

Biosorption of Copper Ions from Aqueous Solution by *Flammulina velutipes* Spent Substrate

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To remove heavy metals from aqueous solution and reclaim valuable materials from mushroom byproducts, *Flammulina velutipes* spent substrate (FVSS) was developed as a novel biosorbent for copper ion removal. Batch experiments demonstrated that ion removal was pH-, biosorbent dosage- and initial metal concentration dependent. The maximum removal capacity of 15.56 mg/g was achieved at pH 6.0 with a biomass dosage of 3.0 g/L and initial copper ion concentration of 50 mg/L. The adsorption data were in compliance with the Langmuir isotherm and a pseudo-second-order kinetic model. Thermodynamic studies revealed the biosorption process was endothermic, random, and spontaneous. FT-IR spectral analysis confirmed that hydroxyl, amino, carbonyl, and phosphate groups on the biosorbent surface were involved in the biosorption. The uneven surface and porous structure of the biosorbent was propitious for quickly capturing the metal ions from aqueous solution. EDX spectra revealed that the copper ions were loaded on the surface of the biosorbent. XRD patterns showed the formation of copper-containing compounds.

Keywords: *Flammulina velutipes* spent substrate; Biosorption; Copper ion; Kinetics; Thermodynamics; Mechanism

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INTRODUCTION

Heavy metal contamination is a serious issue that endangers the ecosystem and humans because of its toxicity and accumulation throughout the food chain (Kandziora-Ciupa *et al.* 2013; Łuszczek-Trojnar *et al.* 2014; Zhang *et al.* 2015). Potential sources of copper originate from anthropogenic activities including mining, copper smelting, metal processing, and electroplating (Aksu and İsoğlu 2005; Ni *et al.* 2012). Other sources of copper in urban runoff include emissions from automobile brake pads and tire wear onto roadways (Lough *et al.* 2005; McKenzie *et al.* 2009), anti-fouling agent application to irrigation plumbing, roofing materials, and boat hull paint (Srinivasan and Swain 2007; Tobiszewski *et al.* 2010; Lifset *et al.* 2012). Elevated copper concentrations in aquatic systems can also be attributed to commercial pesticides and effluent discharge (Gupta *et al.* 2006). Although copper is an essential trace element in plant and animal tissue, coppers entering aquatic systems have severe effects on olfaction and chemically mediated behaviors (Lahman *et al.* 2015); moreover, excessive exposure to copper causes health problems such as anemia, diseases of the liver and kidneys, polyneuritis, and brain damage (Bhatti *et al.* 2009; Şengil *et al.* 2009).

Traditional methods, including chemical precipitation, electrochemical oxidation reduction, chemical coagulation, and filtration, have been used to eliminate copper from

aqueous solutions, but these methods have such disadvantages as high operating costs, low selectivity, and incomplete copper removal. (Bermúdez *et al.* 2012; Gupta and Nayak 2012; Khataee *et al.* 2013). Biosorption is a promising technological alternative to traditional techniques for metal ion removal as it is low cost, highly efficient, and eco-friendly (Gupta and Rastogi 2009). Various biomaterials used as biosorbents have been reported in the literature, including fungus (Zafar *et al.* 2007), bacterium (Iyer *et al.* 2005; Sahin *et al.* 2005), algae (Sulaymon *et al.* 2013), nutshell (Pehlivan *et al.* 2009), grain husk (Luo *et al.* 2011), and agricultural wastes including rice husk and wood dust (Hansen *et al.* 2010; Yuvaraja *et al.* 2014).

China is the world's largest mushroom producer. Annual production is up to 35,000,000 tons, accompanied by about 60,000,000 tons of spent substrate wastes (Wei *et al.* 2010; Dong *et al.* 2013). Most spent substrates are discarded or burned as fuel, causing economic loss and environmental concerns. The spent substrate of edible fungus is a complex of massive, entangled mycelium residues and their decomposition products, which are derived from cellulose, hemicellulose, and lignin. Substantial numbers of functional groups, such as carboxyls, phosphates, hydroxyls, aminos, and amines, on the surface of this biomass may chelate or precipitate copper ions in aqueous solution (Ramrakhiani *et al.* 2011). *Flammulina velutipes* is a wood-rotting, edible fungi cultivated primarily with rice husk. Therefore, it was deduced that *Flammulina velutipes* spent substrates (FVSS) could potentially be developed as a novel biosorbent for copper ions in aqueous waste.

In this study, FVSS was used as a biosorbent for the removal of copper ions from aqueous solutions. The aims were to ascertain the key factors affecting the adsorption process; describe the adsorption behavior of FVSS according to kinetics, isotherms, and thermodynamic parameters; and further explore the mechanism of the biosorption of copper ions onto the FVSS.

EXPERIMENTAL

Materials

All reagents used in this study were of analytical grade. FVSS was kindly provided by the Xiangfang edible fungi plant, Harbin, China. It was dried overnight in an oven at 60 °C and ground to particles below 0.3 mm in size. The stock solution (1000 mg/L) of copper ions was prepared by dissolving the required amount of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Sinopharm, China) in deionized water. The working solutions were prepared by diluting the stock solution to the desired concentrations.

