

# Determination of Adsorption Isotherms and Kinetic Parameters for Biosorption of Cu (II) on Raw Pine Needles: An Experimental Study

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**ABSTRACT:** An experimental study was performed to investigate the potential of raw Chir pine needles (*Pinus roxburghii*) for biosorption of Cu(II) from its aqueous solutions. Biosorption was carried out under varying pH, contact time, biosorbent doses, and initial metal concentrations to achieve optimal condition for metal uptake. Biosorption of metal at equilibrium was tested by Langmuir and Freundlich adsorption isotherms. Both isotherms showed significant  $R^2$  value, though Langmuir isotherm was found most significant ( $R^2=0.96$ ). The maximum biosorption capacity ( $q_{max}$ ) of *P. roxburghii* was 4.03 mg/g at pH 6.5, while the constant  $b$  at the same pH was  $0.298 \text{ Lmg}^{-1}$ . The value of separation coefficient also favours the adsorption process which ranges between 0.869-0.250 with initial metal ion range of 0.5 to 10 mg/L. The constants obtained with Freundlich isotherm,  $K_f$  (0.88) and  $n$  (1.10) also favours the biosorption process. Parameters of kinetic studies suggest pseudo second order kinetic as a most favourable model for present biosorption process with  $R^2=0.99$ . Functional groups such as hydroxyl (OH), amine (NH), carboxylic (COO), aromatic (CH), amide (NH) and carbonyl (CO), obtained in FTIR confirm the presence of potential ligands in raw pine needles, FTIR studies indicated the presence of functional groups like on the surface of biosorbent.

**KEYWORDS:** Biosorbent; isotherm; kinetic study; FTIR; ligands

## I. INTRODUCTION

Elevated concentration of metallic substance in aquatic environment poses threat to the life of aquatic organisms. Higher concentrations of all metals are toxic for living organisms. Due to their higher solubility nature, these are considered toxic for living forms. Metals persist in living organisms' body at low concentrations. Toxic metals (Cu, Cr, Pb, Cd, Hg, As, Ni) are used by humans for quite long times in industries like electroplating, battery manufacturing, plastic, paint, textile and tannery industries [1]. The respective concentration of metal depends on the industrial operation and nature of wastewater treatment processes, such as most of the industries discharge effluents only after conventional treatment, which produces effluent containing metal concentration beyond the discharge limits. WHO, the permissible level of Cu(II) in drinking water is 2 mg/L and for wastewater and industrial effluents is 3 mg/L [2]. Hence, the removal of metal bearing effluents is necessary before the discharge into environment. Copper is essential element for human life but its excessive concentration can cause irritation, organ dysfunction (kidney and liver) and gastrointestinal disturbance. Many conventional methods have been developed for the removal of heavy metals from water and wastewater like osmosis, membrane process, ion-exchange, chemical precipitation, flotation and adsorption. Despite of high removal efficiency, most of these processes are economically unviable and energy intensive. Therefore a low cost and efficient method to remove Cu (II) has been always become the focus of researchers.

Biosorption of heavy metals have several advantages over convention methods such as low cost, metal recovery, regeneration of biosorbent, easy operation and simplicity of design [3]. The biosorption occurs due to interaction of metal ions with functional groups at the adsorbent surface like carboxylic, amino, phenolic groups, amide, hydroxyl, sulphate and sulphhydryl groups [4]. Researchers have developed various kinds of adsorbent by using sunflower stalk [5], leaf powder corn cobs [6], tree fern [7], Wheat shell [8], papaya wood [9-10], coffee waste [11], mushroom biomass [12], cactus fibers [13], okra biomass [14], ground nut husk [15].

Despite of detailed exploration of plant derived biosorbent only few researchers have focused Chir Pine needles as a biosorbent for metal removal. Chir pine (*Pinus roxburghii*) are found abundantly in Himalayan range from 500-2500 m

which extends from countries India, Pakistan, Nepal, Bhutan and Afghanistan. Pine needles are high susceptible for forest fire which damages forest flora and fauna. As forest waste, pine needles can be used as adsorbent for heavy metal removal from water and wastewater. Thus, the present study deals with the application of pine needle for Cu(II) metal ion removal from aqueous solutions. We studied adsorption of Cu(II) onto pine needle by varying pH, initial concentration, adsorbent dosage and contact time on uptake of metal were also studied. The study also involves isotherm and kinetic study to understand the mechanism and nature of adsorption. On the other hand surface feature of pine needle responsible for metal uptake is observed through FTIR analysis.

