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Biosorption of copper(II) from aqueous solutions by *Pleurotus cornucopiae*

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ABSTRACT

Pleurotus cornucopiae was used as biosorbent for the adsorption of Cu(II) ions in water. The adsorption process was carried out in a batch process and the effects of contact time, initial pH, initial Cu(II) ion concentration, adsorbent amount on the adsorption were investigated. The removal percentage of Cu(II) was increased with an increase in pH, biomass concentration and a decrease in Cu(II). *Pleurotus cornucopiae* exhibited the highest Cu(II) uptake of 25.25 mg · g^{-1} of biomass at pH 5 in the presence of 100 mg l^{-1} Cu(II) at 298 °K. The experimental isotherm data were analysed using the Langmuir, Freundlich and Temkin equations. It was observed that Langmuir model exhibited the best fit to experimental data. The experimental data were analysed using four sorption kinetic models the pseudo first and second order equations, and the Elovich and the Intraparticle diffusion equation to determine the best fit equation for the biosorption of Cu(II) ions onto Pleurotus cornicopiae. Pseudo second order model described well the sorption kinetic of Cu(II) ions in comparison to pseudo first order, Elovich equation and Intra-particle diffusion kinetic model. Fourier transform infrared analysis revealed that hydroxyl, carboxyl, amino functional groups were mainly responsible for Cu(II) biosorption.

Keywords: Biosorption; Copper; Equilibrium studies; Kinetic studies

1. Introduction

Heavy metal pollution is an environmental problem of worldwide concern with effluents from various industrial processes representing one of the most important sources of pollution [1]. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Elevated environmental levels of Cu(II) come from a variety of sources. Mining, metal cleaning, plating baths, pulp, paper and paper board mils, refineries, fertlizer industry, etc. are the potential sources of Cu(II) in industrial effluents [2].

Copper, a widely used metal in industry, is an essential trace element for human health and play an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity. The adult human body contains 100–150 mg of Cu(II), but excess amounts in the body can be toxic [3]. In aqueous environments, the speciation of the metal is dependent both on ligand concentration and pH. While the cupric ion (Cu(II)) is the metallic form most toxic to flora and fauna, it is also a nutrient necessary for algal growth [1].

If allowed to enter the environment excessive amounts of Cu(II) can cause serious potential health issues such as nausea, headache dizziness, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding, liver and kidney failure, and death [4–9]. The world health organization (WHO) recommended a maximum acceptable concentration of Cu(II) in drinking water of 1.5 mg · L^{-1} [5].

In recent year, increasing concern about the effect of toxic metals in the environment has resulted in more strict environmental regulations for industrial applications that discharge metalbearing effluents [10]. Removal of metal ions from wastewater in an effective manner has become an important issue [2]. Efficient methods for the removal of metals have resulted in the development of new separation technologies. Precipitation, adsorption, ion exchange, flocculation, absorption, electrochemical processes and/ membrane processes such as electrodialysis, nanofiltration and reverse osmosis are commonly applied for the treatment of industrial effluents [2,5,7,9,11–19]. However, these techniques have several disadvantages such as high chemical cost, low removal efficiency, low selectivity, high-energy requirements, and generation of secondary toxic slurries. Among these various treatment techniques, activated carbon adsorption is one of the most commonly used due to its high efficiency and easy operation. However, it is expensive and may also require complexing agents to improve its ability to remove inorganic matter [11]. Thus, there is a need to develop a cost effective and an efficient technique for metal removal from wastewaters. That is biosor ption. Biosorption is considered as an alternative process for the removal of heavy metals, metalloid species, and compounds from aqueous solution by biological materials. Compared with conventional methods for the removal of toxic metals from wastewater, the biosorption process offers potential advantages such as low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed of, and high efficiency in detoxifying very dilute effluents [13,19–22,24]. Large number of studies were reported in literature on biosorption of [4,8,10,12,17,20,21,23–46] heavy metals onto different microbial and plant biomass.

