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Biosorption of Cu(II) ions onto the litter of natural trembling poplar forest

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Abstract

The litter of natural trembling poplar (*Populus tremula*) forest (LNTPF) was used for the biosorption of Cu(II) ions in a batch adsorption experiments. The sorption capacity of LNTPF was investigated as a function of pH, particle size, agitating speed, initial Cu(II) concentration, adsorbent concentration and temperature. The efficiency of copper uptake by the used LNTPF increases with a rise of solution pH, adsorbent concentration, agitating speed, temperature, and with a decline of particle size and initial Cu(II) concentration. The biosorption process was very fast; 94% of Cu(II) removal occurred within 5 min and equilibrium was reached at around 30 min.

Batch adsorption models, based on the assumption of the pseudo-first order, pseudo-second order mechanism were applied to examine the adsorption kinetics. The pseudo-second order model was found to best fit the kinetic data. EPR studies combined with FTIR spectroscopy were used to represent the biosorption mechanism.

Thermodynamic parameters such as ΔH°, ΔS° and ΔG° were calculated. The adsorption process was found to be endothermic and spontaneous. Equilibrium data fitted well to Langmuir adsorption model. This study proved that the LNTPF can be used as an effective, cheap and abundant adsorbent for the treatment of Cu(II) containing wastewaters.
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1. Introduction

Biosorption is a new and attractive treatment technology for removing of heavy metals for especially dilute wastewaters. Biosorption and/or bioaccumulation as the ability of biological materials to adsorb pollutant matters have received considerable attention for the development of an efficient, clean and cheap technology for wastewater treatment. The development of inexpensive adsorbents for the treatment of wastewaters is an important area in environmental sciences [1,2]. Different form of inexpensive, easily available and effective biosorbent such as tea factory waste [2], waste acorn of *Quercus ithaburensis* [3], waste biomass of *Sargassum* sp. [4], eucalyptus bark [5], *Hevea Brasilinesis* sawdust [6], oak sawdust [7], cone biomass of *Thuja orientalis* [8,9], *Araucaria angustifolia* tree waste [10],

orange waste [11], *Cassia fistula* waste [12], activated rubber wood sawdust [13], chemically modified corncobs [14], agricultural by-product of *Lentinus edodes* [15], non-living microbial biomass [16], fresh water algae [17–20], the biopolymer of chitin and/or chitosan which extracted from the shells of crustaceans [21–23], aerobic granular sludge [24] have been widely used as potential adsorbents for heavy metals.

Unlike organic pollutants, heavy metals are non-biodegradable materials and hence are accumulated in living organisms by food chains. Some metals such as Cd, Hg, Ag and Pb can become extremely toxic for the cycle of living beings. The others such as Cu, Zn, Mn, Fe, Ni and Co are essential for plant and animals in little quantities but when present in excess concentrations above certain limits, can be very harmful to living organisms [9]. The heavy and toxic metal contaminants in aqueous waste streams can cause serious water pollution problems being faced the world over. Conventional methods for removing dissolved heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology

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and evaporation recovery. However, these technology processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal [22,25]. Adsorption, an alternative technology for conventional wastewater treatment, has received considerable attention for the development of an efficient, clean and cheap technology.

The main sources of copper pollution are metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertilizer industry, etc. The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu(II) in drinking water of $1.5 \, \text{mg L}^{-1}$ [13]. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product such as food, water or drink [8].

In this study, the litter of natural trembling poplar (*Populus tremula*) forest (LNTPF) was used for the biosorption of Cu(II) ions which is known to be major contaminant at many sites around the world.

2. Materials and methods

2.1. Adsorbent preparation

In this study, the litter of natural trembling poplar (*Populus tremula*) forest (LNTPF), a low-cost and abundant adsorbent, were used for removal of Cu(II) ions from aqueous solutions. The LNTPF were collected in October 2004 on the forest floor of the natural-pioneer trembling poplar (*Populus tremula*) forest in the Kargapazarı mountain which is away 15 km from Hasankale district in Erzurum. It take a position between 40°06′07″N latitude and 41°52′01″E longitude (elevation 2111 m).

The LNTPF consists of the O_L (organic litter), the O_F (organic fermentation) and the O_H (organic humus) horizons of the soil profile. The LNTPF was dried at room temperature for a few days and ground in a warring blender to powder and sieved to constant size ($\leq$0,15; 0.15–0.25; 0.25–0.50; 0.50–1 mm). Certain size and portions of the samples were taken for biosorption. Zeta potentials were measured with a Zeta-Meter (ZETAMETER 3.0 + 542, USA). The Physicochemical characteristics of the LNTPF are presented in Table 1.

Table 1
Physicochemical properties of the LNTPF

	Units
Particle size (mm)	0.15–0.25
Moisture content at room temperature (%)	2.89
Ash content (%)	78.90
Total loss of dry ignition (%)	21.10
Bulk density (g cm^{-3})	0.622
BET surface area (m^2 g^{-1})	1.170

2.2. Preparation of Cu(II) solution

A stock of Cu(II) solution ($1000 \, \text{mg L}^{-1}$) is firstly prepared by dissolving 3.930 g CuSO$_4$·5H$_2$O in 1 L distilled water. Cu(II) solutions at the desired concentration are then obtained by successive dilutions. Fresh dilutions were used for each experiment. The initial pH adjustments were carried out either by diluted hydrochloric acid and sodium hydroxide.