Methods

Batch biosorption experiments

Batch biosorption experiments were carried out as functions of pH, contact time, biosorbent dosage, and initial metal ion concentration in 250-mL Erlenmeyer flasks. A weighed amount (0.3 g) of biosorbent was added to the copper sulfate solution (initial concentration: 50 mg/L), and the flasks were agitated with a rotational speed of 150 rpm at 25 °C. The pH (2.0 to 7.0) was adjusted by 0.5 M HCl or 0.5 M NaOH solutions. The influences of contact time (5 to 120 min), biosorbent dosage (0.5 to 5.0 g/L), and initial copper ion concentration (10 to 150 mg/L) were evaluated. The equilibrium (residual) concentration of the filtrate was analyzed using an atomic absorption spectrometer (AA-6800, Shimadzu-GL, Japan). All experiments were conducted in triplicate, and the

averages were used in data analysis. The biosorption rate (R) and quantity (Q) at equilibrium were calculated with Eqs. 1 and 2, respectively,

$$R = \frac{(C_j - C_e)}{C_j} \times 100 \% \quad (1)$$

$$Q = \frac{(C_j - C_e)v}{m} \quad (2)$$

where c_j and c_e are the initial and equilibrium concentrations of copper ion solution, respectively (mg/L); v is the volume (mL) of reaction solution (unified for 100 mL); and m is the dried mass of the biosorbent (g).

Biosorption isotherms

The Langmuir adsorption isotherm model can be expressed as (Langmuir 1918),

$$1/q_e = 1/q_{\max} + 1/q_{\max} b c_e \quad (3)$$

where q_e is the amount of copper ions (mg/g); q_{\max} is the maximum amount of copper ions (mg/g); c_e is the concentration of copper ions (mg/L) at equilibrium; and b is the affinity constant of the isotherm.

The Freundlich adsorption isotherm model is an exponential equation (Freundlich 1906),

$$\ln q_e = \frac{1}{n} \ln c_e + \ln k_f \quad (4)$$

where k_f is a Freundlich constant related to the binding capacity and $1/n$ is an empirical parameter related to the biosorption intensity, which varies with the heterogeneity of the biosorption.

Dubinin and Radushkevich (D-R) developed the following isotherm to account for the effect of the porous structure of an adsorbent (Dubinin and Radushkevich 1947),

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \quad (5)$$

where β is the activity coefficient related to the mean free energy of biosorption and ε is the Polanyi potential, which can be determined from Eq. 6:

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e} \right) \quad (6)$$

Biosorption kinetics

Lagergren's pseudo-first-order equation and the pseudo-second-order equation were used to model the kinetics of copper ion sorption onto FVSS. The linear forms of the pseudo-first-order and pseudo-second-order adsorption equations are depicted in Eqs. 7 and 8, respectively (Lagergren 1898; Ho and McKay 1999):

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1 t}{2.303} \quad (7)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (8)$$

The equation can be transformed as follows,

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

where q_e (mg/g) and q_t (mg/g) are the amount of copper ions adsorbed at equilibrium and at time t , respectively. k_1 (min^{-1}) is the rate constant of first-order kinetics, as determined by the slope of the plot of $\log(q_e - q_t)$ versus t , in the biosorption process. k_2 ($\text{g} / \text{mg} \cdot \text{min}$) is the rate constant of second-order kinetics, which was obtained from the linear plot of $1/q_t$ versus $1/t$, in the biosorption process.

Thermodynamic parameters

Copper solution was kept in contact with FVSS at various temperatures (293, 298, and 303 K) to study the thermodynamics of the reaction (Saini and Melo 2013). Thermodynamic parameters such as the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) in the interaction of copper ions with FVSS were given by the Van't Hoff equations,

$$\Delta G^0 = -RT \ln k^0 \quad (10)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (11)$$

$$\ln k^0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (12)$$

where T is the temperature (K); R is the universal gas constant (8.314 J/mol K); and k^0 (L/g) is an equilibrium constant obtained by multiplying the Langmuir constant q_{max} by b (Ramrakhiani *et al.* 2011).

Biosorption mechanism

Spectral analyses of the FVSS (before and after biosorption) were done using an FT-IR spectrometer (Alpha, Bruker, Germany) in the region of 4000 to 400 cm^{-1} . The biosorbents were pressed into spectroscopic-quality KBr pellets with a sample/KBr ratio of 1/150. The prepared pellets were then scanned. The possible functional groups present on the FVSS biosorbents were determined.

The surface structure of the biosorbent was analyzed with a scanning electron microscope (SEM) (QuANTA200 model, FEI, USA) after fixation with glutaraldehyde. The elements were analyzed by an energy dispersive X-ray analysis system (EDX) (QuANTA200 model, FEI, USA).