In this fundemental work, a biosorption study of Cu(II) on *Pleurotus cornucopiae* was developed. In none of the literature studies, isotherms and the kinetics of biosorption of Cu(II) ions onto *Pleurotus cornucopiae* was investigated as a function of operating parameters. Zeta potential measurements have been used experimentally to predict optimum pH levels on *Pleurotus cornucopiae*. Adsorption equilibrium and kinetic works were carried out to evaluate the removal capacity of *Pleurotus cornucopiae* as a function of pH, biosorbent concentration, initial metal ions concentration and contact time.

2. Material and medhod

2.1. Collection and preparation of biomass samples

Pleurotus species are characterized by a white spore print, attached to decurrent gills, often with an eccentric stipe, or no stipe at all. They always grow on wood on nature, usually on dead standing trees or fallen logs [47]. In this study, *Pleurotus cornucopiae* which was *species of Pleurotus* was used as a biosorbent for the biosorption of Cu(II) ions. Samples of biomass were collected from dense forests covering area of Erzurum Atatürk University Campus, Turkey, in April and May of 2007. All samples were washed in distilled water and then dried in the open air. The dried biomass were cut into small pieces, ground in a motor to a very fine powder and sieved to select particles of less than 0.5 mm for use as a biosorbent in batch studies. The Brunauer- Emmelt, Teller (BET) surface area was measured from N_2 adsorption isotherms with a sorptiometer and the surface area of the biosorbent was determined to be 0.862 m^2/g (BET-N_2).

2.2. Zeta potential measurements

In order to study the possible biosorption mechanism, the zeta potential of the *Pleurotus cornucopiae* was measured before and after the metal ions adsorption using the microelectrophoretic apparatus Zeta Meter (Zeta Meter System 3.0 + 542 USA).

2.3. Fourier transform infrared analysis

Fourier transform infrared (FTIR) study was used to characterize the reaction mechanism of *Pleurotus cornucopiae*. The FTIR spectra was obtained using Perkin-Elmer Spectrum One FTIR spectrometer

2.4. Synthetic wastewater preparation

Synthetic wastewater solutions were prepared by dissolving analytical grade $CuSO_4$. $5H_2O$ in distilled water to obtain 1,000 $mg \cdot l^{-1}$ of Cu(II) solution. The solution was diluted to the required concentration for experiments. The pH of the solution was measured and observed as 5 ± 0.5 and no chemicals were added to change pH.

2.5. Batch biosorption experiments

The factors that affect the biosorption rate and uptake capacity of the biosorbent were examined in a batch system. Batch biosorption tests were conducted by mixing known weight of *Pleurotus cornucopiae* and 50 ml of solution of known Cu(II) ion concentrations used were in the range 50–250 $mg \cdot l^{-1}$. The mixture was shaken in a mechanical shaker (Thermolyne ROSI 1000) samples were taken at known time intervals. Preliminary experiments showed that biosorption is fast and the removal rate is negligible after 60 min. Therefore, contact time of 60 min were used for batch tests. The sample was filtered to remove any fine particles (Whatman, 110 mm Ø and 11 μm pore size) and analyzed for the Cu(II) ion. The Cu(II) concentration in the supernatant solution was determined using flame atamic absorbtion spectrophotometry (Shimadzu AA-670) at 324.8 nm. Series of experiments were conducted to determine the effect of adsorbent dose, initial metal ion concentration, contact time and initial pH on biosorption. Effect of initial solution pH on biosorption was determined by mixing

0.2 g of biosorbent with 50 mL of solution containing metal concentration of 100 mg · l^{-1} at various pH values ranging from 2 to 5. Solution pH was adjusted with 0.5 M, HCI and NaOH solutions. The mixture was shaken for 1 h and the solution was filtered and analysed. All the experiments were conducted at 25°C. Biosorption experiments were carried out in duplicate.

The metal concentration in the liquid phase was determined at beginning (*Co*) and equilibration (*Ce*) in mg · l^{-1}. The following equation was used to compute biosorbent uptake capacity at equilibrium q_{eq} (mg · g^{-1}):

$$q_{eq} = (Co - Ce) \times \frac{V}{M}$$

Where *M* is the dry mass of biomass in grams and *V* is the volume of solution in litres.