2.3. Batch adsorption experiments

The batch biosorption experiments were conducted in 250 mL conical erlenmeyer flasks using an orbital shaker. Pre-weighted sample of the adsorbent and a measured volume of Cu(II) solution were taken in 250 mL Erlenmeyer. The mixture was agitated 300 rpm for 120 min to ensure equilibrium and filtered through (Schleicher&Schüll589) filter paper. Samples (5 mL) were taken before mixing the adsorbent solution and Cu(II) ion bearing solution and at pre-determined time intervals (1, 3, 5, 7, 10, 20, 30, 60 and 120 min) for the residual Cu(II) ion concentration in the solution. Cu(II) in the adsorbate was analyzed by standard complexometric methods [26]. All the experiments were carried out twice. The values used in calculations were mostly the arithmetic average of the two experimental data.

2.4. FTIR and EPR analysis

Fourier transform infrared (FTIR) and electron paramagnetic resonance (EPR) spectroscopy studies were used to characterize the reaction mechanism of LNTPF. The FTIR spectra were obtained (and transferred to Microsoft Excel) using Perkin-Elmer Spectrum One FTIR spectrometer. The EPR spectra were obtained an *x*-band EPR spectrometer at 9.53 GHz using Varian E104 EPR spectrometer.

3. Results and discussion

3.1. Influence of biomass concentration

This study was carried out at 25 °C and at pH 4.5 by varying the adsorbent amount 2, 5 and $10 \, \text{g L}^{-1}$ at constant initial Cu(II) concentration. The results are graphically shown in Fig. 1. It is apparent that the percent removal of copper increases with increase in the adsorbent dose from 2 to $5 \, \text{g L}^{-1}$ due to the increase in surface area of the adsorbent. In general, a high biomass dose is synonymous with a higher number of active sites and, in turn, of a high metal recovery. The 5 and $10 \, \text{g L}^{-1}$ adsorbent dose have remaining similar trends. This occurrence could be explained to many reasons, such as availability of solute, electrostatic interactions, interference between binding sites, and reduced mixing at high biomass densities. Thus, the adsorption sites remain unsaturated during the sorption process due to a lower adsorptive capacity utilization of the sorbent, which decreases the adsorption efficiency [20]. Since the $5 \, \text{g L}^{-1}$ adsorbent dose was determined sufficient for this research, the other research steps were conducted at this adsorbent concentration.
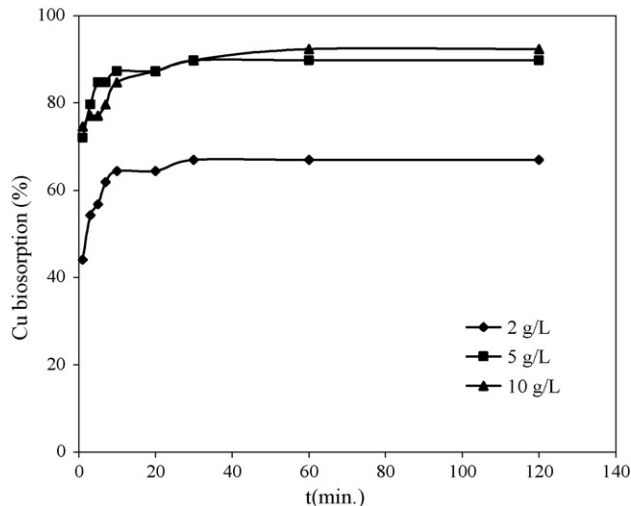
Fig. 1. Influence of adsorbent concentration on adsorption of Cu(II) by LNTPF (pH 4.5, agitating rate = 300 rpm, initial Cu(II) concentration = 50 mg L^{-1}).

However, copper(II) uptakes showed a reverse trend to the percentage adsorptions. With increasing adsorbent dosage from 2.0 to 10 g L^{-1}, the adsorption of copper(II) ion per unit weight of adsorbent decreased from 16.74 to 4.62 mg g^{-1}.

3.2. Influence of particle size

The experiments were carried out for four different particle sizes (Ø): ≤0.15, 0.15–0.25, 0.25–0.50 and 0.50–1.0 mm, under constant initial Cu(II) concentrations (50 mg L^{-1}) as in Fig. 2.

It reveals that the adsorption of copper on LNTPF decrease from 94.92 to 74.58% with the increased particle size from ≤0.15 to 0.50–1.0 mm. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity. Since there were significant removing differences between various particle sizes, the other research steps were conducted at high removing particle size as ≤0.15.

