

Biosorption of Zn^{2+} and Pb^{2+} from aqueous solutions using native and microwave treated *Flammulina velutipes* stipe

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(Received 26 September 2013 • accepted 8 February 2014)

Abstract—Native stipe (NS) and microwave treated stipe (MTS) of *Flammulina velutipes* were utilized for the biosorption of Zn^{2+} and Pb^{2+} ions from aqueous solution. The effects of pH, contact time, and initial concentration on the biosorption were studied for each metal separately. The desired pH of aqueous solution was found to be 6.0 for the removal of Zn^{2+} ions and 5.0 for the removal of Pb^{2+} ions. The percent removal of both metals was found to increase with the increase in contact time; biosorption equilibrium was established in about 60 min. The maximum biosorption of Zn^{2+} and Pb^{2+} ions from single component systems can be successfully described by Langmuir and Freundlich models; the biosorption kinetics can be accurately described by a second-order kinetic model. The present data from these studies confirms that the native and microwave treated forms of *Flammulina velutipes* stipe have the potential to be used for the biosorption of Zn^{2+} and Pb^{2+} ions from aqueous solution. The metal biosorption capacities of NS for Zn^{2+} and Pb^{2+} were 58.14 and 151.51 mg g^{-1} , respectively, while the biosorption capacities of MTS for the both metals were 95.24 and 172.41 mg g^{-1} , respectively.

Keywords: *Flammulina velutipes*, Stipe, Zn^{2+} , Pb^{2+} , Biosorption

INTRODUCTION

The presence of toxic heavy metals in water resulting from rapid industrialization and technological advances has been a worldwide environmental problem. The removal and recovery of heavy metals from wastewater significantly protects the environment and human health [1-3]. Currently, many physicochemical and biological methods have been developed for metal removal from aqueous solutions, such as chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment, activated carbon adsorption [4-8]. However, they can be expensive and not fully effective. Biosorption with microbial biomasses has become an alternative to traditional methods because of its eco-friendly nature, excellent performance, and cost-effectiveness [9-12].

Among heavy metals, Zn^{2+} and Pb^{2+} are a widespread concern to human health. Despite an essential micronutrient for life, excessive quantities of Zn^{2+} can lead to both acute and chronic toxicity. Prolonged intake of Zn^{2+} ranging from 100 to 150 mg day^{-1} interferes with copper metabolism and causes low copper status, reduced iron function, red blood cell microcytosis, neutropenia, reduced immune function and reduced levels of high-density lipoproteins [13]. Pb^{2+} poisoning can affect almost all parts of the body, but its effects are most pronounced on the central nervous system and kidneys. Pb^{2+} can result in cognitive difficulties, reading problems, development defects, and mental retardation. Chronic, low-level Pb^{2+} exposure can be asymptomatic until kidney function starts to deteriorate [14, 15]. Hence, it is urgent to remove Zn^{2+} and Pb^{2+} from the polluted

water before transformation into environment.

Fruit bodies of macrofungi are considered ideal for the purpose of evaluation as biosorbents, because many fungal species exhibit high biosorption potential [16-20]. *Flammulina velutipes* is a common edible basidiomycete fungus which has easy cultivation and high output and is widely distributed around the world. *Flammulina velutipes* has a long, slender and hollow stipe, most of which is usually discarded before cooking. However, the waste parts can be an attractive and inexpensive option for the biosorption. To the best of our knowledge, the utilization of *Flammulina velutipes* stipe has not been reported in the literature. Thus, native stipe (NS) and microwave treated stipe (MTS) were first utilized in present work for the removal of Zn^{2+} and Pb^{2+} from single metal solutions.

In this study, the structure of *Flammulina velutipes* stipe is demonstrated, and the biosorption capacities of the absorbent for metal ions are investigated under different conditions, such as solution pH, contact time and metal ions concentration. The theoretical isotherm models and kinetic properties of biosorption of Zn^{2+} and Pb^{2+} are also assessed.

MATERIALS AND METHODS

1. Preparation of Biosorbent

Fruit bodies of *Flammulina velutipes* were purchased from Metro Supermarket in Hefei. The bottom of the stipe was cut off and washed thoroughly with deionized water to remove dirt and impurities. The stipes were dried in an oven at 40 °C for 24 h and referred to as NS. The remaining stipes were dried in an oven at 40 °C for 2 h, and treated in a microwave at 500 W for 30 s. These steps were repeated twice. Finally, the stipes were dried in an oven again at 40 °C for 18 h, and referred to as MTS. Both of the dried stipes were cut into pieces.