## II. RELATED WORK

Pine cone biomass tested for the uptake of methylene blue dye in aqueous solutions [16]. The maximum monolayer adsorption capacity of pine cone biomass was 109.89 mg/g at 30 °C. Dod et al. [17] used green pea peels (*Pisum sativum*) for methylene blue dye removal from wastewater. They studied the adsorption affecting parameter like initial dye concentration, pH, contact time, adsorption dosage, agitation speed, particle size and temperature. The maximum adsorption capacity was found upto 163.94 mg in 7h contact time at 30 °C. *Imperata cylindrical* (cogon grass), common weed, was utilized as adsorbent for the removal of methylene blue [18]. They found that adsorption dosage and pH affected the adsorption process. The maximum colour removal was found to be 99.09 % at shaking speed of 100 rpm, pH 9, 40 min contact time and adsorption dosage of 1.0 g. Ghosh et al. [19] assessed the potential of tobacco stem ash as an adsorbent for uptake of methylene blue dye from aqueous media. The maximum adsorption was 35.7 mg/g. The dimensionless separation factor ( $R_L$ ) was found to be 0.137, which supported the MB dye removal from wastewater.

## III. MATERIAL AND METHODS

### Preparation of Adsorbent

Pine needles were collected from Garhi Cantt, Dehradun, India and then washed with several times with double distilled water. After that material grinded into powder and sieved 75-150 mesh size. The sieved material again washed with double distilled water to remove dirt and colour. Then, material again dried in oven (105°C) and packed in air tight plastic container.

### Adsorbent solution

The chemicals used in experiment were analytical grade. The stock solution of Copper (II) was prepared by dissolving 3.929 g of copper sulphate ( $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ ) in 1 litre triple distilled water. The required concentrations (1-10 mg/L) were prepared by further dilutions.

### Instrumentation

A ELICO SL 160 model atomic spectrophotometer was used to determine the copper concentrations in solution. Fourier transform infrared spectroscopy (FTIR) spectra of before and after adsorption were recorded using KBr pellets on Shimadzu-8400S model over 400-4000  $\text{cm}^{-1}$ . The surface structural modification of adsorbent was visualized by SEM (JSM- JEOL, Japan).

### Adsorption studies

Adsorption of Cu(II) metal ions on raw pine needles was performed in batch mode sorption equilibrium experiments with series of Erlenmeyer flasks of 250 mL capacity. 0.1 g of pine needle adsorbent was placed in 250 mL conical flasks containing 100 mL of Cu(II) solution of desired concentration. The flasks were shaken in digital shaken at 110 rpm. After the equilibrium time flasks were taken out and samples were analyzed by AAS.

The percentage of Cu(II) removal was calculated by formula as:

$$\text{metal removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \dots \dots \dots (1)$$

Where,  $C_o$  and  $C_e$  are the liquid-phase dye concentration at initial stage and equilibrium stage respectively.

The amount of Cu(II) adsorbed per unit mass was computed by using equation as:

$$q_e = \frac{C_o - C_e \times V}{W} \dots \dots \dots (2)$$

Where,  $q_e$  (mg/g) is the equilibrium amount of copper metal ions adsorbed per unit mass of pine needle,  $V$ (L) is the volume of solution and  $W$ (g) is the mass of adsorbent.

