

Biosorptive Removal of Copper (II) ion from Aqueous Solution using *Lawsonia Inermis* Plant Leaf Biomass

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Abstract

The present study investigates the biosorptive removal of Copper (II) ion from aqueous solution using plant leaf biomass under various conditions. Biosorption studies have been carried out to determine the effect of pH, Cu (II) metal concentration, contact time, temperature and biomass dose on the biosorption capacity of Cu (II) ions by the biomass. The process was investigated using concentrations of Cu (II) ions ranging from 10-125 mg/L in equilibrium batch tests for Langmuir and Freundlich isotherm models. The biosorption data was better fitted to Langmuir isotherm model, and the maximum biosorption capacity (q_{max}) was 6.06 mg/g. The optimum pH for the removal of Cu (II) ions was around pH 5.0 and the removal of Cu (II) ions was 85.6%. The biosorption kinetics followed the pseudo-second order model. FTIR clearly showed that -OH, -CH and C=O group are likely to participate in Cu (II) ion adsorption. The results demonstrated that plant leaf biomass was a economic and eco-friendly biosorbent possessed strong biosorption characteristics for Cu (II) ions.

Keywords: *Lawsonia Inermis*. Cu (II) removal, Biosorption, Isotherm.

1. INTRODUCTION:

Copper is one of the most common toxic metals that finds its way to water sources from various industries, i.e. electroplating, mining, electrical and electronics, iron and steel production, non-ferrous metal industry, printing and photographic industries. On the other hand, Cu²⁺ is a mineral that is naturally found in the human body and is a necessary microelement. It participates in hematopoietic functions, mainly the synthesis of hemoglobin [1]. However, copper concentrations in humans have increased to toxic levels causing various diseases and disorders, such as liver damage, gastrointestinal problems, and continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers[2][3].

According to U.S. Environmental Protection Agency (EPA) standards, the permissible limit of copper discharge in industrial effluents into water bodies is limited to 1.3 mg/L. World Health Organization (WHO) defines the Cu (II) permissible limit of 1.5 mg/L in drinking water [4]

A large number of technologies have been used to remove Cu (II) from the environment. The main treatment processes for the removal of Cu (II) ions include: chemical precipitation, Chelation/complexation Reverse osmosis, Electrochemical treatments, membrane separation, and sorption/ion exchange [5]. Among the processes used for the removal of Cu (II) from wastewater, adsorption is an effective and eco-friendly treatment method for metal removal from aqueous solutions. The use of biomass is preferred because it does not require nutrients, it is not affected by toxic pollutants, and may be regenerated and reused in a number of adsorption-desorption cycles [6].

In this study, the Leaf biomass of *Lawsonia Inermis* adsorbent for removal Cu (II) ion was used to determine adsorption efficiency as a function of pH, temperature, biomass dose, contact time and initial metal concentration and constants of the adsorption isotherm and investigated its adsorption kinetics for removal of copper ions from aqueous solutions. FTIR analysis was carried out to understand the functional group of biomass.

2. Material and methods:

2.1. *Lawsonia Inermis* Biomass: *Lawsonia Inermis* biomass (LIB) used in this work was collected, processed and stored as described earlier [7]

2.2. Reagents: All chemicals were of an analytical grade. Solutions of 0.01 M NaOH and HCl (from Merck) were used for pH adjustment. Stock solutions of Cu (II) containing 1,000 mg/L, were prepared by dissolving appropriate metal (chloride) salts in Milli-Q ultrapure water. The stock solution was diluted as required to obtain standard solutions with Milli-Q ultrapure water when needed.

2.3. Analysis for metal biosorption tests: The concentrations of Cu (II) in the solutions before and after equilibrium were determined by flame atomic absorption spectrometry (FAAS), using Atomic adsorption spectrophotometer AAS4129D, ECIL India which operates in flame mode and controlled by Intel personal computer.