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Stipe particles with 1-2 mm size were used for the study.

2. Preparation of Zn^{2+} and Pb^{2+} Solutions

The aqueous solutions of Zn^{2+} and Pb^{2+} used in the present investigation were prepared using ultrapure water (Millipore Mili-Q, USA). Stock solutions of Zn^{2+} and Pb^{2+} were prepared by dissolving 2.274 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.799 g of $\text{Pb}(\text{NO}_3)_2$ in 1 L ultrapure water. The stock solutions were diluted to prepare different working concentrations. All chemicals were analytical grade reagents.

3. Biosorption Studies

Biosorption experiments of Zn^{2+} and Pb^{2+} on NS and MTS of *Flammulina velutipes* were performed in a 100 mL Erlenmeyer flask adding 0.2 g of the biosorbent in 50 mL of Zn^{2+} and Pb^{2+} solutions separately at 27 °C on a rotary shaker at 100 rpm. The effect of pH on the biosorption was investigated in the pH range 2.0-7.0. The pH was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards. The effect of the initial ion concentration on biosorption was studied at pH 6.0 and 5.0 for Zn^{2+} and Pb^{2+} ions, respectively. The metal ion concentration was varied between 10 and 500 mg L^{-1} . To collect enough coherent data points for biosorption of Zn^{2+} and Pb^{2+} (500 mg L^{-1}), samples were collected at definite time intervals (10, 20, 30, 40, 50, 60, 90, and 120 min). Blank trials without adding biosorbent were performed simultaneously to determine adsorption of the metal on the walls of the conical flask. After the desired biosorption period (up to 120 min) of each experiment, the metal solution was filtered and residual metal concentration in the filtrate was measured by inductively coupled plasma (XSP Intrepid II, Thermo Electron Corporation, USA). The biosorption experiments were triplicated and the average values are

reported.

The amount of adsorbed metal ions (mg g^{-1}) on NS and MTS was obtained as:

$$q = \frac{(C_0 - C)V}{m}$$

where C_0 (mg L^{-1}) and C (mg L^{-1}) are the concentrations of each metal ion in the solution before and after biosorption, respectively, q (mg g^{-1}) is the amount of metal ion adsorbed on the unit dry mass of the stipe, V (L) is the volume of the metal ion solution, and m (g) is the weight of the dry stipe.

4. Characterization Studies

The dry NS and MTS particles were attached to a stub and coated with gold-palladium under reduced pressure prior to obtaining their scanning electron micrographs by scanning electronic microscopy (SEM) (S-4800, Hitachi Ltd., Japan) at an accelerating voltage of 5.0 kV.

RESULTS AND DISCUSSION

1. Characterization of the Stipe Using SEM

The cross-section and side micrographs of NS and MTS before biosorption are exemplified by SEM in Fig. 1. Fig. 1(a) and (b) show that the hollow structure of NS almost remained unchanged after oven drying. There were some pores in the cross-section and fibrous structure in the side surface. As clearly seen from Fig. 1(c) and (d), more pores and folds were observed in the cross-section of MTS compared with NS, the wall of the pores was thin, and a large num-