The crystalline structure of the biosorbent was investigated using an X-ray diffraction (XRD) apparatus (D/max2200 model, Hitachi, Japan) equipped with a Cu-K α radiation source. The operating conditions were $U = 40$ kV and $I = 30$ mA. The scans were performed between 5° and 40° with a scan rate of 5°/min and a step size of 0.02° at room temperature.

RESULTS AND DISCUSSION

Batch Biosorption Experiments

Effect of pH

The pH value is a key parameter greatly affecting the removal efficiency and adsorption capacity of metallic ions from aqueous solution (Benaïssa and Elouchdi 2011). Increasing the pH from 2.0 to 6.0 raised the biosorption capacity of copper ions onto the

FVSS from 12.78 to 21.68 mg/g, as shown in Fig. 1a. Such results could be assigned to the competition of high-density H^+ with Cu^{2+} for the active sites on the biosorbent surface at low pH (Guiso *et al.* 2012). As the pH was decreased, the overall surface charge became almost positive, inhibiting the approach of positively charged ions such as copper ions. As the pH increased, more carboxyl acid groups dissociated on the substrate surface, which resulted in an increasing ion exchange capacity of the biosorbent, favoring the combination of copper ions and the anionic ligands (Hubbe *et al.* 2011). In addition, electrostatic repulsion also decreased with the reduction of amine groups on the biosorbent at higher pH values, accelerating the loading of copper ions onto the FVSS surface. The biosorption capacity achieved a maximum for the partial hydrolysis formation of $Cu(OH)^+$, which was more attractive for ligands when the pH was 6.0. Moreover, the ionic exchange ability of the biosorbent also increased with increasing pH (Lodeiro *et al.* 2006). Above pH 6.0, precipitation of heavy metals occurred. This is related to insoluble metal hydroxide precipitation from the solution at higher pH and should be avoided during sorption experiments to effectively distinguish between adsorption and precipitation (Onundi *et al.* 2010). It is clear that pH significantly impacted the biosorption of copper ions onto FVSS and that the optimum pH was 6.0. This is consistent with the results of previous reports (Nakbanpote *et al.* 2007; Iskandar *et al.* 2011).

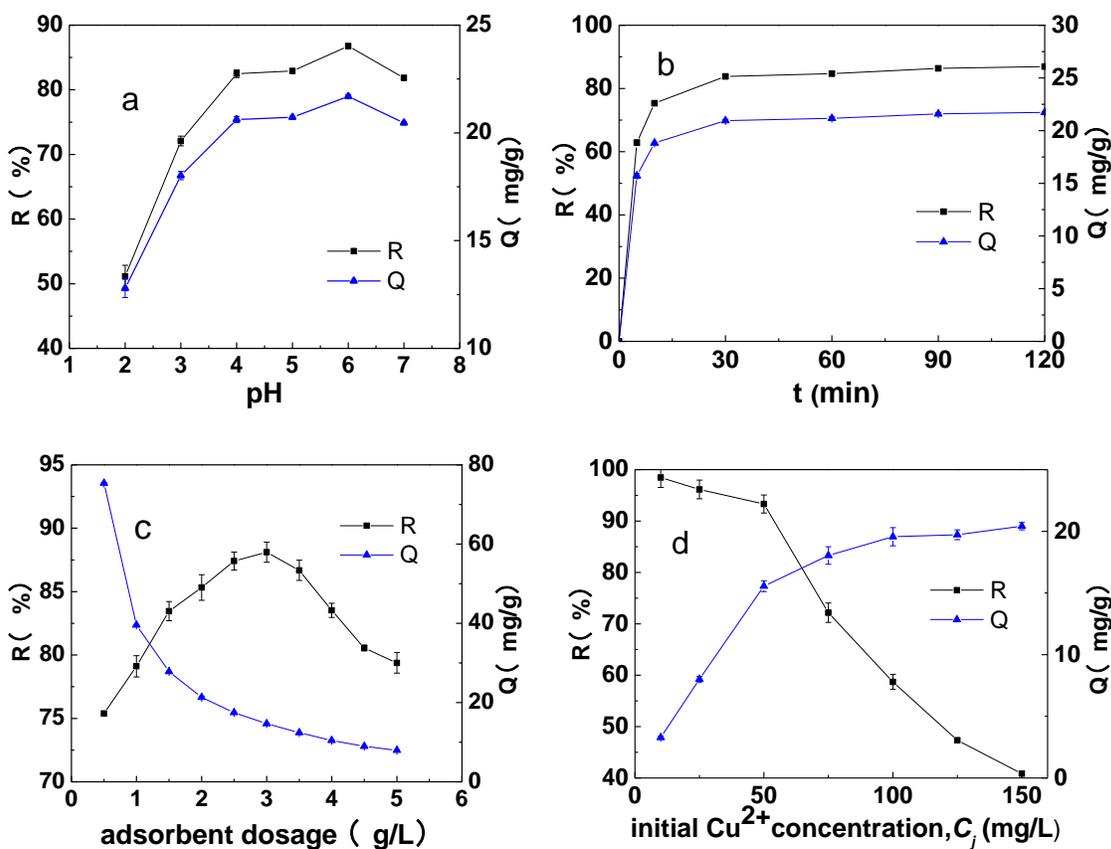


Fig. 1. Effect of parameters on copper biosorption onto FVSS (agitation speed: 150 rpm, T : 298 K): (a) C_j : 50 mg/L, contact time: 2 h, m : 2 g/L; (b) C_j : 50 mg/L, pH 6.0, m : 2 g/L; (c) C_j : 50 mg/L, pH 6.0, contact time: 30 min, (d) pH 6.0, m : 3 g/L, contact time: 30 min