3.3. Influence of initial Cu(II) concentration

The effect of adsorbate concentration on the removal efficiency is shown in Fig. 3. Adsorbate concentrations were varied
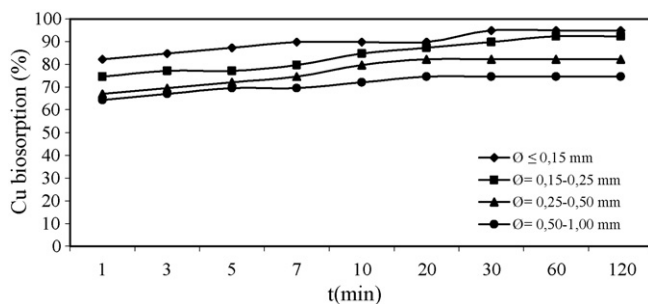

Fig. 2. Influence of adsorbent size on percentage adsorption (pH 4.5, temperature = 25 °C, initial metal concentration = 50 mg L^{-1}, adsorbent concentration = 5 g L^{-1}, agitating speed = 300 rpm).
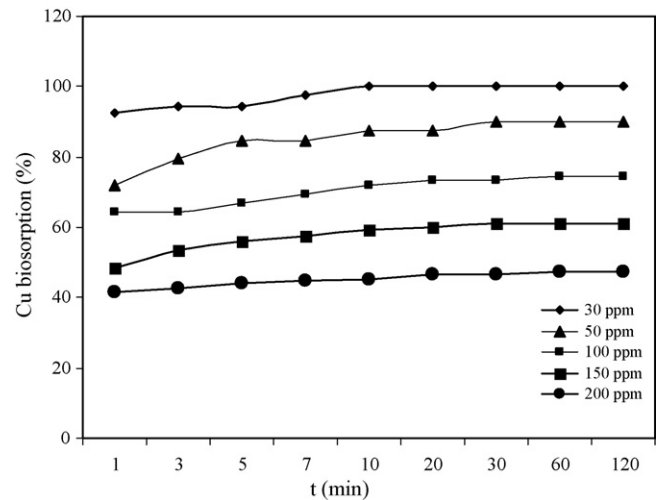

Fig. 3. Influence of initial Cu(II) concentration on Cu(II) biosorption efficiency (pH 4.5, temperature = 25 °C, particle size = 0.15–0.25 mm, adsorbent concentration = 5 g L^{-1}, agitating speed = 300 rpm).

from 30 to 200 mg L^{-1} (ppm). The equilibrium concentration of Cu(II) increased with increasing adsorbate concentration, because of decreasing surface area per unit adsorbent. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases [27]. As shown in figure, when the initial Copper(II) ion concentration was increased from 30 to 200 mg L^{-1}, the removal of metal ion decreased from 100 to 47.2%.

The biosorption capacities of Cu(II) onto LNTPF are presented in Fig. 4. As is shown in figure, when the initial Cu(II) concentration was increased from 30 to 200 mg L^{-1}, the adsorption capacity of LNTPF increased from 6 to 18.92 mg g^{-1}.

3.4. Influence of temperature

The influence of temperature on the removal of Cu(II) was investigated as a function of contact time. The results were graphed in Fig. 5. From this figure, the adsorption of metal ions
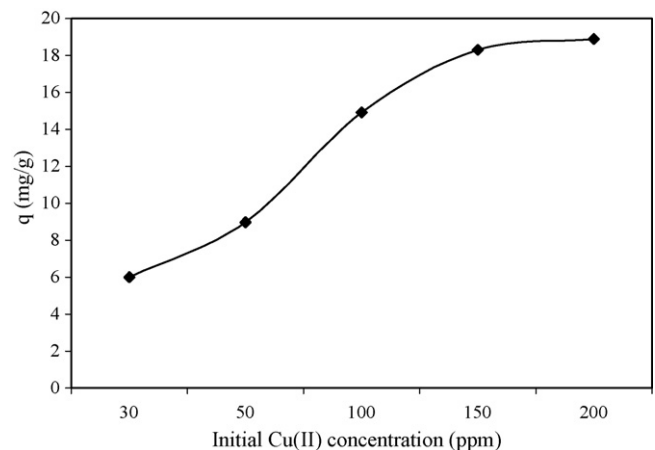

Fig. 4. The biosorption capacities of LNTPF at different initial Cu(II) concentrations (pH 4.5, temperature = 25 °C, particle size = 0.15–0.25 mm, adsorbent concentration = 5 g L^{-1}, agitating speed = 300 rpm).
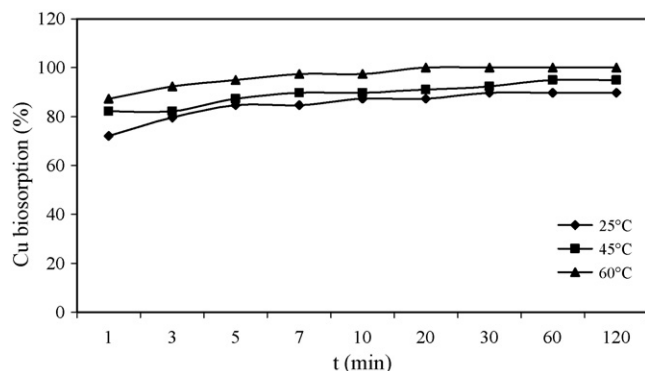
Fig. 5. Influence of temperature on Cu(II) biosorption efficiency ($C_0 = 50\,mg\,L^{-1}$, agitation speed = 300 rpm, pH 4.5, biosorbent concentration = 5 g L^{-1}, particle size = 0.15–0.25 mm).