Percent removal of Cu(II)(%) is

$$\frac{Co - Ce}{Co} \times 100$$

2.6. Equilibrium isotherms and kinetics of biosorption

Equilibrium studies were carried out by agitating 50 ml of copper solutions of initial concentrations varying from 50 to 200 mg · l^{-1} with 0.025–0.3 g of *Pleurotus cornucopiae* at 25°C for 60 min at a constant stirring speed at a pH of 5.

It is important to point out that the equilibrium sorption studies determine the capacity of the sorbent, which can be described by a sorption isotherm, characterized by certain constant whose values express the surface properties and affinity of sorbent. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface [2]. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, many different isotherm models have been proposed for the biosorption of solutes in a liquid solution onto a solid surface. Three isotherm equations have been tested in the present study, namely, Langmuir, Freundlich and Temkin.

2.6.1. Langmuir isotherm

The Langmuir isotherm was used to describe observed sorption phenomena and suggests that uptake occurs on a homogeneous surface by monolayer sorption with out interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The linear form of the equation can be written as Eq. (1)

$$\frac{Ce}{q_{eq}} = \frac{1}{b \cdot q_{\max}} + \frac{Ce}{q_{\max}} \tag{1}$$

where C*e* is the equilibrium concentration of Cu(II), q_{eq} is the amount of adsorption at equilibrium, $q_{\max}$ is the maximum monolayer capacity, and *b* is an equilibrium constant of Langmuir. The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process. The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) that can be defined by the following Eq. (2) [8].

$$R_L = \frac{1}{(1 + b \cdot Co)} \tag{2}$$

where Co is the initial concentration (mg · l^{-1}) and *b* is the Langmuir equilibrium constant (l · mg^{-1}). It is reported that, when $0 < R_L < 1$, the sorption system is a favorable isotherm. It can be explained apparently that when b > 0, sorption system is favorable [9].

2.6.2. Freundlich isotherm

The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The linear form of the equation can be written as Eq. (3)

$$\ln q_{eq} = \log K_F + \frac{1}{n} \log Ce \tag{3}$$

where, K_F (mg·g^{-1}) is the adsorption capacity and *n* is related to the adsorption intensity of the adsorbent; and where, K_F and $\frac{1}{n}$ can be determined from the linear plot of log (q_{eq}) versus log (C*e*).

2.6.3. Temkin isotherm

Another model, Temkin isotherm, was also used to fit the experimental data. Unlike the Langmuir and Freundlich equation, the Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [9]. The isotherm can be written as Eq. (4)

$$q_{eq} = \frac{R \cdot T}{b_T} \ln(A_T Ce) \tag{4}$$

where A_T is the equilibrium binding constant corresponding to the maximum binding energy, b_T is the

Temkin isotherm constant, T is the temperature (K), and R is the ideal gas constant (8.315 J $mol^{-1} \cdot K^{-1}$). The isotherm constants were determined from linear isotherm graphs for each of the isotherm equations tested.

In order to quantitatively compare the applicability of each isotherm [5], the standart deviation (S.D.) is calculated by Eq. (5).

$$\text{S.D.} = \sqrt{\frac{\sum [(q_{eq,\exp} - q_{eq,cal}) \,/\, q_{eq,\exp}]^2}{(n-1)}} \tag{5}$$

where n is the number of data points.

In order to examine the mechanism of biosorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyse the rate data. In this work, four kinetic models were applied to our experimental data.

The pseudo-first order kinetic model [5] has the following form.

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

where q_{eq} and q_t($mg \cdot g^{-1}$) is the amount of adsorbed Cu(II) on the biosorbent at equilibrium ($mg \cdot g^{-1}$) and at time (t), espectively, and k_1 is the rate constant of pseudo-first order adsorption process (min^{-1}). The integrated form of Eq. (6) is represented as Eq. (7)

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2,303} \times t \tag{7}$$

A straight line of $\log(q_{eq} - q_t)$ versus t suggests the applicability of this kinetic model, q_{eq} and k_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo-second order kinetic model as developed by Ho and McKay [48] has the following form;

$$\frac{dq}{dt} = k_2(q_{eq} - q_t)^2 \tag{8}$$

where k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is the equilibrium rate constant of pseudo-second order biosorption ($g.mg^{-1} \cdot min^{-1}$). Eq. (8) can be rearranged and linearized to obtain Eq. (9):

$$\frac{t}{q_t} = \frac{1}{k_2(q_{eq})^2} + \frac{t}{q_{eq}} \tag{9}$$

The plot $\frac{t}{q_t}$ versus t should give a straight line if second-order kinetics are applicable and q_{eq} and k_2 can be determined from the slope and intercept of the plot, respectively.