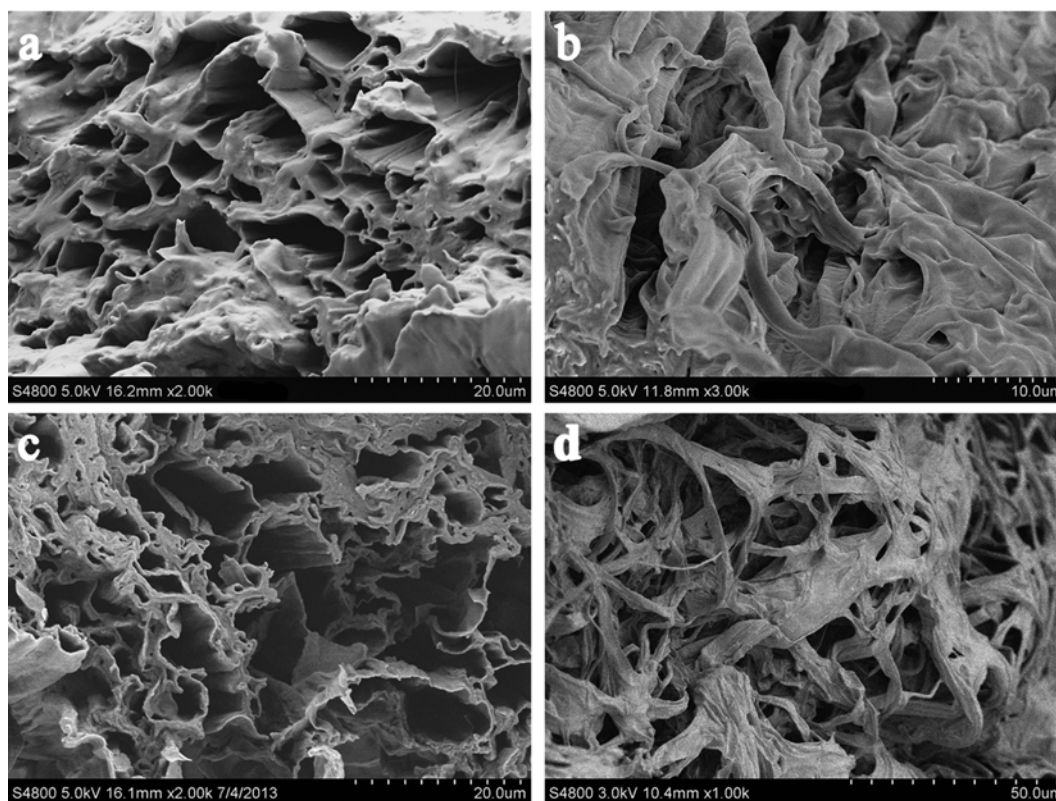


Fig. 1. SEM images of NS and MTS before biosorption. (a) SEM image of the cross-section of NS, (b) SEM image of the side of NS, (c) SEM image of the cross-section of MTS, (d) SEM image of the side of MTS. (Yun Wu)

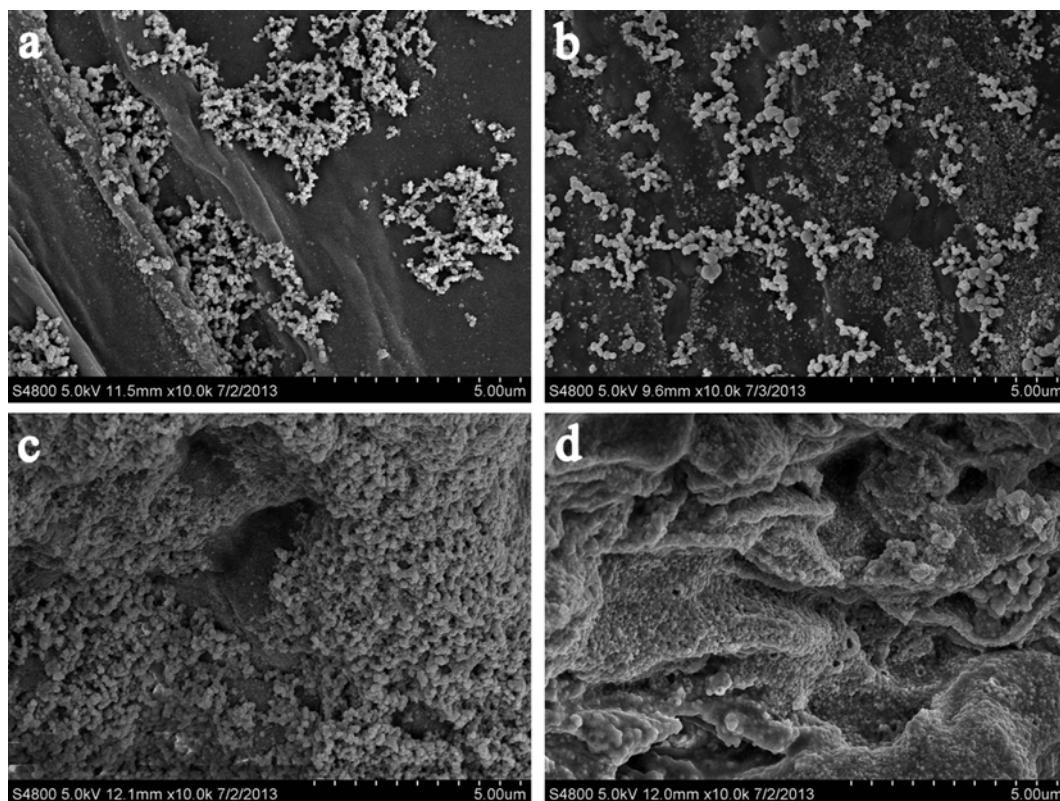


Fig. 2. SEM images of NS and MTS after biosorption. (a) SEM image of Zn^{2+} ions adsorbed on NS, (b) SEM image of Zn^{2+} ions adsorbed on MTS, (c) SEM image of Pb^{2+} ions adsorbed on NS, (d) SEM image of Pb^{2+} ions adsorbed on MTS. (Yun Wu)