Fig. 6. Influence of agitating speed on Cu(II) biosorption efficiency ($C_0 = 50\,mg\,L^{-1}$, $T = 25\,°C$, pH 4.5, biosorbent concentration = 5 g L^{-1}, particle size = 0.15–0.25 mm).

has been found to increase with an increase in temperature from 25 to 60 °C. Equilibrium was established in 20 min at the end of a rapid biosorption for 60 °C and 30 min for 25 and 45 °C. After an equilibrium time, no more Cu(II) was adsorbed.

The increase in adsorption capacity of LNTPF with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. At higher temperatures the possibility of diffusion of solute within the pores of the adsorbent may not be ruled out. Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperature [28].

The adsorption of Cu(II) on LNTPF increased from 8.98 mg g^{-1} (89.83% removal) to 10.0 mg g^{-1} (100% removal) when temperature was increased from 25 to 60 °C at an initial concentration of 50 mg L^{-1}.

3.5. Influence of agitating speed and contact time

The effect of agitating speed on biosorption was shown in Fig. 6. The agitation speed varied from 180 to 420 rpm. The adsorption efficiency increased with increase agitation speed and Cu(II) adsorption efficiency was maximal at 420 rpm. It reveals that the copper adsorption on LNTPF increase from 84.75 to 94.92% with the increased agitating speed from 180 to 420 rpm.

The influence of the contact time on adsorption of Cu(II) on LNTPF has been shown in Figs. 1–3, 5–7 where the adsorption rate of metal uptake was very fast, significant rate of Cu(II) removal occurred within 5 min and adsorption equilibrium was reached at 30 min. Further increase in contact time did not show an increasing in biosorption. These results show that the actual adsorption of metal ion binding to the biomass is a rapid phenomenon. The very fast sorption and settling for the LNTPF make this material suitable for continuous flow water treatment systems [29].
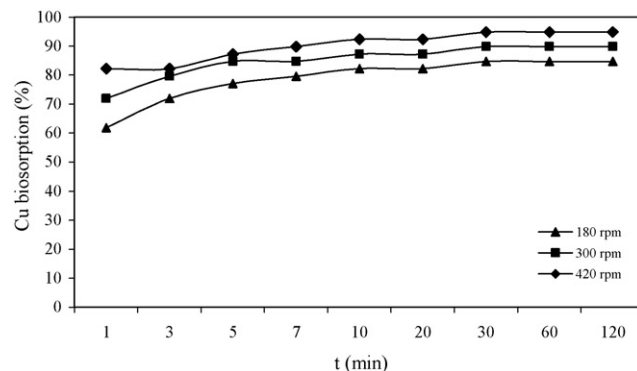
3.6. Influence of pH on Cu(II) biosorption

The solution pH affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbates [30]. Since pH is one of the main controlling parameter affecting the adsorption process, the optimum pH for the biosorption of Cu(II) was determined. The influence of pH on the adsorption of copper(II) onto LNTPF is presented in Fig. 7.

These results indicate that an increase in pH has a positive effect on metal uptake up to pH 4.5, since the competition between protons and metal cations for the active sites of the biomass decreases. The maximum adsorption of copper(II) ions on LNTPF were observed at pH 4.5. Above pH 4.5, Cu(II) biosorption significantly decreased. A significant reduction in copper biosorption capacity was observed at pH 5.0. Also, beyond pH 6.0 the copper(II) was precipitate as its hydroxide complexes [9]. These results seem to suggest that the adsorption of Cu(II) to biomass is mainly due to ionic attraction. The medium pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups. The carboxylate and phosphate groups carry negative charges that allow the cell wall components to be able removers of cations [31].
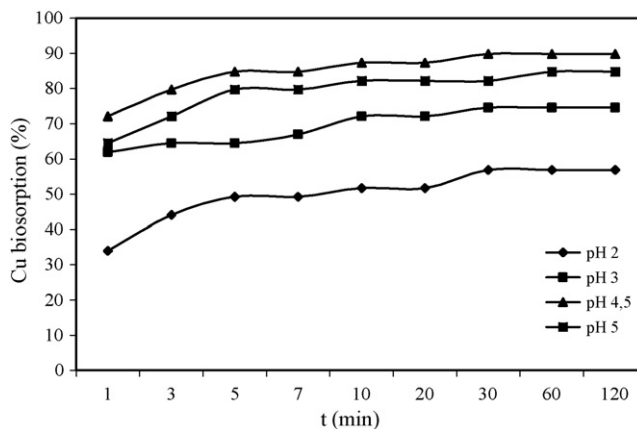

Fig. 7. The influence of pH on Cu biosorption (initial Cu(II) concentration = 50 g L^{-1}, adsorbent dosage = 5 g L^{-1}, temperature = 25 °C, agitating rate = 300 rpm, particulate size = 0.15–0.25 mm).