Effect of contact time

The effect of contact time on the removal of copper ions by FVSS is described in Fig. 1b. The biosorption capacity and efficiency reached 20.95 mg/g and 83.8%, respectively, at 30 min. Subsequently, the biosorption capacity reached only 21.73 mg/g at 120 min, only 3.7% higher than that at 30 min. It is obvious that rapid biosorption of copper ions occurred during the first 30 min of biosorption, followed by slower biosorption, until equilibrium was reached. Generally, the fast stage involved physical sorption or ion exchange with the biomass and the slow stage involved complexation or micro-precipitation, primarily in the microporous structure (Verma *et al.* 2013; Ding *et al.* 2014). In this case, the amount of copper ion biosorption did not exhibit time-dependent change after 30 min. In practical applications, long-time treatment is power-wasting and uneconomical (Lan *et al.* 2014). The most suitable contact time was therefore 30 min.

Effect of biosorbent dosage

The biosorbent dosage determines the amount of sorption sites available for copper ions on the FVSS surface (Akar *et al.* 2012a). As can be seen from Fig. 1c, when the biosorbent dosage rose from 0.5 to 3.0 g/L, the biosorption rate increased from 75.39% to 88.11%. However, the biosorption capacity declined from 75.39 to 14.68 mg/g. The biosorption rate and capacity both declined with the further increases in the adsorbent biomass concentration, when the biomass dosage was 5.0 g/L, the biosorption rate was reduced to 79.38% and the biosorption quantity was reduced to 7.94 mg/g. This could have been caused by the equilibrium adsorption when the biosorption capacity reached a maximum. The aggregation or overlapping of biosorbent surface area and competition for available sorption sites for metal ions adversely impacted the biosorption efficiency (Bhatti *et al.* 2009). Based on the aforementioned results, the best biosorbent dosage was 3.0 g/L. According to recent studies of copper ion biosorption with fungi and rice husk as potential biosorbents, their biosorption capacities were 20 and 7.1 mg/g, respectively, much lower than that of FVSS (Nakbanpote *et al.* 2007; Iskandar *et al.* 2011).

Effect of initial metal ion concentration

Experiments were conducted to investigate the effect of the initial copper ion concentration which was adjusted to the range of 10 to 150 mg/L under optimal pH, contact temperature and biosorbent dosage. Figure 1d illustrates that the biosorption capacity increased from 3.28 to 20.42 mg/g and the biosorption rate decreased from 98.46% to 40.83% with the copper ion concentration ranging from 10 to 150 mg/L. However, the increase leveled off after the concentration exceeded 50 mg/L, which may be due to the lack of adequate active sites to accommodate much more copper ions in the solution when biomass had become saturated. Furthermore, the increase of metal uptake was a result of the increase in the driving force (Das *et al.* 2012; Xue *et al.* 2013). The concentration of metal ions thus play a significant role in determining the feasibility and efficiency of a biosorption process. To balance the biosorption capacity and the removal efficiency, the suitable initial metal ion concentration was set as 50 mg/L, under this condition, biosorption capacity and biosorption rate were 15.56 mg/g and 93.32%, respectively.

Biosorption Isotherms

The biosorption of copper ions onto FVSS at 293, 298, and 303 K was analyzed using the Langmuir, Freundlich, and D-R isotherm models. The parameters of these isotherm models are displayed in Table 1. The Langmuir isotherm is often adopted to describe the adsorption of a solute from liquid solution. The Langmuir isotherm model represents the equilibrium of adsorbate between the solid and liquid phases. The q_{\max} of the Langmuir isotherm increased with increasing temperature, indicating that hyperthermia would facilitate biosorption capacity. The q_{\max} of FVSS, based on the Langmuir isotherm, was 40 mg/g at pH 6.0 and temperatures of 298 and 303 K.