The Elovich kinetic model [5] is given by Eq. (10)

$$q_t = \frac{1}{\beta} In(\alpha\beta) + \frac{1}{\beta} Int \tag{10}$$

where α is the initial sorption rate constant (g^{-1} min^{-1}), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g^{-1}).

The plot q_t versus Int should give a straight line if the Elovich kinetic model is applicable and $\frac{1}{\beta}$ and α can be determined from the slope and intercept of the plot, respectively.

Intra-particle diffusion model [24] is given by Eq. (11)

$$q_t = k_{\text{int}} t^{1/2} \tag{11}$$

where k_{int} is the intraparticle diffusion rate constant, ($mg \cdot g^{-1} \cdot min^{-1/2}$).

3. Result and discussion

3.1. Characterization of the biosorbent

Changes in the functional groups and surface properties of the biosorbent were confirmed by FTIR spectra before and after Cu(II) adsorption. The FTIR spectral characteristics of *Pleurotus cornicopiae* before and after adsorption are listed in Table 1. As can be seen from

Table 1
The FTIR spectral characteristics of Pleurotus cornicopiae before and after adsorption

Absorption bands (cm^{-1})		
Before adsorption	**After adsorption**	**Assignment**
3875.41	3835.93	OH groups
3521.50	3508.68	OH group
3394.54	3336.65	Bonded hydroxyl groups, –NH stretching
3177	3141.43	=C–H stretching
3017	2952.85	=C–H stretching
1583.76	1522.63	–NH– bending, Amide II band
1454.15	1441.01	C–H bending
1142.60	1131.84	–C–O–C group
1010.50	980.86	–C–O stretching
950.68	919.13	C=C–H bending, N-H stretching
866.93	847.40	S=O stretch
730.32	692.05	C=C stretching, CH_2 rocking

Table 1, the analysis of the FTIR spectra showed the presence of ionizable functional groups (like hydroxyl, carboxyl, amino) that are able to interact with protons or Cu(II) metal ions. The spectra of raw biomass exhibits a broad band between 3,000–3,875 cm^{-1} due to the presence of hydroxyl groups on the biomass surface and are attributed to water molecules hydrogen bonded with -OH groups on the biomass surface. Also, at around 3,300–3,110 cm^{-1} band is a result of N–H stretching in resonance with overtone. The wave number observed at 1,010.50 cm^{-1} is due to C–O group in carboxylic and alcoholic groups. The =C–H stretching bonds due to unsaturated acyl chains are found at 3,177–3,017 cm^{-1}. In summary, the biomass contains –OH, –NH stretching, =C–H stretching, –NH bending, Amide II bond, –C–O–C group, –C–O stretching, C=O–H Bending, S=O stretch, C=C stretching and CH_2 rocking.

3.2. Effect of biosorbent dose

Effects of biosorbent dose on percentage of Cu(II) ion removal and the amount of Cu(II) adsorbed (q_{eq}) at equilibrium conditions are shown in Fig. 1. Biosorbent dose seemed to have a great influence in biosorption process. Dose of biomass added into the solution determine the number of binding sites available for adsorption. Percentage of Cu(II) ion removal increased from 17.45 to 100% when the biosorbent dose per 50 ml of solution was increased from 0.025–0.35 g. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal removal at a high dose. However, as shown in Fig. 1, the amount of metal ions adsorbed per unit weight of adsorbent (q_{eq}) decreases with the adsorbent dose.

This is due to the fact that at higher biosorbent dose the solution ion concentration drops to a lower value and the system reaches equilibrium at lower of q_{eq} indicating the adsorption sites remain unsaturated.