Zeta potential is one of the most useful parameters to characterize the surface charge of biomaterials [24]. Since there was a close relationship between the zeta potential and the biosorption capacity of biomaterials, the zeta potentials of LNTPF were measured. The zeta values were -7.66, -9.13, -15.9, -18.2, -20.4, -19.1 mV at pH 2, 3, 4, 5, 6, 7, respectively. These results demonstrated that the zeta potential of LNTPF depended on the solution pH and had a negative charge at all pH values. The zeta potentials of the LNTPF at all pH values had negative charges might be causes of the very fast Cu(II) biosorption process.

At the research pH (pH 2–7) there are three copper species present in aqueous solution: Cu^{2+}, $CuOH^+$ and $Cu(OH)_2$. These species are adsorbed an electrostatically interaction at the surface of the biosorbent. The heavy metal cations are completely released under circumstances of extreme acidic conditions. At lower pH values and higher (H^+) ion concentrations, the surfaces of LNTPF were partially neutralized yielding negative surface charges and therefore H^+ ions compete with metal cations for the exchange sites in the system, and thus became lower attraction forces between the adsorption sides and Cu^{2+} ions. While pH increased the biosorbent surface became more and more negatively charged and therefore the biosorption of positively charged Cu^{2+} and $Cu(OH)^+$ species were more favorable [8].

3.7. Adsorption mechanism determined by FTIR and EPR analysis

Before recording the FTIR spectra of the copper binding LNTPF, it has recorded the spectrum of the LNTPF alone in order to determine the main functional groups of LNTPF participate in copper adsorption. The FTIR spectra before and after adsorption of LNTPF are shown in Fig. 8a and b. There were clear band shifts and intensity decrease the band at 1645, 1387 and 782 cm^{-1}. These bands are the main functional groups of LNTPF participate in copper adsorption which are shown in Table 2.

From the FTIR spectra, three band decreases of the functional groups on the biomass were detected at 1645, 1387 and 782 cm^{-1}. These decreases were attributed, respectively, to C=O stretching, carboxylate functional group and the –C–C– group participate in Cu(II) biosorption.

Electron paramagnetic resonance (EPR) is the resonant absorption of electromagnetic radiation by a paramagnetic particle (an atom, molecule or ion), having a nonzero electronic spin due to unpaired electrons in its outer shells, and it is a very powerful nondestructive technique used for the study of the electronic structure of paramagnetic centers, e.g., transition
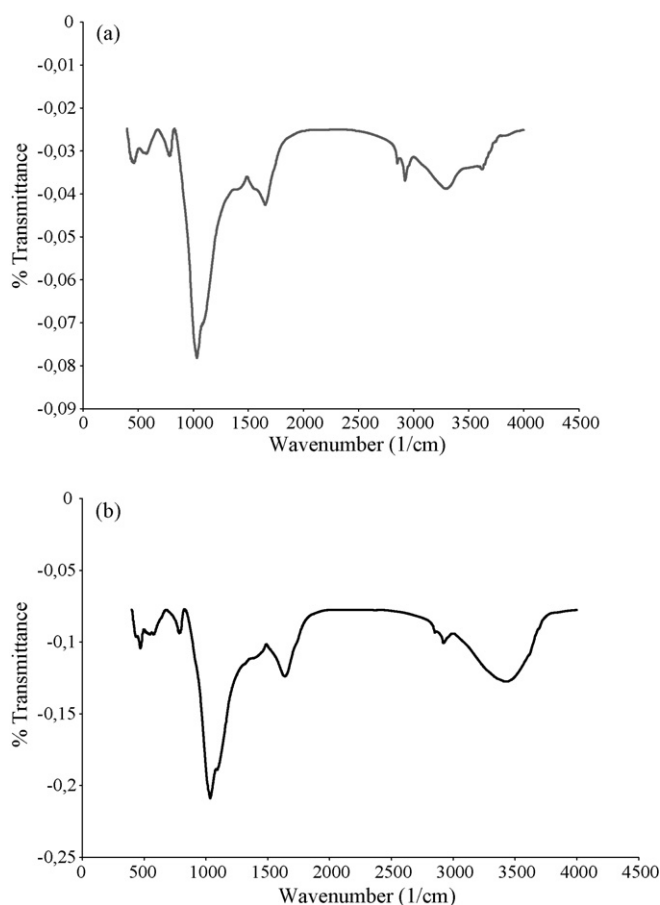

Fig. 8. The FTIR spectra of LNTPF (a, before and b, after adsorption).

metal ions such as copper, chromium, nickel, etc. in a large variety of organic and inorganic compounds. The flipping of spins induced in a paramagnetic system embedded in a static magnetic field by the absorption of the electromagnetic radiation is the physical principle behind the EPR technique. For a system with a spin $S = 1/2$, e.g. a free electron or a radical, there are two energy levels corresponding to the spin parallel and antiparallel to the static magnetic field, the latter being of lowest energy [32].