Table 1. Isotherm Model Constants of Copper Ion onto FVSS at Various Temperatures (pH: 6.0, m : 3.0 g/L, contact time: 30 min)

Temperature (K)	Langmuir Constant			Freundlich Constant			D-R Constant		
	b (L/mg)	q_{\max} (mg/g)	R^2	n	K_F	R^2	q_{\max} (mg/g)	R^2	E (KJ/mol)
293	0.0269	38.46	0.997	1.329	0.0288	0.992	22.111	0.893	12.98
298	0.0303	40	0.997	1.321	0.0418	0.993	22.87	0.896	15.81
303	0.0279	40	0.998	1.317	0.0655	0.992	23.364	0.89	15.81

The Freundlich isotherm is applied under the assumptions of a heterogeneous adsorption surface and active sites with different energies involved (Freundlich 1906). As shown in Table 2, all values of constant n at different temperatures were more than 1.0; thereafter, it was inferred that the removal of copper ions by FVSS was a physical process and was not linearly related to the copper ion concentration (Mohamad *et al.* 2012; Awwad and Salem 2014). The K_F value rose with increasing temperature, suggesting that the kinetic energy sped up the mobility of the copper ions and facilitated the arbitrariness and heterogeneity of the biosorption system (Sulaymon *et al.* 2013). Furthermore, R^2 values of 0.992, 0.993, and 0.992 meant the experimental data fit this model well and also proved the heterogeneous features of FVSS sorption system for copper ions.

The Dubinin-Radushkevich isotherm was developed to account for the effect of the porous structure on adsorption (Dubinin and Radushkevich 1947). The mean adsorption energy (E) in the D-R isotherm provides useful information with regard to chemical or physical processes (Vijayaraghavan *et al.* 2006). An E value between 8 and 16 kJ/mol suggests the biosorption process might follow a chemically ionic exchange process (Erkaya *et al.* 2014).

The R^2 and q_{\max} values suggest that the Langmuir isotherm may be the most suitable model for the data in this study because of the high coefficients of determination. It was concluded that monolayer biosorption occurred at specifically homogeneous sites on the surface of the FVSS (Chergui *et al.* 2009). According to the Langmuir model, once a copper ion occupies in a site, no further adsorption can take place in that site, and all sites are identical and energetically equivalent. FVSS is structurally homogeneous. There is no interaction between molecules adsorbed on neighbouring sites. The maximum monolayer biosorption capacities were found to be between 38.46 and 40 mg/g at the various temperatures studied in the Langmuir isotherm. The biosorption capacity of

FVSS was moderately higher in this study than in those of other agricultural waste adsorbents in (Table 2).

Table 2. Biosorption Capacity of Various Biosorbents for Copper Ions in the Literature

Biosorbent	q_{max} (mg/g)	References
Rice bran	33.58	Wang and Qin 2005
Cotton boll	11.4	Ozsoy and Kumbur 2006
Chestnut shell	12.56	Yao <i>et al.</i> 2010
Peanut hull	21.25	Zhu <i>et al.</i> 2009
Cashew nut shell	17.82	Kumar 2014
Pine bark	6.05	Ronda <i>et al.</i> 2014
Wheat straw	5.0	Gorgievski <i>et al.</i> 2013
Water hyacinth roots	22.7	Zheng <i>et al.</i> 2009
NaOH treated pine cone	26.32	Ofomaja <i>et al.</i> 2010
Sugar beet pulp	28.5	Aksu and Isoğlu 2005
Mansonia sawdust	36.91	Ofomaja 2010
Sour orange residue	21.7	Khormaei <i>et al.</i> 2007
Banana peel	4.75	Annadurai <i>et al.</i> 2002
<i>Flammulina velutipes</i> spent substrate	40	Present study

Biosorption Kinetics

The kinetic study was carried out to describe the behavior of the biosorption of copper ions onto FVSS. In this study, kinetic data were tested using Lagergren's pseudo-first-order model, in addition to a pseudo-second-order kinetic model (Ho 2006). The results in Table 3 indicate that the biosorption capacity increased with increasing temperature.

Table 3. Kinetic Equations Parameters for Copper Ion Biosorption onto FVSS at Various Temperatures (C_j : 50 mg/L, pH: 6.0, m : 3.0 g/L)

Temperature (K)	Experimental	Pseudo-first-order Kinetics			Pseudo-second-order Kinetics		
	q_e (mg/g)	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
293	37.74	1.6×10^{-3}	33.42	0.6843	2.3099×10^{-4}	36.50	0.9907
298	39.84	1.6×10^{-3}	35.23	0.6985	2.4819×10^{-4}	36.76	0.9917
303	40.00	1.6×10^{-3}	35.35	0.7176	2.5222×10^{-4}	37.31	0.9910

The theoretical q_e values, estimated from the pseudo-first-order kinetics model, were different from the experimental values, while the coefficients of determination (R^2) (<0.72) were also lower than those for the pseudo-second-order kinetic model. These results indicate that pseudo-first-order kinetics model did not well describe the biosorption of copper ion by the FVSS. In addition, the theoretical q_e value was closer to the experimental q_e values in the case of pseudo-second-order kinetic model, and the R^2 value above 0.99 attests that the kinetic data were well-correlated with the pseudo-

second-order kinetic model. One possible explanation is that two adjacent functional groups at the surface, acting independently, govern the adsorption rate at the biosorbent surface; however it is difficult to understand how two such bound groups could act as independent entities in determining the rate of adsorption. An alternative explanation is that the remaining sites become increasingly reluctant to be filled because of charge repulsion or the time required for diffusion to sites located deep within a network of mesopores and micropores (Hubbe *et al.* 2012).