### Study of isotherms

Isotherms describes the interaction between the biosorbent and biosorbate and determine the maximum biosorption capacity. The Langmuir and Freundlich models are commonly used to describe biosorption process. The Langmuir [20] isotherm describes monolayer coverage of the biosorbate on the surface of biosorbent. The Langmuir isotherm, non-linear form is shown as:

$$q_e = Q^0 b C_e / (1 + b C_e) \dots\dots\dots(3)$$

The linear form of Langmuir isotherm equation can be represented as:

$$1/q_e = 1/Q^0 + 1/bQ^0 C_e \dots\dots\dots(4)$$

Where  $q_e$  is the amount of adsorbent on the fiber at equilibrium (mg/g),  $C_e$  (mg/L) and  $b$  (L/mg) are the monolayer biosorption capacity, respectively. The values of  $Q^0$  and  $b$  were calculated from the slope and intercept of the plot. The dimensionless equilibrium parameter ( $R_L$ ) is used to describe whether the Langmuir biosorption process is favourable or not, which can be represented as:

$$R_L = 1 / (1 + b C_0) \dots\dots\dots(5)$$

Where  $C_0$  is the initial concentration of the biosorbate (mg/L). For favourable condition  $R_L$  value should be ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ) and irreversible ( $R_L = 0$ ). On the other hand, Freundlich model describes heterogeneous surfaces, general form of Freundlich can be expressed as:

$$q_e = K_F C_e^{1/n} \dots\dots\dots(6)$$

The logarithmic (linear) form of the Freundlich equation can be written as:

$$\ln q_e = \ln K_F + 1/n \ln C_e \dots\dots\dots(7)$$

Where  $q_e$  is the amount of metal biosorbed per unit weight of biosorbate (mg/g),  $C_e$  is the equilibrium liquid phase concentration (mg/L),  $K_F$  is the Freundlich constant (mg/g) and  $1/n$  is the heterogeneity factor. The values of  $K_F$  and  $n$  (Table 1.) were obtained from the slope and intercept of a plot of  $\log q_e$  vs  $\log C_e$ .

#### **Biosorption kinetics**

Biosorption kinetic models are used to describe the biosorption mechanism and affecting parameters in the biosorption process [21]. Pseudo first order and pseudo second order kinetic model were used to test the experimental data. The Lagergren pseudo-first order equation can be represented as:

$$\log q_e (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \dots\dots\dots(8)$$

Where  $k_1$  is the rate constant of pseudo-first order biosorption and  $q_e$  and  $q_t$  express the amount metal biosorbed at time  $t$  and  $k_1$  ( $\text{min}^{-1}$ ) is the equilibrium rate constant. The pseudo-second order equation can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots(9)$$

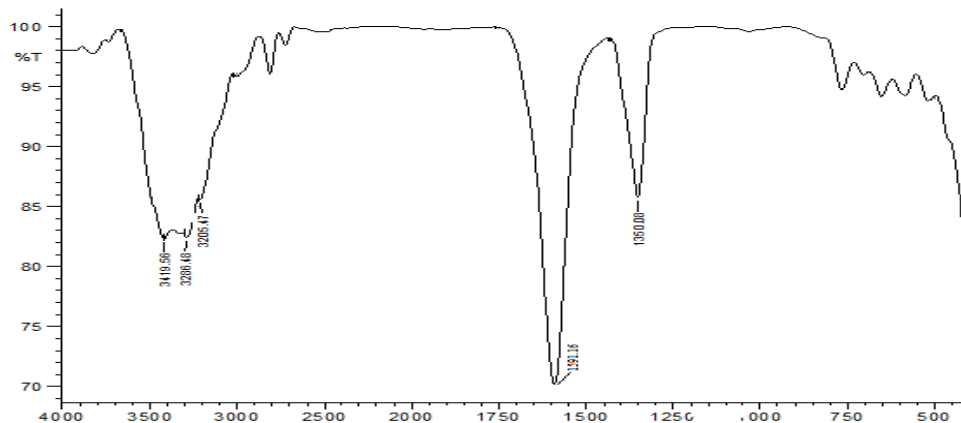
Where  $q_e$  and  $q_t$  are amount of metal ion biosorbed (mg/g) at equilibrium at time  $t$  respectively.  $K_2$  (g/mg min) is the rate constant of pseudo-second order biosorption.