3.3. Effect of initial metal ion concentration

The effects of initial metal concentration on the biosorption capacity and percentage of Cu(II) ion removal at equilibrium conditions are shown in Fig. 2.

Biosorption experiments were carried out at different initial Cu(II) concentrations ranging from 50 to 250 mg · l^{-1}. Ion removal percentage increases from 34.7% to 87.4 % when the initial ion concentration decreases. At low ion concentrations the ratio of surface active sites to the metal ions in the solution is high and hence metal ion may interact with the adsorbent and be removed from the solution. However, amount of metal adsorbed per unit weight of adsorbent q_{eq}, is higher at high concentrations as shown in Fig. 2 and with increase in initial concentration the amount of Cu(II) adsorbed increases from 11 to 22 mg · g^{-1}.

3.4. The effect of pH

pH is one of the most important environmental factor influencing not only site dissociation, but also the solution chemistry of the heavy metals; hydrolysis, complexation by organic and/or inorganic ligands. Redox reactions, precipitation are strongly influenced by pH and, on the other site, strongly influence the speciation and the biosorption availability of the heavy metals [9]. The pH value of the solution was an important controlling parameter in the adsorption process.

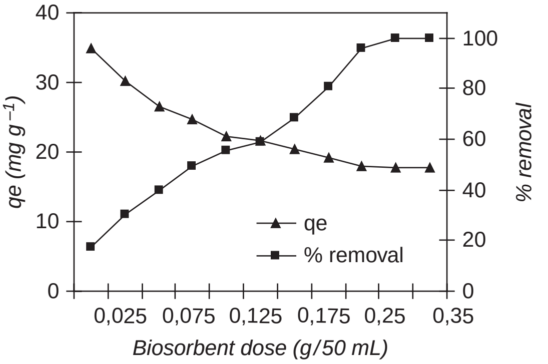

Fig. 1. Effect of biosorbent dose on percent Cu(II) ion removals and biosorbed Cu(II) ion concentrations with the amount of the biosorbent (q_e) (initial Cu(II) concentration = 100 mg · l^{-1}, pH = 5, T = 25 °C, stirring speed = 150 rpm).

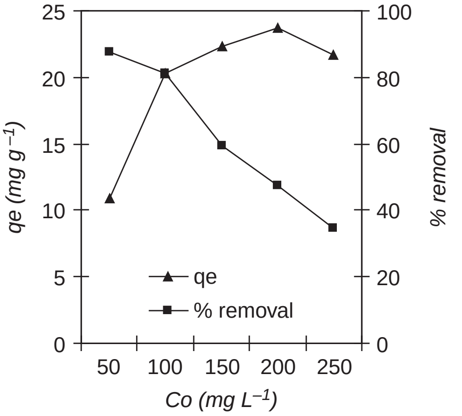

Fig. 2 Effect of initial Cu(II) ion concentration removals and biosorbed Cu(II) concentrations with the amount of the biosorbent (qe) (pH = 5, biosorbent dose = 0.2 g /50 ml, T = 25 °C, stirring speed = 150 rpm).

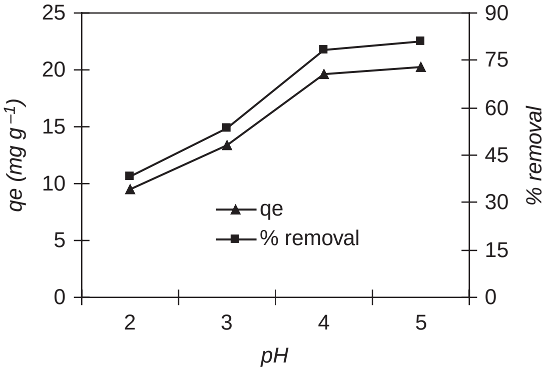

Fig. 3. Effect of pH on percent Cu(II) ion removals and biosorbed Cu(II) ion concentrations with the amount of the biosorbent (qe) (initial Cu(II) concentration = 100 mg · l^{-1}, biosorbent dose = 0.2 g/50 ml, stirring speed = 150 rpm, T = 25 °C).