EPR can be applied to the investigation of metal-charged biomasses. For this aim, the main information provided by this technique are the chemical identity, valence states and relative concentration of the metals involved in the biosorption processes [32]. In the early researches, the adsorption data were combined with EPR spectroscopy to obtain structural information about the metal binding and estimate of adsorption mechanism [33–37]. In this research, in order to compare the natural and copper binding LNTPF and estimate mechanism of copper ion biosorption, the

Table 2
The FTIR spectral characteristics of LNTPF before and after adsorption

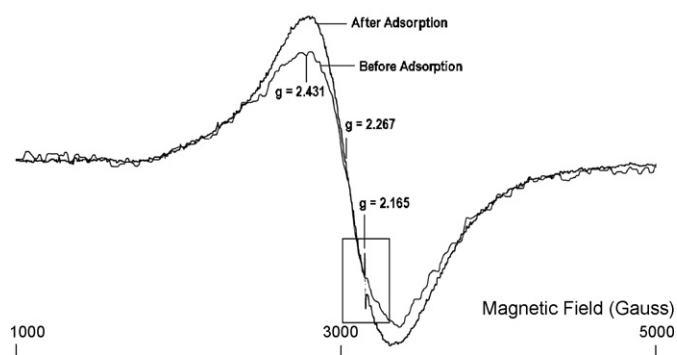| IR peak	Absorption bands (cm^{-1})			Assignment
	Before adsorption	After adsorption	Differences	
1	1645	1621	-24	C=O or C=C stretching
2	1387	1371	-16	Carboxylate functional group
3	782	775	-7	–C–C– group

Fig. 9. EPR spectra of LNTPF were measured at room temperature ($25 \pm 2\,^\circ$C) with a microwave frequency of 9.53 GHz.

EPR spectra were taken from the alone and copper loading. The EPR spectra before and after adsorption of LNTPF are shown in Fig. 9.

By comparing the natural and copper loading EPR signal, it was observed that the amplitude of EPR signal decreased after adsorption. The broad EPR lines stem from strong dipolar interactions of their unpaired magnetic moments. The capture of copper(II) by biomasses is also observed by using EPR spectroscopy to study copper adsorption on LNTPF samples were measured using an x-band (9.53 GHz) EPR spectrometer with modulation of magnetic field of 10 kHz. The microwave frequency was recorded. EPR spectra were measured with attention of 23 dB to avoid microwave saturation of resonance absorption curves. Fig. 9 shows the EPR spectra for Cu-charged LNTPF measured at room temperature. With $S = 1/2$(Cu(*II*)), $I = 3/2$ for Cu(II) with 100% natural abundance. g-Factor was calculated from resonance conditions as seen in follows:

$$g = \frac{h\nu}{\beta B_r} \tag{1}$$

where h is the Planck constant, ν the microwave frequency, β the Bohr magnethon and B_r is the resonance magnetic field.

Two lines were observed in these resonance absorption curves in Fig. 9. Free radicals of Cu(II) are responsible for two EPR components. EPR line unresolved hyperfine structure are characteristics for free radicals of Cu(II). Band centered at about 2788 G ($g = 2.431$) and 3142 ($g = 2.165$) with peak-to-peak line width of 354 G. It can be seen from Fig. 9, that free radicals with g equal to 2.165 at 3142 G are present in the LNTPF after biosorption. The g-value close to 2 confirms that the free radicals or transition metal ions do have $g \approx 2$, but there are also systems which show marked deviations from this value [38]. Free radicals are generally highly unstable and its have very short residence time. However, the certain free radicals have persisted for much longer duration because they were trapped in a stable cell wall matrix [39]. The EPR analysis indicates that one probable sorption sites consist of carboxylate moieties of alginic acid functional groups [40]. This occurrence was confirmed FTIR analysis as seen in Table 2. The fast biosorption kinetics observed is typical for biosorption of metals involving no energy-mediated reactions, where metal removal from

solution is due to purely physico-chemical interactions between biomass and metal solution [40,41].

3.8. Adsorption isotherms

An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants [42]. Several mathematical models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. The most widely used models are the Freundlich, the Langmuir and the Temkin adsorption isotherm model. In order to determine the mechanism of Cu(II) adsorption on the LNTPF and evaluate the relationship between adsorption temperatures, the experimental data were applied to the Langmiur, Freundlich and Temkin isotherm equations. The contact time of 30 min and pH values of 4.5 were chosen as the experimental conditions for the determination of adsorption isotherms of Cu(II) ions. The constant parameters of the isotherm equations for this adsorption process were calculated by regression using linear form of the isotherm equations. The constant parameters and correlation coefficient (R^2) are summarized in Table 3.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L, which is defined by:

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

where b is the Langmuir constant and C_0 the initial metal ion concentration (mg L^{-1}). R_L value indicates the type of isotherm. R_L values between 0 and 1 suggest favorable adsorption. As seen in Fig. 10, R_L values for copper(II) at various temperatures were found to be between 0 and 1.

As seen from Table 3, the Langmuir isotherm was generates a satisfactory fit to the experimental data as indicated by correlation coefficients. Except for 60 $^\circ$C, the Langmuir isotherm shows a better fit to adsorption data than the Freundlich isotherm.