### **IV. RESULT AND DISCUSSION**

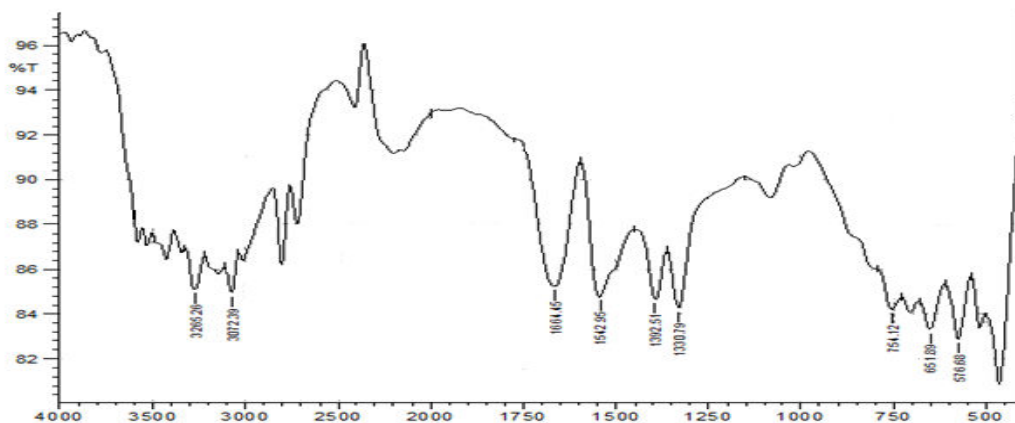
#### **FTIR analysis before and after biosorption of Cu(II)**

The functional groups that are found on the surface of pine needle biosorbent are responsible for chemical reactivity at the surface. FTIR spectra analyzed on biosorbent raw and Cu(II) loaded biomass by use of KBr and pine needle adsorbent (Fig 1 and 2). There were displacements of IR bands found between raw and treated samples for Cu biosorption. A characteristic peak at  $576.68 \text{ cm}^{-1}$  was due to C-Cl stretching, and peak at  $651 \text{ cm}^{-1}$  indicates the stretching of NH group and CH bending. The peak present at  $754.12 \text{ cm}^{-1}$  indicates aromatic CH bending. The peaks at  $1350.08 \text{ cm}^{-1}$  and  $1330.79 \text{ cm}^{-1}$  were due to -CH and -CN stretching. The peaks at  $1542.95 \text{ cm}^{-1}$  and  $1591.16 \text{ cm}^{-1}$

were attributed to stretching vibration of  $-\text{NO}_2$  and  $\text{C}=\text{C}$  groups. The bands observed at  $3205.47\text{ cm}^{-1}$  was assigned to aliphatic  $\text{NO}_2$  stretching. The peaks at  $3072.39\text{ cm}^{-1}$  corresponds to  $-\text{CH}$  stretching, and peaks at  $3419.95\text{ cm}^{-1}$  and  $3265.25\text{ cm}^{-1}$  indicating presence of  $-\text{OH}$  group. The results indicated that the functional groups OH, NH, COO and CO were mainly involved in the biosorption of  $\text{Cu}(\text{II})$ .



**Fig.1 FTIR spectra of Pine needles adsorbent before adsorption**



**Fig.2 FTIR spectra of Pine needle adsorbent after adsorption of  $\text{Cu}(\text{II})$  metal ion**

### Effect of pH

The biosorption process was influenced by pH of the system; it affects the functional group properties on the adsorbate surface [22]. Fig. 3 shows the influence of pH on  $\text{Cu}(\text{II})$  sorption by pine needles. It was evident from the figure that sorption was pH dependent and maximum sorption occurs at pH 6.5. The percentage of  $\text{Cu}(\text{II})$  ion removal increased from 80% to 99% with an increase of pH from 4.0 to 6.5 and thereafter removal decreased from 99% to 73.05% with an increase of pH from 7 to 10. Cellulose, hemicelluloses and lignin are common materials in plant cell wall. Cellulose hemicelluloses and lignin have hydrophobic and aromatic properties which are binding sites for metal uptake [23-24]. The adsorption capacity decreased at lower pH value was due to the higher concentration of  $\text{H}_3\text{O}^+$  ions present in the aqueous solution, which compete with the  $\text{Cu}(\text{II})$  ions for the adsorption sites of pine needles [25]. At higher pH value,  $\text{H}_3\text{O}^+$  ions are become available in solution resulting in a higher sequestration of metal ions.