Fig. 3 shows the effect of pH value of solution on the biosorption of Cu(II) on the *Pleurotus cornicopiae* at 25 °C, 100 mg · l^{-1} of initial Cu(II) ion concentration and 0.2 g of adsorbent dosage with 50 ml Cu (II) solution. The pH values ranging from 2.0 to 5.0 were studied in the experimental run. Cu(II) removal sharply increased from 38.21% at pH 2.0 to 81% at pH 5.0 (Fig. 3). It can also be seen from Fig. 3 that the adsorption capacity of Cu(II) onto *Pleurotus cornicopiae* increases significantly with increasing pH. From the Figure, it may be observed that amount of Cu(II) adsorbed increases with increase in pH and reaches maximum 9.55–20.25 mg · g^{-1}. The increase in biosorption levels with an increase in pH can be explained by the surface charge of the adsorbent and the H$^+$ ions present in the solution. At low pH values, the surface of adsorbent would also be surrounded by hydronium ions, which decrease the Cu(II) interaction with binding sites of the *Pleurotus cornicopiae* by greater repulsive forces and therefore lower adsorption. In contrast, when the pH was increased, the competing effect of hydrogen ions decreased. Therefore, at high pH values, the overall surface on the *Pleurotus cornucopiae* became more negative and adsorption increased. The study at pH higher than 5 were not conducted because insoluble copper hydroxides get precipitated and restricted the true biosorption studies [3].

Zeta potential is one of the most useful parameters to characterize the surface charge of biomaterials. There is a close relationship between the zeta potential and the biosorption capacity of biomaterials. Zeta potential values were determined at various pH for deionized water and Cu (II) solution, while zeta potentials of *Pleurotus cornucopiae*'s particles at pH 3, 4 and 5 are –20, –24 and –26 mM, for Cu(II) solution, zeta potential at pH 3, 4 and 5 are –2, –4 and –8, respectively. These results demonstrated that the zeta potential of *Pleurotus cornucopiae* depended on the solution pH and had a negative charge at all pH (3, 4 and 5) values. Zeta potential values at pH 2 were not observed.

3.5. Sorption isotherm models

The equilibrium data were analysed using three isotherm equations, namely, Langmuir, Freundlich and Temkin isotherm models and the evaluated constants are given in Table 2. Fig. 4 shows the sorption isotherms of Cu(II) ions on the *Pleurotus cornucopiae*. The sorption capacities Cu(II) increased with an increase in the equilibrium metal concentration in solution.

The best-fit equilibrium model was determined based on the linear regression correlation coefficient r^2. The isotherm constants, correlation coefficient (r^2) and standard deviation (S.D) are summarized in Table 2.

As shown in Table 2, it was observed that the Langmuir was better fits the experimental equilibrium adsorption data than the Freundlich and Temkin isotherm equation for Cu(II) sorption according to the values of r^2 and S.D. In Langmuir isotherm, the highest value of r^2 and the lowest values of S.D were

Table 2
Langmuir, Freundlich and Temkin isotherm constants

Langmuir			
Q_{max} (mg . g^{-1})	b (L · mg^{-1})	r^2	S.D.
25.2	0.146	0.99	0.0759
Freundlich			
K_F (mg · g^{-1})	N	r^2	S.D.
7.67	3.85	0.83	0.14
Temkin			
B	A (L · g^{-1})	r^2	S.D.
4.30	2.99	0.87	0.124

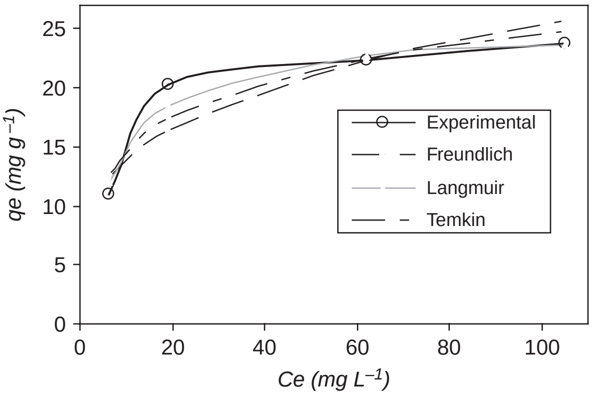

Fig. 4. Equilibrium curves for Cu(II) on to *Pleurotus cornucopia* (pH=5, initial Cu(II) concentration = 100 mg · l^{-1}, biosorbent concentration = 0.2 g/50 ml, stirring speed = 150 rpm).