ber of pinholes appeared among the folds. Meanwhile, the side surface appeared micro-fibrous interlaced and porous. The highly porous structure in Fig. 1(c), (d) was possibly from massive and fast vaporization during microwave drying. Vapor bubbles could increase total pressure gradient inside the stipe and therefore enhanced the porosity [21,22].

The scanning electron micrographs of NS and MTS after biosorption are shown in Fig. 2. A large number of well-developed metal ion grains were present on the surface of the stipe after Zn^{2+} and Pb^{2+} biosorption. Zn^{2+} ions were equally distributed on MTS (Fig. 2(b)), contrary to NS which shows uneven distribution (Fig. 2(a)). As shown in Fig. 2(c), (d), a large number of Pb^{2+} ions were adsorbed on the inside wall of the pores on MTS in comparison with NS, probably because microwave energy broke the bond from the inside out, and supplied more binding sites inside MTS. That was also the reason why there were more Pb^{2+} ions inside the pores than outside the surface of MTS.

2. Influence of pH

Biosorption of heavy metal ions depends on the pH of the solution. The pH affects the speciation of metal ions in the solution and the metal binding sites on biosorbent surface. Fig. 3(a) shows that Zn^{2+} and Pb^{2+} adsorption sharply increased from pH 2-5 for NS and MTS. The biosorption of metal ions reached equilibrium at pH 6.0 for Zn^{2+} and pH 5.0 for Pb^{2+} . In the lower pH region, the dominant protons impede the biosorption of metal ions because protons occupy most of the biosorption sites on the biosorbent surface and enhance the repulsion between the biosorbent surface and metal ions [23]. Higher pH is favorable for the biosorption due to higher

surface negative charges which depend on the dissociation of functional groups [24]. The main functional groups in the ion exchange reactions at mild acidic pH values are the carboxyl and phosphate groups present in plant cell wall components. Therefore, metal binding mainly occurs with these groups at weakly acidic conditions (pH 3.5-6.5) [25]. Decrease in biosorption of both metal ions at higher pH is due to the formation of soluble hydroxylated metal complexes which would compete with the active sites and a corresponding decrease of the retention.

The metal ions absorbed on NS and MTS were 56.3 and 89.0 mg g^{-1} for Zn^{2+} at pH 6.0, and 147.1 and 164.0 mg g^{-1} for Pb^{2+} at pH 5.0, respectively. The biosorption capacities of NS and MTS for two different metal ions were in the order: $\text{Pb}^{2+} > \text{Zn}^{2+}$, $\text{MTS} > \text{NS}$.

3. Influence of Contact Time

Biosorption of Zn^{2+} and Pb^{2+} by NS and MTS as a function of time is depicted in Fig. 3(b). Initially (initial 30 min), the removal rate of metal ions by both biosorbents increased rapidly due to the abundant availability of active binding sites on the biomass, while gradual occupancy of these sites decreased the biosorption in the later stage. The biosorption equilibrium of Zn^{2+} and Pb^{2+} was reached at about 60 min by the two biosorbents. The equilibrium biosorption quantity on NS and MTS was found to be 56.3 and 89.0 mg g^{-1} for Zn^{2+} , 147.1 and 164.0 mg g^{-1} for Pb^{2+} .