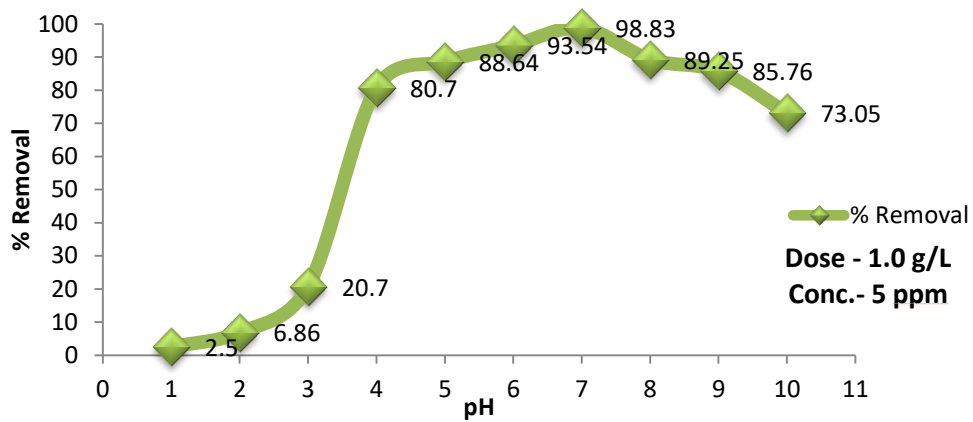


Fig. 3 Effect of pH on adsorption of Cu(II) ions onto Pine needle adsorbent (Conditions: Concentration =5 ppm, Doses= 1.0 g/L, Temperature 25°C, pH =6.5, volume= 100 mL, contact time 350 min)

**Effect of initial metal concentration**

The effect of Cu(II) concentration on the sorption by pine needle sorbent was investigated by varying the Cu(II) from 1-10 mg/L at pH 6.5 (Fig.4). Copper metal uptake increases rapidly as concentration increase from 1 to 2.5 mg/L but become slow in the later stage until equilibrium condition obtained. The equilibrium time for copper adsorption on pine needle at different adsorbent concentration was found to be 30 min.

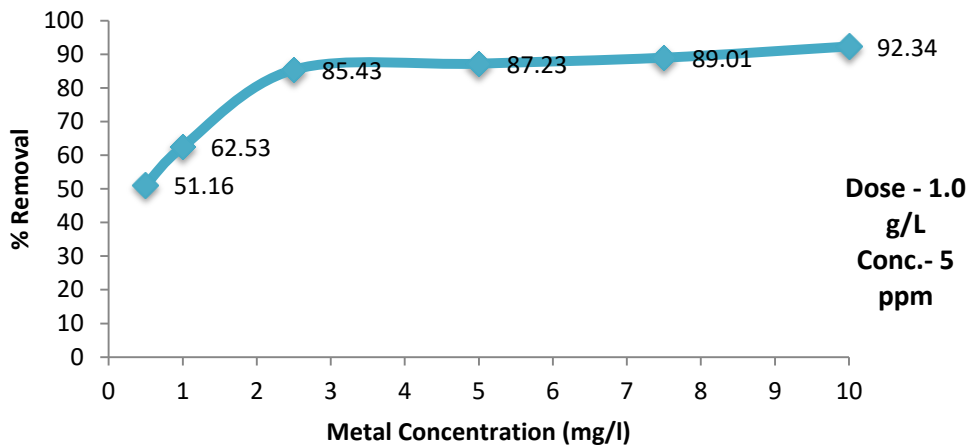


Fig.4 Effect of adsorbent dosage and contact time (Conditions:, Doses= 1.0 g/L, Temperature 25°C, pH =6.5, volume= 100 mL, contact time 350 min)

**Effect of adsorbent doses**

Effect of adsorbent dosage on adsorption of copper was studied by changing the biosorbent dosage from 0.50 to 4 g/L using 5 mg/L of the Cu(II) ion solutions (Fig. 5). The maximum removal was found at 1 mg/L.