2.4. Metal Biosorption Studies: Batch biosorption experiments were conducted in a set of conical flasks

containing 50 mL of solution to investigate the effects of pH (2-7), biomass dose (0.1-0.8 g/L), initial metal ion concentration (10-125 mg/L), temperature (303, 313 and 323 K) and contact time (15-180 min). The adsorbent and solution were separated by filtration through a membrane filter. The metal ion concentration in the original solution and left in bulk solution were determined by the AAS technique. The optimum conditions for the biosorption of Cu (II) ion were determined, and biosorption kinetics was investigated using 50 mg/L initial copper concentration, 0.5g/L biomass dose at solution pH of 5 at 303 K temperature. Biosorption isotherms were examined by mixing a dosage of 0.5 g/L of biomass dose with Cu (II) solution at pH 5 at various initial concentrations in the range of 10-125 mg/L at three different temperatures.

The difference between initial and final Cu (II) concentrations in aqueous solution was used to calculate the biosorbed metal concentrations. Cu (II) ions removal efficiency (% R) is defined as

$$R = \frac{C_o - C_e}{C_o} \times 100\%$$

Where C_o (mg L^{-1}) is the initial and C_e (mg L^{-1}) is the equilibrium concentration of metal ions, respectively. The amount of the metal adsorbed (mg) per unit mass of biomass was obtained by using following equation:

$$q_e = \frac{(C_o - C_e)V}{w}$$

Where q_e (mg g^{-1}) is the adsorption capacity at equilibrium, C_o (mg L^{-1}) is the initial and C_e (mg L^{-1}) is the equilibrium concentration of metal ions, W (g) is the weight of adsorbent used and V (ml) is the volume of sample.

Control samples with no added biomass were used as blanks. Each experiment was repeated for three times.

2.5. Fourier transform infrared (FTIR): In order to identify the functionalities being capable of interacting with copper ions in biomass, FTIR technique was used. FTIR spectrums of raw and metal loaded biomass were recorded with a Thermo Nicolet, Avatar 370 Model FTIR spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$ having resolution 4 cm^{-1} at the SAIF KOCHI, Cochin, Kerala, India.

3. Result and Discussion:

3.1. Effect of pH: The pH effect not only on speciation of copper ions, but also the charges on the active sites of biomass [8]. When the pH of metal ions solution is changed, the hydroxyl group on the surface of biomass is also changed [9]. The effect of solution pH on Cu (II) sorption was evaluated from the pH ranges of 2.0–7.0 and results are depicted in Fig.1. As observed from Fig.1, at lower pH, the biosorption efficiency is low due to the presence of high concentration of H_3O^+ ion which will compete with the Cu (II) present in the solution. As the pH is increased from 2.0 to 5.0 the biosorption efficiency also increases from 40.6% to 85.6%. By further increase in pH from 5.0 to 7.0 causes a decrease in the biosorption efficiency due to precipitation of water insoluble $\text{Cu}(\text{OH})_2$. Based on the high biosorption efficiency by the conjugate adsorbent, the pH 5.0 was chosen for determining the other experimental parameters for subsequent biosorption operation in this study.

3.2. Biosorption time of Cu (II): The biosorption of Cu (II) was studied in order to determine the contact time required to reach the equilibrium. Fig.2. shows the effect of contact time on the biosorption of Cu (II) ions onto *biomass*. From Fig.2, it can be seen that 50% adsorption was completed within 60 min and equilibrium was achieved within 90 min and remained nearly constant afterwards. Therefore, this time value was selected as optimum contact time for sufficient biosorption of the Cu (II) ions.

3.3. Effect of biomass dosage: The effect of biomass dosage on the biosorption of Cu (II) ions was studied using the biomass in the range of $0.1\text{--}0.8\text{g L}^{-1}$ (Fig. 3). From Fig.3, it was observed the biosorption of the metal ions increased with increasing biomass dosage and almost constant at higher than 0.5 g/L. This is because an increase in biomass dosage causes an increase in surface area of the biosorbent, which consequently increases the number of active binding sites on the surface of biomass [10]. Therefore, the amount of biomass was selected as 0.5 g/L for further experiments.