0.99, and 0.076 for Cu(II). It was also seen from Table 2 that, the Langmuir maximum adsorption capacity q_{max} ($mg \cdot g^{-1}$) is 25.2 and the equilibrium constant b ($l \cdot mg^{-1}$) is 0.146. The Freundlich constant K_F indicates the sorption capacity of the sorbent and the value of K_F is 7.67 $mg \cdot g^{-1}$. Furthermore, the value of 'n' at equilibrium is 3.85.

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L). The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values are 0.120, 0.064, 0.043 and 0.033 while initial Cu(II) concentrations are 50, 100, 150 and 200 $mg \cdot l^{-1}$, respectively. All the R_L values were found to be less than one and greater than zero indicating the favourable biosorption of Cu(II) onto *Pleurotus cornucopiae*.

Table 3 lists some reported sorption capacity values for Cu(II) uptake by various biosorbents. In general *Pleurotus cornucopiae* tested in this study exhibited sorption capacity higher than most of the reported biosorbent except *Rhizopus oligosporus*, Duolite GT-73, *Ascophyllum nodosum* and *Rhizopus arrhizus*.

3.6. Kinetics of biosorption

Fig. 5 shows four kinetic models for the biosorption of the Cu(II). The sorption data of Cu(II) uptake by Pleurotus *cornucopia* fitted with pseudo first order and pseudo second order kinetic model parameters are indicated in Table 4. It is clear from the Table 4 that coefficient of correlation (r^2) for the pseudo second order kinetic model is higher in comparison to pseudo first order model, and the estimated value of q_{eq} for the pseudo second order kinetic model for the Pleurotus cornucopia were also closer to the experimental q_{eq} values than those obtained from the pseudo first order kinetic model (Table 4). The parameters of the Elovich Equation model and intra particle diffusion model were also presented in Table 4. Low r^2 values indicated apparently that the model did not fit the data well. It gives an indication that intra particle diffusion and Elovich equation model did not control the rate which consisted with the results taken from the pseudo second order that the biosorption may be a rate limiting step. The maximum removal for all metallic species occurred in 60 min where the uptake was 20.25, 20.32, 20.39 and 20.38 $mg \cdot g^{-1}$, respectively for experimental data. The values, which were derived for the reaction rate constant for pseudo first, second, Elovich and Intraparticle diffussion equations, are shown at Table 4. The results indicated that pseudo first, pseudo second, elovich and intra particle diffusion rate constants were affected by initial Cu(II) ions concentration. The first order rate constant (k_1) and $q_{eq,cal}$ determined from the model are not in good agreement with the experimental values of $q_{eq,exp}$. In the view of these results, it can be said that the pseudo second order kinetic model provided a good correlation for the biosorption of Cu(II) onto *Pleurotus cornicopiae* at different initial Cu concentration in contrast to the other models. This suggests that the rate limiting step in this sorption process may be chemisorption involving valent forces through the sharing or exchange of electrons between sorbent and sorbate, as also reported by Ho and McKay [48].

Table 3
Comparison of the adsorption capacities (Langmuir q_{max}) for Cu(II) ions of various adsorbents

Adsorbent	q_{max}/(mg g^{-1})	Reference
Typha latifolia L.	6.230	48
P. chrysogenum	3.905	49
Bagasse fly ash	2.26	37
A. spinosus	0.206	50
Gonoderma	0.375	51
Rhizopus arrhizus	48.54	16
Ceratophyllum demersum	6.17	16
Rhizopus oligosporus	79.37	16
Duolite GT-73	61.64	51
Pleurotus pulmonarius	6.20	51
Ascophyllum nodosum	29.251	51
Hydrodictyon reticulatum	8.72	51
Pithophora oedogonia	23.08	51
Granular AC	5.08	51
Powdered AC	4.45	51
Pleurotus cornucopiae	25.2	This study