Thermodynamic Parameters

The thermodynamic parameters reflect the feasibility and spontaneous nature of the biosorption process. In the practice of environmental engineering, changes in the Gibbs free energy, enthalpy, and entropy should be considered to determine whether the process occurs spontaneously (Çolak *et al.* 2009). In this study, the standard changes of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were evaluated from the plot of $\ln k^0$ versus $1/T$ at 293, 298, and 303 K. The results are shown in Table 4.

Table 4. Thermodynamic Parameters for the Biosorption of Copper Ions onto FVSS at Various Temperatures

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)
293	-0.0899	11.498	0.03955
298	-0.2879		
303	-0.4856		

The negative values of ΔG° at different temperatures (Table 4) indicate that copper ion biosorption was spontaneous and that the FVSS biosorbent had higher affinity at higher temperatures. The positive value of ΔH° (11.498 kJ/mol) suggests the endothermic nature of the biosorption behavior. Moreover, the positive value of ΔS° illustrates that entropy was increased at the solid/solution interface (Ahmad *et al.* 2013). The decrease in the free energy (ΔG°) with the increase in temperature indicates that the biosorption process was endothermic. Similar results have been reported by Akar *et al.* (2012b) and Saini *et al.* (2013). The thermodynamic study demonstrated that FVSS was suitable for the uptake of copper ions from aqueous solution. The plot of fitted data is shown in Fig. 2.

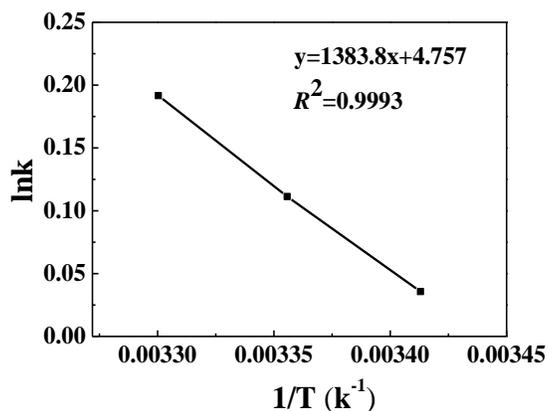


Fig. 2. Plot of fitted data

Biosorption Mechanism

FT-IR spectrum characterization

The FT-IR spectra of the biosorbent unloaded and loaded with copper ions are presented to better understand the biosorption mechanism (Fig. 3). Following loading with copper ions, the absorption spectra dramatically changed: some peaks were shifted and some became weak. It has been reported that biosorbent materials have intense absorption bands around 3500 to 3200 cm^{-1} , which represent the stretching vibrations of amino groups ($-\text{NH}$) and hydroxyl groups ($-\text{OH}$) (Boddu *et al.* 2008). In this experiment, a strong $-\text{NH}$ absorption peak was observed in both copper-unloaded and copper-loaded biomass at 3420 and 3402 cm^{-1} , respectively. The characteristic absorption peaks at about 2921 cm^{-1} for copper-unloaded and at 2922 cm^{-1} for copper-loaded biomass were the stretching vibrations of $-\text{CH}_2$. A strong absorption band, indicating $\text{C}=\text{O}$ vibrations, shifted from 1640 to 1634 cm^{-1} in the FT-IR spectra (Gupta and Rastogi 2009). The band representing $\text{P}-\text{OH}$ stretching vibration moved from 1037 to 1030 cm^{-1} after copper ions were loaded (Akar *et al.* 2012b). The above results indicate that the hydroxyl, amino, carbonyl, and phosphate groups were all involved in the biosorption process. These changes could be attributed to the effective interaction of copper ions with the functional groups on the hyphae. Javaid *et al.* (2011) pointed out the involvement of amine ($-\text{NH}_2$) and carboxylic acid ($-\text{COOH}$) groups in the adsorption process using *Pleurotus ostreatus* as a biosorbent to remove copper ions.

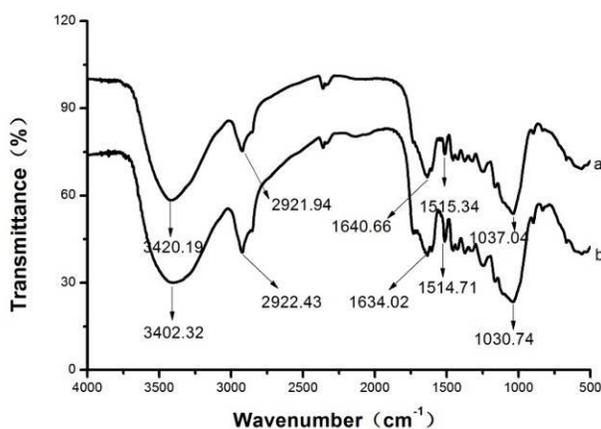


Fig. 3. FTIR spectra of FVSS before (a) and after (b) copper ion biosorption

SEM-EDX analysis

The surface configurations of the FVSS biomass before and after biosorption were observed by scanning electron microscopy and are displayed in Fig. 4. The images show that FVSS biomass before biosorption had an uneven surface morphology with many cracks, broken hyphae filaments, and pores, which greatly increased the surface area of the biosorbent (Fig. 4a) (Chakraborty *et al.* 2011). After biosorption (Fig. 4b), the spatial structure of the substrate surface changed greatly: the uneven surface more obviously protruded, hyphae filaments disappeared and may have been hidden under the raised surface, and some pores were enlarged, revealing the favorable performance of the biosorbent. An irregular, polyporous structure can improve the biosorption capacity by