3.4. Effect of initial metal concentration: In this the effect of initial metal concentration on biomass removal was carried out in the range $10\text{--}125\text{ mg L}^{-1}$ while keeping the other parameters constant. From Fig.4, it is shown that with increase in initial metal concentration causes decrease in biosorption efficiency because all the available sites present in the solution get saturate and no more binding sites are available for biosorption. The biosorption efficiency of metal was 93-37.6 % for $10\text{--}125\text{ mg L}^{-1}$ of Cu (II) solution.

Fig 5 shows the effect of different metal concentration onto biomass with respect to time, from this we can get that maximum biosorption efficiency is achieved at the time of equilibrium i.e. 90 min.

3.5. Kinetics modeling:

The kinetic data was analyzed using pseudo-2nd-order equation (PSE) [11]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

Where, q_t is the amount of metal ion adsorbed at time t (mg g^{-1})

q_e is the amount of metal ions adsorbed at equilibrium (mg g^{-1}).

K_2 is the rate constant of second-order adsorption. ($\text{g mg}^{-1} \text{min}^{-1}$)

By fitting the experimental data to Eq. 1 the second order rate constant (k_2) and q_e were determined.

The plots of t/q_t versus t and values of the constants of PSE kinetic models obtained from the plots are given in Fig.6 and Table 1. The linear plot concluded that PSE kinetic model is appropriate to describe this adsorption. The Value of K_2 can be determined by the intercept of the plot.

3.6. Adsorption isotherms: Adsorption Isotherm studies provide information on the capacity of adsorbent, which is the most important parameter for a biosorption system. The equilibrium adsorption data was described by most frequently used two isotherm models: Langmuir [12] and Freundlich [13] isotherm models:

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Where, C_e is the concentration of the adsorbate at equilibrium in the solution (mg L^{-1}), q_e is the amount adsorbed at equilibrium on the adsorbent (mg g^{-1}), q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}) and K_L = energy of adsorption constant (L mg^{-1}) or Langmuir constant.

Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where, K_F is the constant related to adsorbent capacity (mg g^{-1}) and $1/n$ = is an empirical parameter related to sorption intensity of the adsorbent ($n = 1-10$).

Table 2 lists the calculated parameters and regression coefficients (R^2). The study found that the biosorption of Cu (II) on the biomass was fitted using both the Langmuir and Freundlich models. However, the Langmuir isotherm ($R_2 > 0.99$) correlated better with the experimental data according to the r^2 value. Similar results were reported in the literature for biosorption of Cu (II) onto *Solanum lycopersicum* [14]. Convenience of the experimental data with the Langmuir isotherm model suggested that there is monolayer coverage of the adsorbate on the surface of adsorbent and that adsorption occurs at specific homogeneous sites on the adsorbent. By Comparing the maximum Cu (II) uptake capacity obtained from Langmuir model for biomass with other biosorbents shows that q_m (mg/g) value of the present biomass was 6.06 mg/g while Activated carbon has 3.56 mg/g [15], Red mud (5.34 mg/g) [16], Barley straw (BS) (4.64 mg/g) [17], Almond shell (3.62 mg/g) [18], *Pycnoporus sanguineus* (2.76 mg/g) [19]. From these results, it is clear that the present biomass can be used as an adsorbent as the adsorption capacity of this higher than the other adsorbent reported by various scientists.

3.7. FTIR results:

Fig.7. shows the FTIR spectra of biomass before and after adsorption and FTIR spectroscopic characteristics are shown in Table 3. The vibrating signals before and after adsorption of Cu (II) was different. The adsorption band at 3350-3380 cm^{-1} is due to banded -OH groups [20]. The weak band at 2922-2933 cm^{-1} could be assigned to the aliphatic C-H group [21]. The adsorption band at 1670-1820 cm^{-1} are attributed to C=O strong stretching Vibration. The trough at 1620-1680 cm^{-1} are characteristics of C=C in aromatic ring [22]. The Peak observed at 1033 cm^{-1} corresponds to C-O stretching in carboxylic group present in biomass containing aromatic ring.