4. Influence of Initial Metal Concentration

Fig. 3(c) shows that biosorption capacities of NS and MTS increased with initial concentration of both metal ions. The maximum capacities of Zn^{2+} and Pb^{2+} on NS were 56.3 and 147.1 mg g^{-1} , while on MTS were 89.0 and 164.0 mg g^{-1} , respectively. The increase in

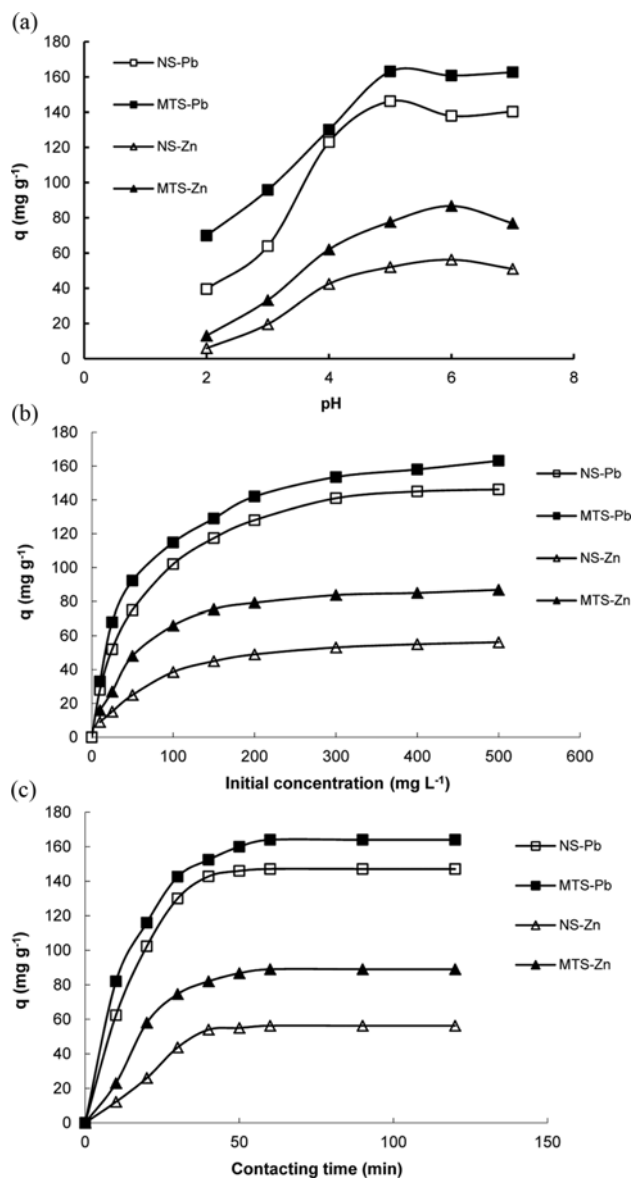


Fig. 3. (a) Effect of pH on Zn^{2+} and Pb^{2+} biosorption capacity of NS and MTS (initial concentration of metal ions: 500 mg L⁻¹, biosorbent dosage: 0.2 g, contact time: 120 min), (b) Effect of contact time on Zn^{2+} and Pb^{2+} biosorption capacity of NS and MTS (initial concentration of metal ions: 500 mg L⁻¹, biosorbent dosage: 0.2 g, pH 5.0 for Zn^{2+} , pH 6.0 for Pb^{2+}), (c) Effect of initial metal concentration on Zn^{2+} and Pb^{2+} biosorption capacity of NS and MTS (biosorbent dosage: 0.2 g, pH 5.0 for Zn^{2+} , pH 6.0 for Pb^{2+} , contact time: 120 min). (Yun Wu)

metal uptake with initial metal concentrations is due to higher availability of Zn^{2+} and Pb^{2+} for the sorption. Moreover, higher initial concentration provides increased driving force to overcome the mass transfer resistance between the aqueous and solid phase, also resulting in higher metal uptake [26].

The biosorption capacities of Zn^{2+} and Pb^{2+} ions on MTS were about 1.5 and 1.1 times higher compared to NS, respectively. The microwave treatment of the plant biomass results in not only higher surface pores but also internal changes. Heating effect of microwave causes water to vaporize suddenly, which leads to the plasmolysis of cells and destruction of organelle, slacking the cell structure; in addition, non-heating effect of microwave weakens the hydrogen bonding between the cells, which leads to the bursting of cell membranes [27]. The heating temperature or thermal effect of the microwave denature the protein molecules and degrade the polysaccharide compounds, which produces additional available binding sites such as amino group, carboxyl group and hydroxyl group [28,29].

5. Biosorption Kinetics

To determine the rate constants of the biosorption process, the kinetic models—pseudo-first order, pseudo-second order and intra-particle diffusion were employed.