Table 3
Isotherm constants for Cu(II) sorption on LNTPF

Isotherm equations	Temperature ($^\circ$C)		
	25	45	60
Langmuir isotherm			
Q_0 (mg g^{-1})	19.531	29.761	29.325
b (L g^{-1})	0.166	0.186	0.3574
R^2	0.9914	0.9952	0.9719
Freundlich isotherm			
K (L g^{-1})	6.14	8.316	14.184
n	3.897	3.307	5.568
R^2	0.9664	0.8745	1.000
Temkin isotherm			
A (L g^{-1})	0.869	2.433	233.43
B	4.3857	5.3991	2.9309
R^2	0.9442	0.8613	0.9724
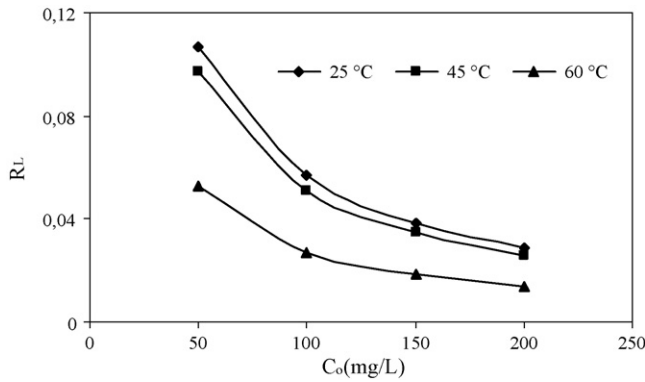
Fig. 10. R_L values for the adsorption of copper(II) onto LNTPF at various temperatures.

Fig. 11. $\ln K_C$ vs. $1/T$ for the adsorption of Cu(II) by LNTPF from aqueous solution.

The Langmuir model also seemed to agree well with the experimental data of the copper(II) considering that obtained linear regression coefficients are greater than 0.99 at 25 and 45 °C. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the adsorbent surface; since the Langmuir equation assumes that the surface is homogenous [43].

3.9. Adsorption thermodynamics

The values of the thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS) were determined using the following equation and presented in Table 4.

The standard Gibb's energy:

$$\Delta G^\circ = -RT \ln K_C \tag{3}$$

where ΔG° is standard free energy change, J; R the universal gas constant, 8.314 (J/mol K) and T is the absolute temperature, K.

The apparent equilibrium constant (K_C) of the adsorption is defined as:

$$K_C = \frac{C_{ad,eq}}{C_{eq}} \tag{4}$$

where $C_{ad,eq}$ and C_{eq} are the concentration of Cu(II) on the adsorbent and residual Cu(II) concentration at equilibrium, respectively. In this case the activity should be used instead of concentration in order to obtain the standard thermodynamic equilibrium constant (K_C) of the adsorption system.

$$\ln K_C = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

Table 4
Thermodynamic parameters of LNTPF at initial Cu(II) concentration of 200 mg L^{-1}, pH 4.5

T (K)	ΔG° (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J/mol K)
298	−2.502		
318	−4.804	25.188	93.18
333	−5.665		

The plot of $\ln K_C$ as a function of $1/T$ yields is shown in Fig. 11, a straight line from which ΔH° and ΔS° can be calculated from the slope and intercept, respectively.

Table 4 shows the ΔG° values at all temperatures have negative values. This occurrence indicates that the adsorption of Cu(II) is spontaneous nature and a better adsorption is actually obtained at higher temperatures. The positive value of ΔH indicates the endothermic adsorption nature. The positive value of ΔS° shows the affinity of the LNTPF for Cu(II) ions and suggests some structural changes and irreversibility in copper adsorption onto LNTPF.

3.10. Adsorption kinetics

Adsorption kinetics describes the solute uptake rate which intern controls the equilibrium time [44,45]. In order to investigate the adsorption processes of Cu(II) on the LNTPF, pseudo-first-order, pseudo-second-order kinetic models were used. The pseudo first-order rate Lagergren model is:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{6}$$

where q_t (mg g^{-1}) is the amount of adsorbed Cu(II) on the adsorbent at time t and k_1 (min^{-1}) is the rate constant of first-order adsorption. The integration of Eq. (6) with the initial condition, $q_t = 0$ at $t = 0$ leads to [28]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

A straight line of $\log(q_e - q_t)$ versus t suggests the applicability of this kinetic model. q_e and k_1 can be determined from the intercept and slope of the plot, respectively [9]:

The kinetic data were further analyzed using a pseudo second-order relation, the linear form of which is as follows [46]:

$$\frac{dq}{dt} = k_2(q_e - q_t) \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{9}$$

where k_2 (g/mg min) is the rate constant of second order adsorption. The plot t/q_t versus t should give a straight line if second

Table 5
A comparison of the first and second-order kinetic model parameters obtained at different initial Cu(II) concentrations and at different temperature