When compared the two spectra in Fig shows that there was some peak that were shifted to another wavelength. The adsorption peak of bonded -OH group get shifted from 3380 cm^{-1} to 3370.35 cm^{-1} in case of FTIR spectra after adsorption which showed that Hydroxyl polymerization in biomass was decreased by the addition of Cu (II) ions. This shows that Cu (II) ions can be bonded to the hydroxyl groups. The similar result was observed by [23]. The another change in peak was observed in C-H group where the peak in case of FTIR spectra after adsorption get shifted to lower wavelength i.e. 2921 cm^{-1} . The peak at 1726 cm^{-1} which corresponds to C=O stretching vibration become weak in case of FTIR spectra after adsorption. This indicates that the free

carbonyl changes to coordinated COO⁻ group.

This change in peak shows that -OH, -CH and C=O group are likely to participate in Cu (II) ion adsorption. The ion exchange process may be the mechanism involved in the biomass and Cu (II) interaction.

4. CONCLUSION

In this study, the adsorption of Cu (II) ions from aqueous solution by using *Lawsonia Inermis* leaf biomass as an adsorbing agent was implemented successfully. The biosorption characteristic has been examined at various pH, biomass dose, initial concentrations, temperature and contact time and the following conclusions can be made

1. It was found that maximum biosorption of Cu (II) ion was obtained in pH 5 with 85.6% removal efficiency. Thus, metal ion uptake was found as pH-dependent, with that the contact time also affects biosorption results.
2. Adsorption isotherm has been carried out using the Langmuir and Freundlich isotherm models. The Langmuir model was determined as the best fit for the biosorption data and the isotherm constants were used to compare the adsorptive capacity of *Lawsonia inermis* biomass.
3. The maximum biosorption capacity of the biomass was 6.06 mg g⁻¹ which can be compared with other biosorbents.
4. Pseudo-second order kinetic models were used to test the biosorption kinetics. It was shown that the biosorption of Cu (II) ion onto biomass could provide the best results by the pseudo-second order model, showing that chemical sorption can control the biosorption.
5. Thus, the present biosorbents can be used as an effective and economically feasible biosorbent to remove Cu (II) ion from aqueous solutions as is cheap can be locally available and does not produce any kind of waste.

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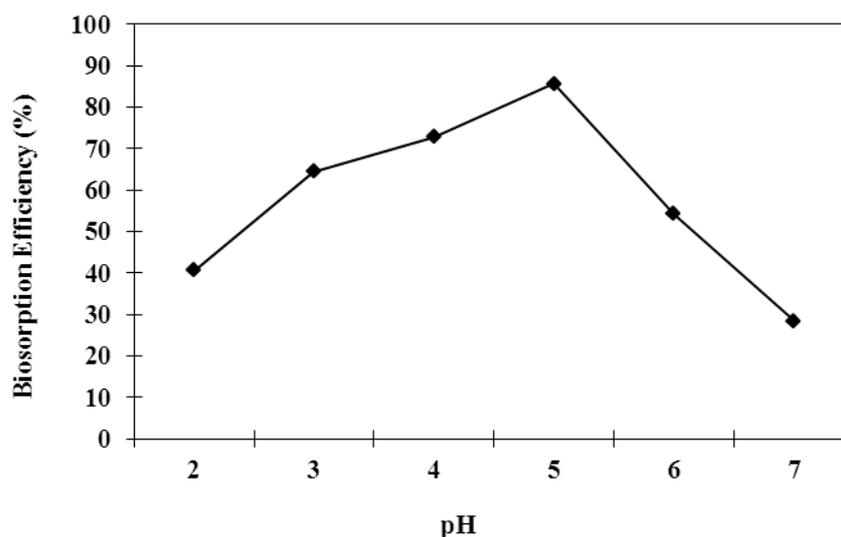


Fig. 1. Effect of pH on Cu (II) uptake onto biomass.
($C_0 = 50 \text{ mg L}^{-1}$; $W = 0.5 \text{ g}$; $T = 303 \text{ K}$; $V = 50 \text{ ml}$, contact time = 90 min.)