increasing the potential energy of molecules, subsequently absorbing more tiny materials (Ramrakhiani *et al.* 2011).

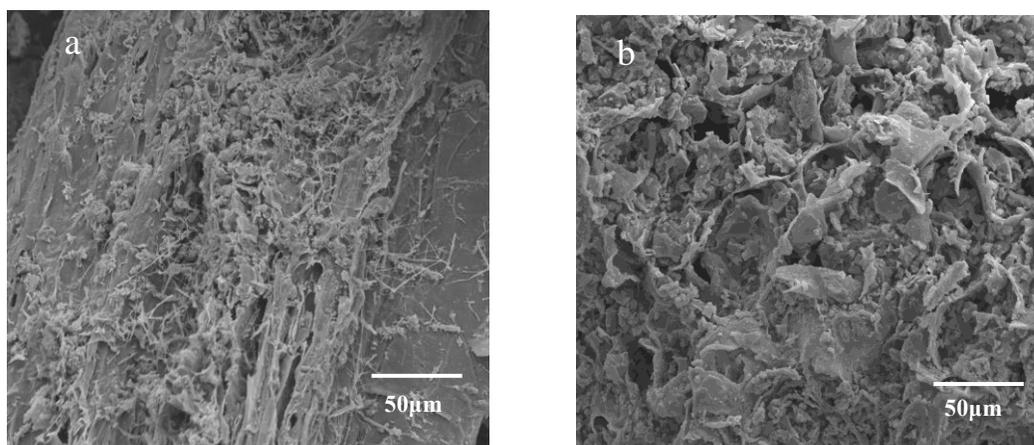


Fig. 4. Characteristics of FVSS surface before (a) and after (b) copper ion biosorption

EDX analyses were conducted to understand the elemental variations in the biosorbent before and after copper ion biosorption. The EDX spectra of the samples and the atomic mass ratios of elements are presented in Fig. 5 and Table 5, respectively.