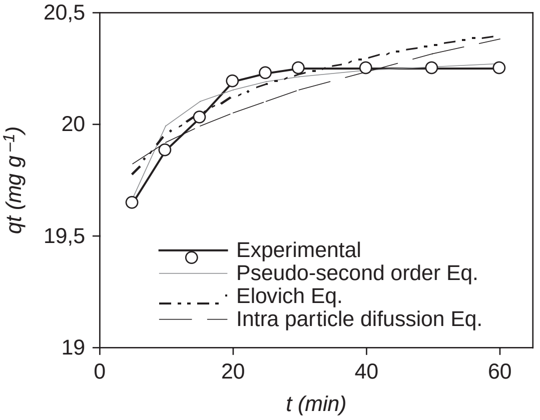

Fig. 5. Comparison between the measured and modelled time profiles for the biosorption of Cu(II) on *Pleurotus cornucopiae* (initial Cu(II) concentration = 100 $mg \cdot l^{-1}$).

Table 4
Variation of the pseudo first, second order, Elovich, intraparticle diffusion rate constants with Cu(II) concentration

		Pseudo first order equation				Pseudo second order equation				Elovich equation					Intraparticle diffusion equation			
C_o (mg·l^{-1})	$q_{eq,exp}$ (mg·g^{-1})	k_1 (min^{-1})	$q_{eq,cal}$	r^2	S.D.	k_2 (gmg1.min)	$q_{eq,cal}$ (mg·g^{-1})	r^2	S.D.×10^{-3}	α (mg·g^{-1}·min)	β (g·min^{-1})	r^2	$q_{eq,cal}$	S.D.×10^{-3}	K_{int} (mg g^{-1}. min$^{1/2}$)	r^2	$q_{eq,cal}$	S.D.×10^{-3}
50	10.925	0.1660	0.93	0.99	1.03	0.570	10.96	1	5	1.9×10^{26}	6.57	0.80	11.10	11	0.0598	0.63	11	7.4
100	20.25	0.1637	1.73	0.96	1.06	0.295	20.33	1	2.7	8.8×10^{30}	3.16	0.88	20.39	5	0.1015	0.73	20.38	170
150	22.31	0.0893	1.66	0.96	1.4	0.13	22.47	1	6.7	5.8×10^{28}	2.32	0.93	22.46	1	0.1804	0.84	22.51	6.4
200	23.75	0.0804	1.60	0.98	1.11	0.11	23.92	0.99	7.3	3×10^{20}	3.21	0.93	23.85	2.7	0.1296	0.83	23.89	12

4. Conclusion

The obtained results strongly demonstrated from batch adsorption studies that pH, biomass dose, initial metal concentration and contact time affect the metal ions uptake capacity of biosorbents. The maximum uptake capacity for Cu(II) was 20.25 $\mathrm{mg \cdot g^{-1}}$ at pH 5, initial concentration 100 $\mathrm{mg \cdot l^{-1}}$ for 60 min. The suitability of sorption isotherm models for the sorption of Cu(II) are Langmuir and Temkin, respectively. And the best isotherm models described the isotherm data with high R^2 and low values of S.D. The experimental data better fitted well to the Langmuir isotherm models. The total capacity (monolayer saturation at equilibrium) of the *Pleurotus cornucopiae* biomass for Cu(II) ions was 25.2 $\mathrm{mg \cdot g^{-1}}$. Metal ion uptake capacity tests have shown that the biosorption process can be better described by pseudo second order kinetic model rather than by pseudo first order Elovich and Intra particle diffussion models. The maximum uptake capacity of *Pleurotus cornucopiae* for Cu(II) cells was found to occur at pH 5. The presence of Cu(II) affected the zeta potential profiles which suggest that the metallic species uptake may be related to the electrostatic interaction of the metal species with the negatively charged functional groups on the *Pleurotus cornucopiae* surface cell. *Pleurotus cornucopiae* demonstrated a good capacity of Cu(II) biosorption and it may be used as a feasible biosorbent for the removal of heavy metal ions.

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