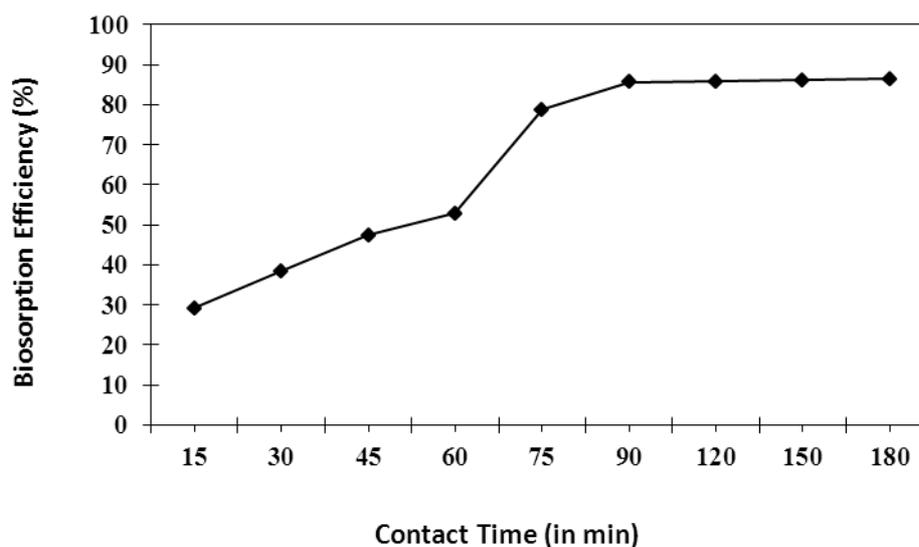


Fig. 2. Effect of Contact time on Cu (II) uptake onto *biomass*.
($C_0 = 50 \text{ mg L}^{-1}$; $W = 0.5 \text{ g}$; $T = 303 \text{ K}$; $V = 50 \text{ ml}$, $\text{pH} = 5.0$)

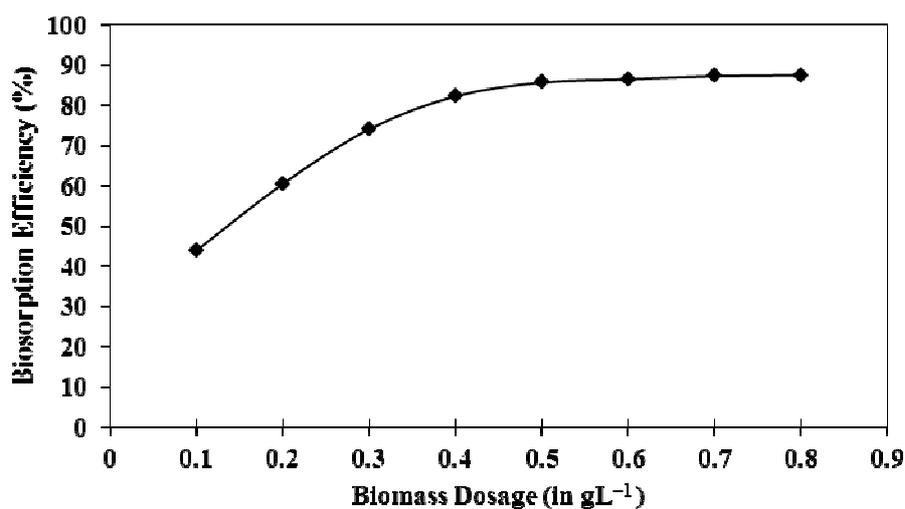


Fig. 3. Effect of biomass dosage on Cu (II) uptake onto *biomass*.
($C_0 = 50 \text{ mg L}^{-1}$, $T = 303 \text{ K}$, $V = 50 \text{ ml}$, $\text{pH} = 5.0$, contact time = 90 min.)