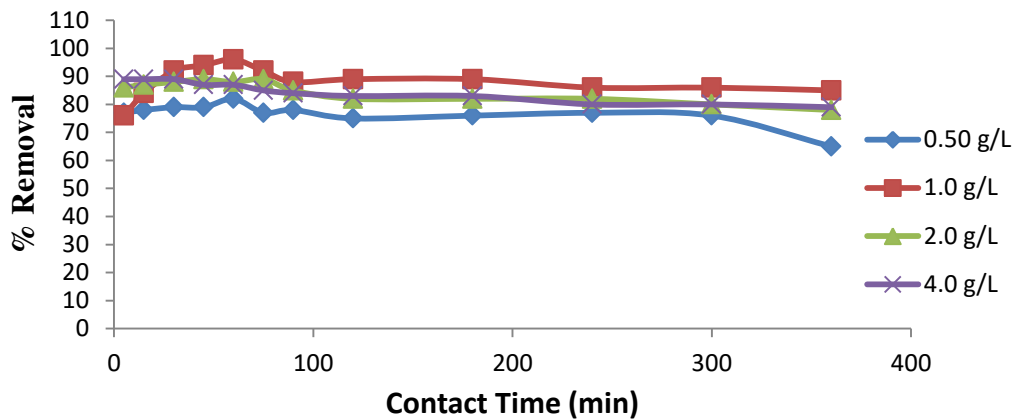


Fig. 5 Effect of adsorbent dosage on adsorption of Cu(II) ions onto Pine needle adsorbent (Conditions: Concentration =5 ppm, Temperature 25°C, pH =6.5, volume= 100 mL, contact time 350 min)

**Biosorption mechanism**

We used two biosorption isotherm to describe the biosorption mechanism, which were fitted in the present study by the widely used Langmuir and Freundlich isotherms. Fig. 6 shows the Langmuir isotherm and Fig 7 shows the Freundlich isotherm for Cu(II) uptake on pine needle sorbents. Table 1 shows the maximum biosorption capacity ( $q_{max}$ ), bonding energy constant ( $b$ ) and correlation coefficient ( $R^2$ ) were 4.03 mg/g, 0.298 L/mg and 0.9 for Langmuir isotherm. The Freundlich constant ( $K_F$ ),  $n$  and correlation coefficient ( $R^2$ ) were found to be 0.88, 1.10 and 0.95. The value of  $n$  found between 0 to 10 indicates a favourable biosorption by the pine needle biosorbent for Cu(II) uptake. Langmuir isotherm ( $R^2=0.96$ ) describes the Cu(II) uptake better than Freundlich isotherm ( $R^2=0.95$ ). The parameter,  $R_L$ , dimensionless parameter or separation factor, represent the shape of isotherm and nature of sorption process [21]. The values of  $R_L$  for Cu(II) were calculated and plotted on the bases of different initial metal concentrations. In this work, the calculated  $R_L$  values ranged from 0.869-0.250 with initial metal ion range of 0.5 to 10 mg/L (Table 2), which suggests that favourable adsorption of Cu(II) onto the pine needle adsorbent, under the test conditions.

