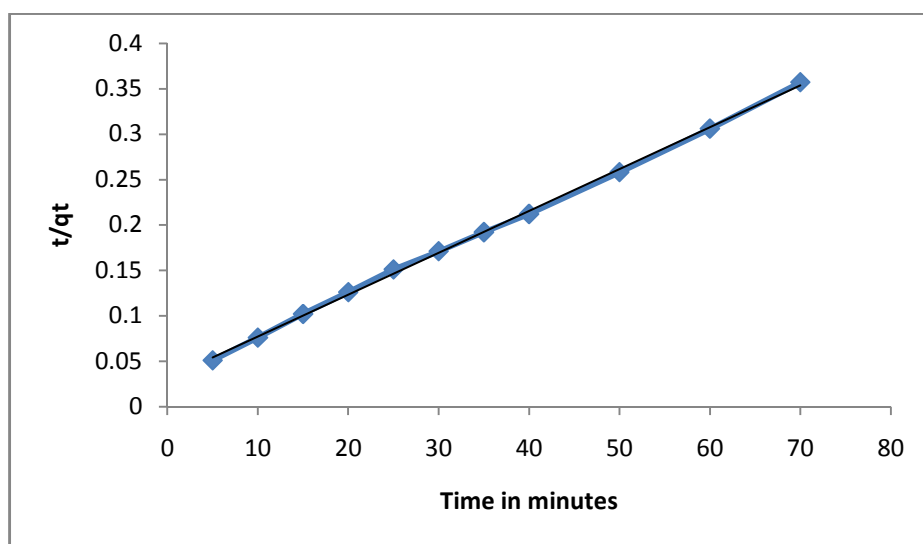


Fig.7. Pseudo second– order sorption Kinetics for Zn (II) by A.cookii

Isotherm studies

The equilibrium between an adsorbate in the active site of an adsorbent and the adsorbent remaining in aqueous phase is usually presented by adsorption isotherm. The effect of contact time on the biosorption of Zn^{2+} by *A.cookii* was studied and the results shown in Fig.8. In order to describe the adsorption mechanism of low-cost adsorbents used for water and waste water treatment experimental equilibrium data are most frequently modeled by the relationship developed by Langmuir isotherm [38] which is expressed as follows.

$$C_e / q_e = 1/ q_0b + C_e / q_0 \quad (7)$$

Where, C_e and q_e are the residual and metal uptake capacity mg/L⁻¹ respectively, b is the adsorption equilibrium constant (L/mg) related to adsorption and q_0 is the maximum monolayer capacity of the adsorbent (mg/g). The constant b and q_0 are calculated from slope and intercepts of the plot between C_e / q_e v/s C_e and are 0.0520 and 1.26, respectively where co-efficient is found to be close to unity(0.9986) (Table 3).

Table 3: Langmuir and Freundlich constants for Zn (II) biosorption by A. cookie

Metal	Langmuir			Freundlich		
	q_{max}	b	R^2	K_f	$1/n$	R^2
Zn(II)	21.73	0.0520	0.998	18.20	0.9666	0.999