C_0 (mg L^{-1})	First-order kinetics		R^2	Second-order kinetics		R^2
	k_1 (min^{-1})	q_e		k_2 (g/mg min)	q_e	
25 °C						
50	0.379	2.773	0.8964	0.394	8.326	0.9999
100	0.221	3.000	0.8987	0.177	14.850	0.9998
150	0.140	3.210	0.9188	2.278	18.500	0.9999
200	0.156	2.350	0.9945	0.185	18.83	0.9999
45 °C						
50	0.080	0.899	0.5885	0.327	9.276	0.9997
100	0.082	1.189	0.9296	0.262	18.520	0.9999
150	0.131	3.856	0.9797	0.091	24.937	0.9997
200	0.275	3.122	0.8862	0.240	25.910	1.0000
60 °C						
50	0.078	0.918	0.7262	0.342	10.000	0.9998
100	0.096	1.365	0.9585	0.234	19.120	0.9999
150	0.119	1.753	0.7243	0.224	25.250	1.0000
200	0.133	3.084	0.9536	0.124	29.32	0.9999

order kinetics are applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively [9].

The kinetics of biosorption of copper on LNTPF is studied using two kinetic models, which are the pseudo-first-order and pseudo-second-order [3,20,47], have been applied for the experimental data The linear form plots of pseudo-second-order for the adsorption of different initial Cu(II) ions were obtained at the different temperatures as 25, 45 and 60 °C. The kinetic parameters for the adsorption of Cu(II) onto LNTPF are given in Table 5 and the pseudo-second-order plots are given in Fig. 12.

The plots for the pseudo-first-order equation are not shown as a figure because the correlation coefficients for the pseudo-first-order model are lower than that of the pseudo-second-order model.

As seen from Table 5, the pseudo-first-order model is not suitable for modeling the adsorption of Cu(II) onto LNTPF. In contrast, the application of a pseudo second-order model leads to much better regression coefficients, all greater than 0.99. Furthermore, the values of q_e are very close, as indicated in Table 5, thus, the pseudo-second-order kinetic model is well suitable to model the sorption curves of Cu(II) onto LNTPF. In accordance with the pseudo second-order reaction mechanism, the overall rate of Cu(II) sorption processes appear to be controlled by the chemical processes.
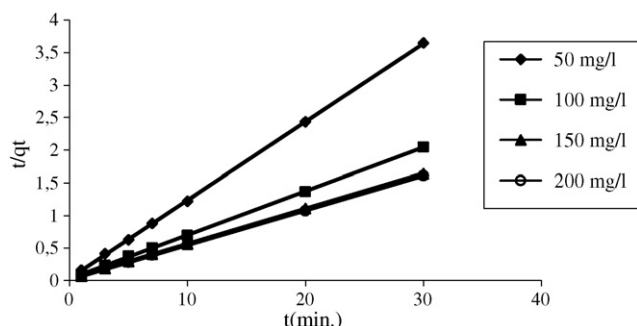

Fig. 12. The pseudo-second-order plots of different initial Cu(II) ions.

4. Conclusions

The present study shows that the litter of natural trembling poplar forest is an effective and inexpensive adsorbent for the removal of Cu(II) ions from aqueous solutions. The following conclusions were drawn from the present study:

- The efficiency of copper uptake by the used LNTPF increases with a rise of solution pH, adsorbent concentration, agitating speed, temperature, and with a decline of particle size and initial Cu(II) concentration. The maximum copper biosorption occurred at initial pH 4.5. The biosorption process was very fast; 94% of Cu(II) removal occurred within 5 min and equilibrium was reached at around 30 min. The adsorption of Cu(II) on LNTPF increased from 8.98 mg g^{-1} (89.83% removal) to 10.0 mg g^{-1} (100% removal) when temperature was increased from 25 to 60 °C at an initial concentration of 50 mg L^{-1}. The adsorption of copper(II) ion per unit weight of adsorbent decreased from 16.74 to 4.62 mg g^{-1} with increasing adsorbent dosage from 2.0 to 10 g L^{-1}. The LNTF has high adsorption capacity and rapid adsorption rate. Thus, it may be promising and economical alternative biosorbent for Cu(II) removal.
- The zeta potential of LNTPF depended on the solution pH and had a negative charge at all pH values. This occurrence might be causes of the very fast Cu(II) biosorption processes.
- From FTIR study, C=O stretching, carboxylate functional group and –C–C– group were participated in Cu(II) biosorption.
- The EPR study are shown that free radicals with g equal to 2.165 at 3142 G are present in the LNTPF after biosorption, and metal removal from solution is due to physico-chemical interactions between biomass and metal solution.
- The pseudo-second order equation provided the best correlation for the adsorption data.
- The Langmuir, Freundlich and Temkin adsorption models were used to represent the experimental data. The Langmuir

isotherm was generates a satisfactory fit to the experimental data.

- Thermodynamic calculations showed that the sorption process by LNTPF has endothermic and spontaneous nature.
- These results demonstrate the LNTPF is great potential and low-cost heavy metal adsorbents. The LNTPF could be used to as an effective, cheap and abundant adsorbent for the treatment of Cu(II) containing wastewaters.

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