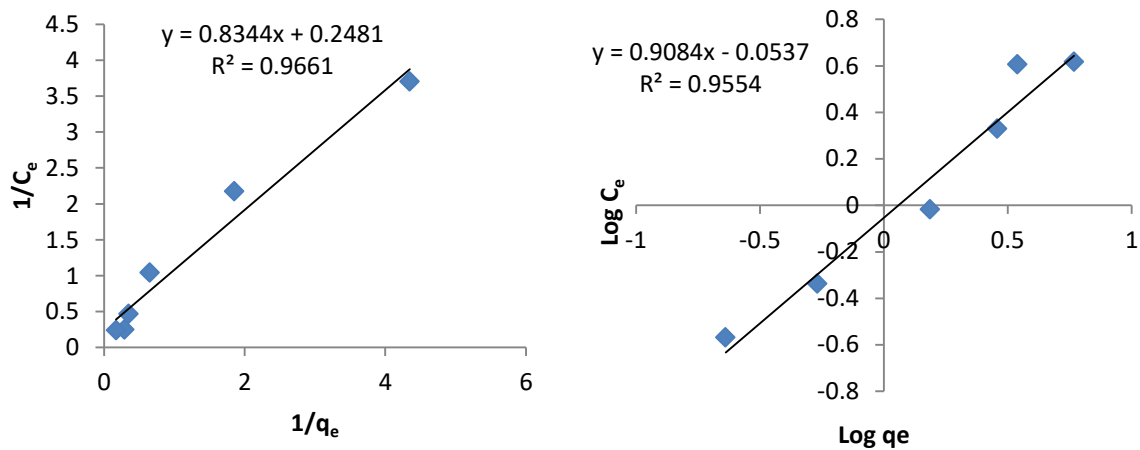


Fig.6 &7 Langmuir plot of  $C_e/q_e$  vs  $C_e$  and Freundlich plot for Cu metal uptake by pine needle

Table 1 Equilibrium model parameters for the removal of Cu(II) onto pine needle

Langmuir constant			Freundlich constant		
$q_{max}$ (mg/g)	B (L/mg)	$R^2$	$n$	$K_F$ (mg/g)	$R^2$
4.03	0.298	0.96	1.10	0.88	0.95

Table 2 Value of separation parameter ( $R_L$ ), based on the Langmuir isotherm equation

Initial Cu(II) concentration (mg/L)	$R_L$ value
0.5	0.869
1.0	0.769
2.5	0.571
5.0	0.400
7.5	0.307
10	0.250

**Biosorption kinetics**

The study of biosorption kinetics reveals the solute uptake rate, mechanism of biosorption that controls the biosorption process. For this, Pseudo-first order and pseudo-second order kinetic models were tested with the experimental data. The plot of  $\text{Log}(q_e - qt)$  vs  $t$  and  $t/qt$  vs  $t$  were shown in Fig. 8 and 9. A plot of Pseudo first-order and pseudo second-order (eq. 8 and eq. 9) gave straight lines with good correlation values. Pseudo second order correlation was found higher ( $R^2=0.99$ ) than Pseudo second order ( $R^2=0.75$ ). Table 3 shows the pseudo first order and pseudo second order kinetic parameters. The values of  $q_e$  obtained in pseudo second order model were in better agreement with the adsorption data than those obtained in pseudo-first order model.