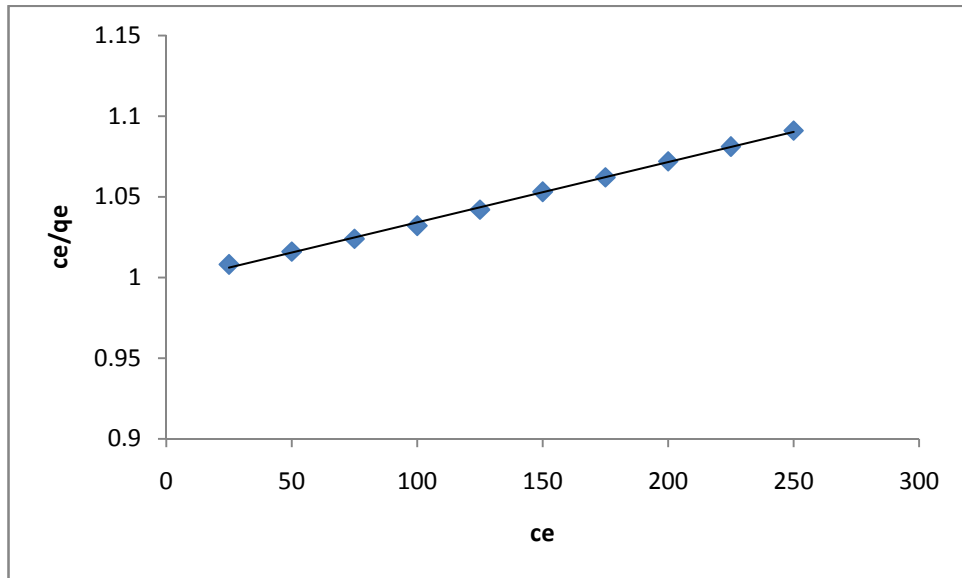


Fig.8. The linearized Langmuir adsorption isotherms of Zn (II) by A.cookii

The Freundlich isotherm [39] model describes multi layer adsorption with the assumption of heterogeneous surface in which the energy, a term in the Langmuir equation varies as a function of the surface area. The model can be represented as

$$q = K_f C_e^{1/n} \quad (8)$$

And the linearized form can be represented as

$$\log(q) = \log(K_f) + 1/n \log(C_e) \quad (9)$$

Where, q is the amount of metal adsorbed per unit weight of the adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium of metal concentration (mg l^{-1}), K_f is the measurement of adsorption capacity (mg g^{-1}) based on Freundlich isotherm, n is the adsorption equilibrium constant shown in Fig. 9. The results are represented in Table 3.

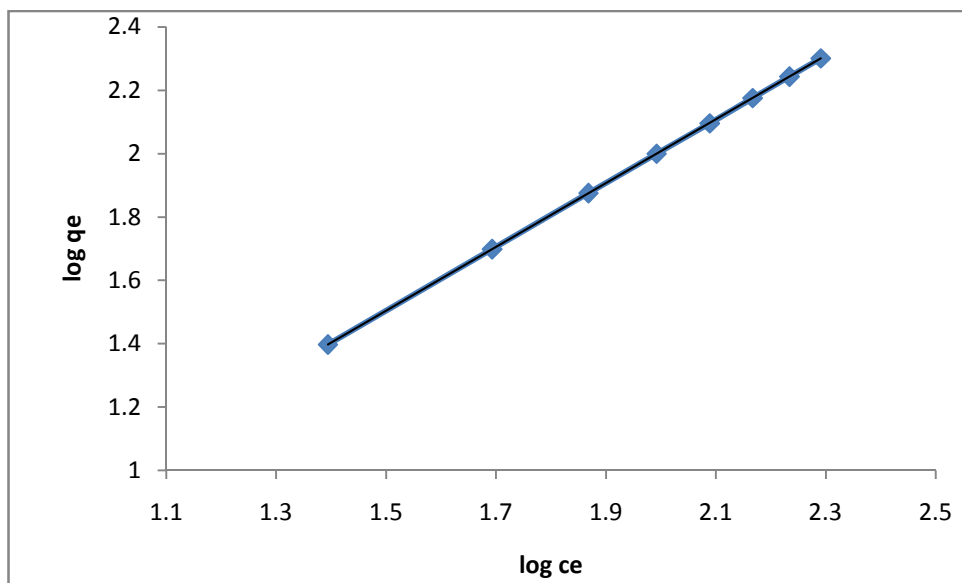


Fig.9. The linearized Freundlich adsorption isotherms for Zn (II) by A.cookii

Removal of Zinc (II) ions from Industrial waste water

The removal of Zn (II) ions from industrial waste water was carried out by batch method under optimum conditions. Hundred ml of electroplating waste water was taken in a 250 ml conical flask. The pH was adjusted to 9 using 0.1 N NaOH. The removal of Zn (II) was carried out as described in adsorption experiments. Removal of Zn (II) by A.C. from industrial waste water was found to be 86%.

CONCLUSION

- (1) The present study reveals that the leaves of the *Araucaria cookii* can be used as biosorbent for the removal of Zn (II) ions from the industrial effluent.
- (2) This adsorption process is influenced by factors like pH, adsorbent mass, contact time and metal ion concentration. Maximum adsorption was achieved at pH 9 and the optimum dosage of adsorbent mass was 2g.
- (3) Removal of Zn (II) increases with the increase in length of time. Maximum removal was observed at 70 min and this remains constant under all other optimum conditions.
- (4) Maximum removal was 97.9% at the concentration of 200 ppm. The Adsorption of biomass also depends on the particle size. The smaller the particle size larger the surface area and optimum particle size was 100 µm.
- (5) The adsorption capacity is in accordance with Langmuir and Freundlich isotherms.
- (6) The leaves of the A.C. are found to be the best biosorbents to remove the Zinc in the industrial effluents and the leaves are non edible and at the same time are of low cost.

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