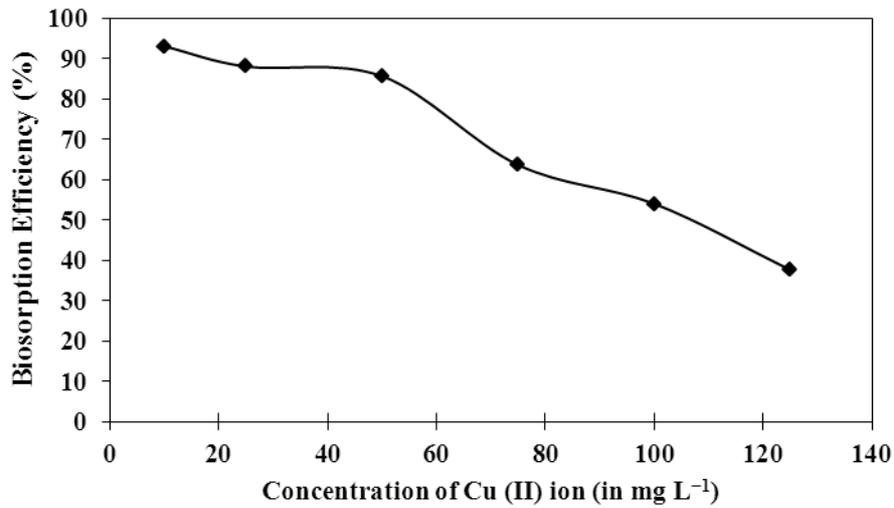


Fig. 4. Effect of initial metal concentration on Cu (II) uptake onto *biomass*. (W= 0.5 g, T = 303 K, V = 50 ml, pH = 5.0, contact time = 90 min.)

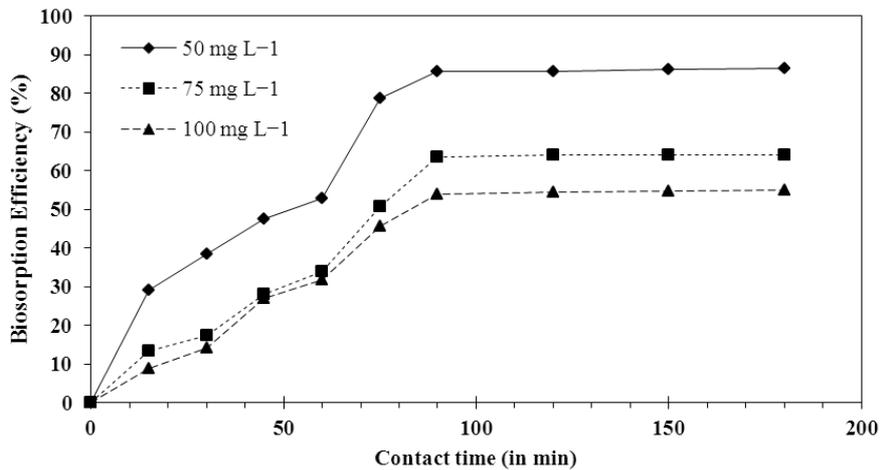


Fig. 5. The Effect of different metal concentration onto *biomass* with respect to contact time