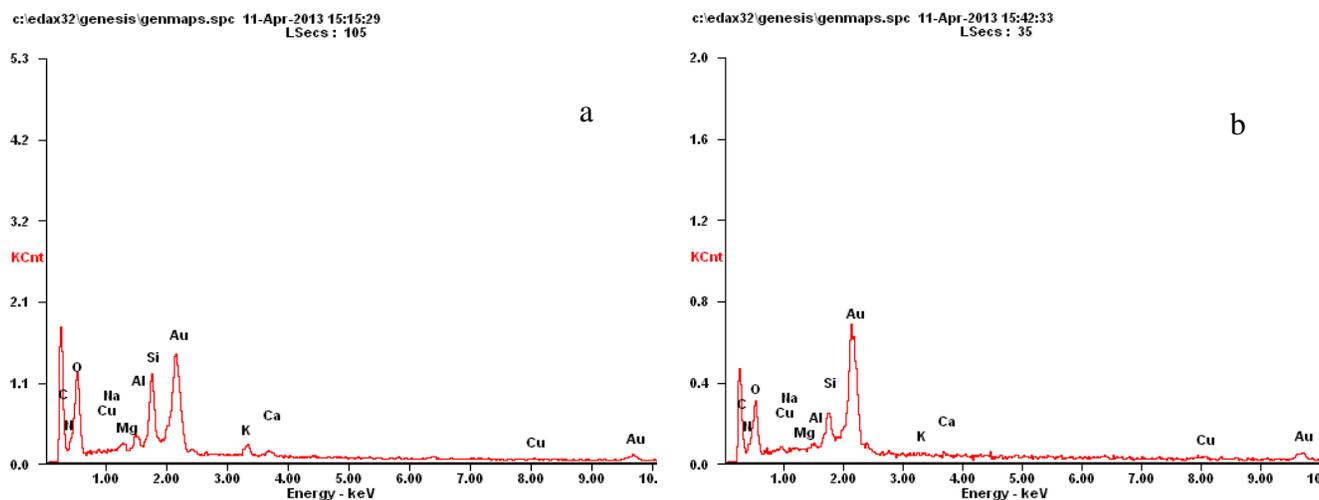


Fig. 5. EDX of FVSS before (a) and after (b) copper ion biosorption

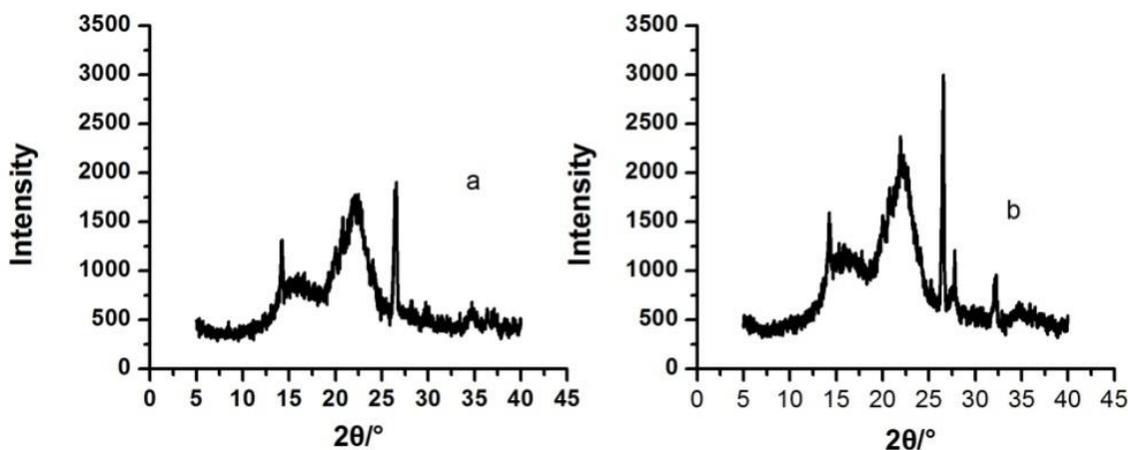
The copper peak was detected only after biosorption (Fig. 5a), which again indicates that the copper ions may combine with functional groups on the surface of the biomass. The high values of the C, N, and O peaks in both the unloaded and copper-loaded biomass suggest that these elements were present extensively on the FVSS surface. As the main component of rice husk, Si also exhibited an intense peak. Other distinctive metal peaks such as Al, Mg, and Na were the trace elements needed for *Flammulina velutipes* growth. The major decreases in the Mg, Al, K, Ca, and Si peaks (Fig. 5b) indicate that the biosorption process included chemically ionic exchange processes with the FVSS surface. Manasi *et al.* (2014) also found this mechanism when they investigated cadmium removal from electronics industry effluent.

Table 5. Atomic and Mass Ratio Analyses of FVSS Before and After Copper Ion Biosorption

Before Biosorption			After Biosorption		
Element	Wt. %	At. %	Element	Wt. %	At. %
CK	45.35	54.89	CK	43.55	53.94
NK	14.61	15.16	NK	17.25	18.32
OK	25.89	23.52	OK	23.18	21.55
NaK	00.09	00.06	NaK	00.27	00.18
MgK	00.73	00.44	MgK	00.64	00.39
AlK	01.20	00.65	AlK	00.85	00.47
SiK	07.24	03.75	SiK	05.36	02.84
KK	01.82	00.67	KK	00.80	00.30
CaK	01.18	00.43	CaK	00.85	00.31
CuK	01.90	00.43	CuK	07.24	01.69
Matrix	Correction	ZAF	Matrix	Correction	ZAF

X-ray diffraction analysis

The X-ray diffraction patterns of FVSS before and after copper ion biosorption are displayed in Fig. 6.

**Fig. 6.** X-ray diffraction patterns of FVSS before (a) and after (b) copper ion biosorption

Compared to the absorption peaks of unloaded biosorbent (Fig. 6a), in the pattern of the copper-loaded (Fig. 6b) some new peaks emerged, indicating higher crystallinity (Silva *et al.* 2012). The increase in crystallinity as shown by the XRD spectrum may have been caused by copper ions loading the FVSS in a larger diffractive range of 15° to 40°. In comparison with XRD standards stored in the JCPDF database of compounds, the peaks exhibited at 2θ values of around 14.133°, 27.295°, and 30.625° suggested the formation of copper-containing compounds.

CONCLUSIONS

1. The biosorption of copper ions onto FVSS was highly dependent on the initial pH and biosorbent dosage. The maximum removal capacity of 15.56 mg/g was achieved at pH 6.0 with a biomass dosage of 3.0 g/L and initial copper ion concentration of 50 mg/L. Biosorption reached equilibrium within 30 min.
2. The biosorption behavior of copper ions onto FVSS fit well with the Langmuir isotherm. The calculated maximum capacity for copper biosorption was 38.46 mg/g above 293 K, much higher than values found in literature.
3. The kinetic data correlated best with a pseudo-second-order model. The process was endothermic, random, and spontaneous according to thermodynamic parameter analysis.
4. The biosorption of copper ions onto FVSS involved its protruded surface structure and hydroxyl, amino, carbonyl, and phosphorus functional groups favorable for metal ion capture. Ionic exchange and complexation occurred between copper ions and FVSS in this biosorption process.

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