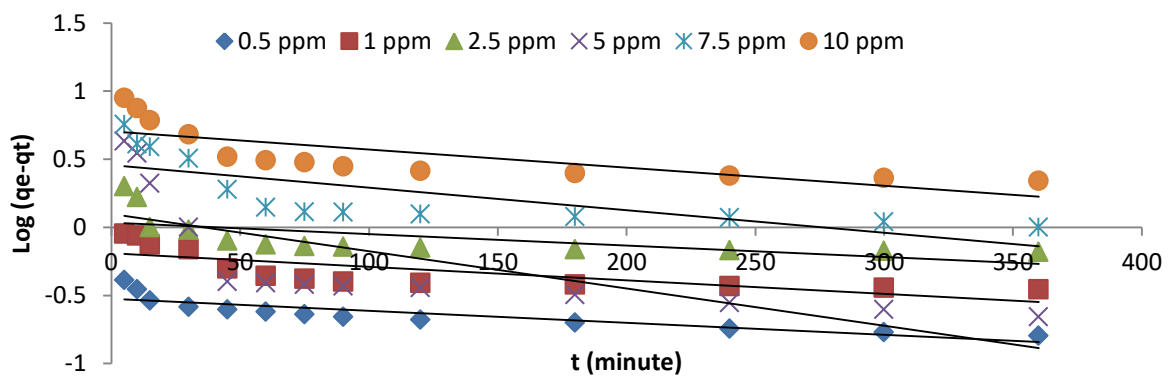


Fig. 8 Lagergren pseudo first order kinetic order model

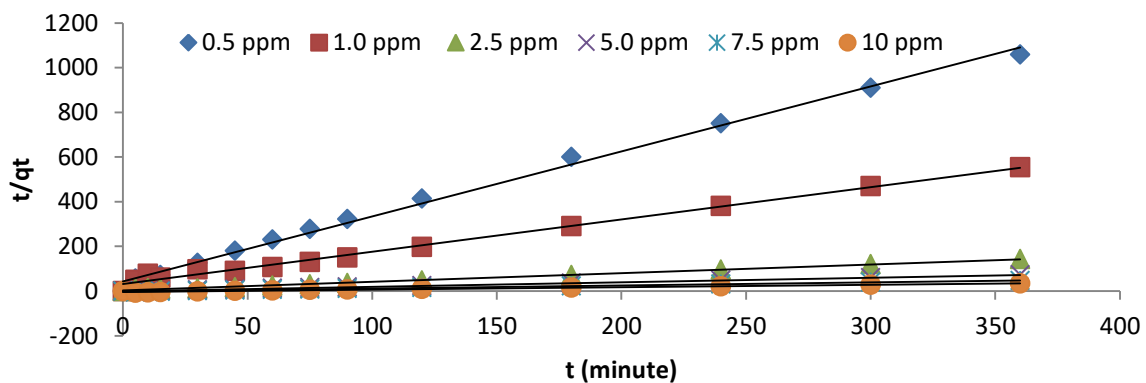


Fig. 9. Ho's pseudo second order kinetic model

Table 3 Pseudo-first order and pseudo-second order kinetic parameter for adsorption of Cu(II) metal ion

Concentration (mg/L)	$q_{e\text{ exp}}$ (mg/g)	Pseudo first order kinetics			Pseudo-second order kinetic		
		$q_{e(\text{cal})}$ mg/g	$K_1$ (/minute)	$R^2$	$q_{e(\text{cal})}$ mg/g	$K_2$ (g/mg/min)	$R^2$
0.5	0.34	0.298745	0.002073	0.75	0.343773	8.459081	0.99
1.0	0.96	0.645803	0.002303	0.58	0.692617	2.084558	0.99
2.5	1.84	1.085176	0.018424	0.4	2.581978	0.150001	0.99
5.0	4.978	1.251699	0.003685	0.52	4.86618	0.04223	0.99

7.5	6.1	2.856933	0.003685	0.55	7.147963	0.019572	0.99
10.0	7.8	5.066406	0.002994	0.58	9.149131	0.011946	0.97

#### Comparison of Pine needles with other adsorbents

In the present study, the Cu(II) metal ion efficiencies were obtained from Langmuir isotherm ( $q_e$ ) of different adsorbents were represented in Table 4. It was found from Table that pine needle adsorbent capacity was higher with some other adsorbents.

**Table 4 Comparison of biosorption capacities of various biosorbents for removal of Cu(II) metal ion**

Biosorbent	pH	Adsorption capacity (mg/g)	Reference
Barley straw	6	4.64	[24]
Cashewnut shell	5	20.0	[26]
Chestnut shell	5	12.56	[27]
Loofah powder	8	14.49	[28]
Olive stone	5	2.0	[29]
Pine bark	5	11.9	[29]
Pine needle	6.5	4.03	Present study
Pomegranate pulp	5.3	7.30	[30]
Rape straw	5	7.3	[31]
Sawdust	6	5.4	[32]

#### V. CONCLUSION

The leaves of *Pinus roxburghii*, a forest waste, can be used as effective biosorbent for the removal of Cu(II) metal ions from aqueous solutions. The biosorption of metal was found to be dependent on contact time, pH, biosorbent doses and initial metal concentrations. It was observed that an increase in the amount sorbed Cu(II) as increase in initial metal concentrations, and the equilibrium conditions were almost achieved after 30-60 min contact time. The highest metal uptake was found to be 4.03 mg/g at 6.5 pH. The equilibrium data of Cu(II) sorption was fitted well with both Langmuir and Freundlich isotherms. Pseudo second order kinetic model was fitted well than pseudo first order kinetic model. Infra-red spectroscopy revealed that various functional groups present on surface of biosorbent interact with Cu(II) binding on pine needle such as hydroxyl (OH), amine (NH), carboxylic (COO) aromatic (CH), amide (NH) and carbonyl (CO). Thus, it can be concluded that the forest waste biomass can be used as biosorbent to remove metals from water and wastewater.

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