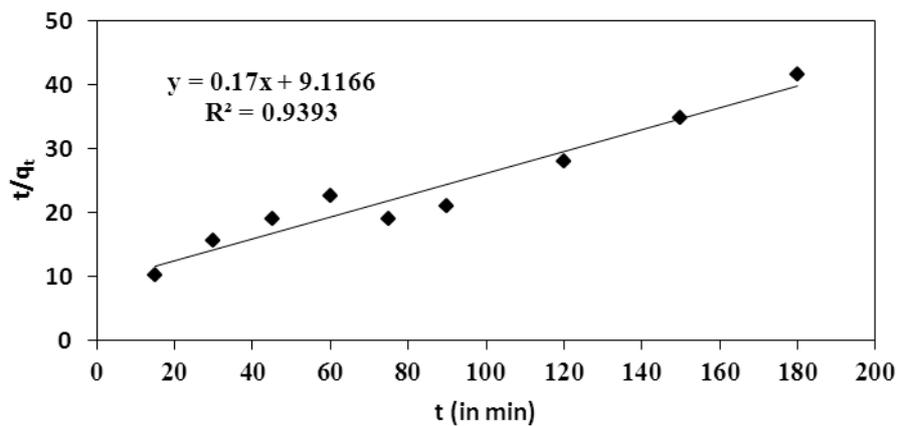


Fig.6. Pseudo-second order kinetic model of Cu (II) uptake onto *biomass*.

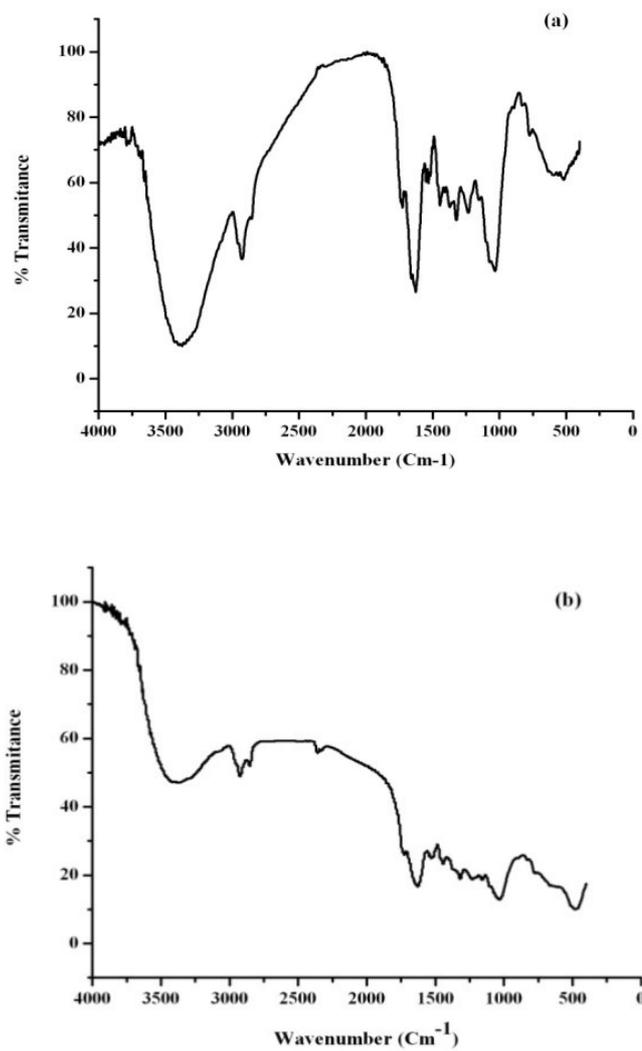


Fig.7. FTIR spectrum of BTLP (a) before and (b) after adsorption.

Table.1. Values of rate constant of adsorption

Experimental	Pseudo second order kinetic model		
q_e (mg g ⁻¹)	K_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
4.28	0.006	5.882	0.939

Table.2. The Values of Constant parameters and correlation coefficients for Langmuir and Freundlich adsorption models at different temperatures.

Isotherm Models	303 K	313 K	323 K
Langmuir			
q_m (mg/g)	5.025	5.617	6.06
K_L (L/g)	0.534	0.475	0.509
R^2	0.99	0.99	0.99
Freundlich			
K_F (mg g ⁻¹)	1.396	1.496	1.713
n	2.873	2.724	2.808
R^2	0.84	0.84	0.88

Table.3. The FTIR spectral characteristics of Biomass

Frequency (cm ⁻¹)	Functional Group
3370	bonded -OH group
2922	Aliphatic -CH group
1720	Stretching C=O group
1626	Aromatic C=C group
1033	C-O stretching of Carboxylic group

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