The pseudo-first order (1), pseudo-second order (2) and intra-particle diffusion (3) models are represented as [30–33]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

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

$$q_t = k_t t^{0.5} + C \quad (3)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the amounts of metal ions adsorbed per unit weight of sorbent at equilibrium and at time t , respectively. k_1 (min⁻¹), k_2 (g mg⁻¹ min⁻¹) and k_t (mg g⁻¹ h^{-0.5}) are the rate constants of pseudo-first order, pseudo-second order and intra-particle diffusion models, respectively. C (mg g⁻¹) is a constant.

To describe the biosorption process by a model, the corresponding variables should follow a linear relationship. The pseudo-second order equation assumes that the biosorption process involves chemisorption and the rate of site occupation is proportional to the square of the number of unoccupied sites [34]. The intra-particle transport is supposed to be the rate-controlling step. The particle transport rate is slower than adsorption on the exterior surface site of the adsorbent [35].

The kinetic parameters are shown in Table 1. Based on the correlation coefficient (R^2), there is no evident linear correlation between the $\log(q_e - q_t)$ and t in the pseudo-first order model, whereas the

Table 1. The first-order kinetic, second-order kinetic and intra-particle diffusion models for biosorption of Zn^{2+} and Pb^{2+} ions on NS and MTS

Metal ions	Stipe forms	First-order			Second-order			Intra-particle diffusion		
		$k_1 \times 10$ (min ⁻¹)	q_e (mg g ⁻¹)	R^2	$k_2 \times 10^3$ (min ⁻¹)	q_e (mg g ⁻¹)	R^2	k_t (mg g ⁻¹ min ⁻¹)	C (mg g ⁻¹)	R^2
Zn^{2+}	NS	0.357	25.07	0.65	0.426	76.34	0.89	5.465	7.62	0.687
	MTS	0.394	40.48	0.76	0.476	108.69	0.95	7.347	23.69	0.662
Pb^{2+}	NS	0.412	42.45	0.67	0.622	163.93	0.99	9.604	62.44	0.643
	MTS	0.435	65.69	0.79	0.644	178.57	1	9.746	76.49	0.711

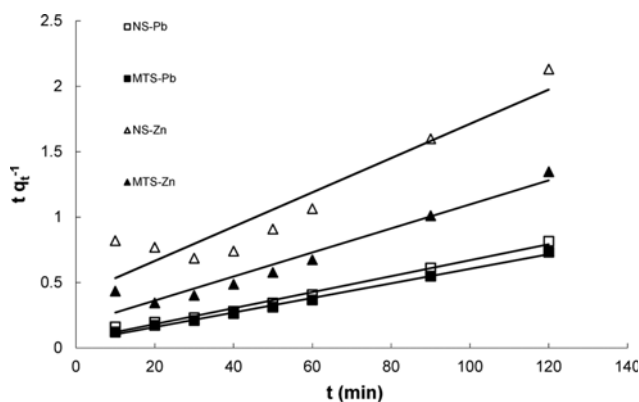


Fig. 4. Pseudo-second order plot of Zn^{2+} and Pb^{2+} biosorption on NS and MTS (initial concentration of metal ions: 500 mg L^{-1} , biosorbent dosage: 0.2 g , pH 5.0 for Zn^{2+} , pH 6.0 for Pb^{2+}). (Yun Wu)

correlation coefficients (R^2) of the pseudo-second order kinetics are high (Fig. 4). The results suggested that the removal of Pb^{2+} and Zn^{2+} on adsorbent followed the second-order kinetics over the entire sorption range, and chemisorption was involved in the removal of metal ions [34].

The k_f is also calculated and tabulated in Table 1. The results indicate that the intra-particle diffusion rate equation does not fit the biosorption process for both metal ions.

6. Biosorption Isotherms

To optimize the design of a biosorption system to remove metal ions, it is important to establish the appropriate equilibrium correlations. Langmuir and Freundlich isotherms are used to represent adsorption of components from the liquid phase on to the solid phase [36,37].

The Langmuir (4) and Freundlich (5) isotherm are represented as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (4)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where C_e (mg L^{-1}) is the equilibrium concentration of metal ions in the solution, and q_e (mg g^{-1}) is the equilibrium adsorption capacity. q_m (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants which indicate the adsorption capacity and the affinity of biosorbent for the metal ions. K_f (mg g^{-1}) and n are the Freundlich constants which indicate the adsorption capacity and adsorption intensity; they are related to the distribution of bonded ions on the sorbent surface [38].

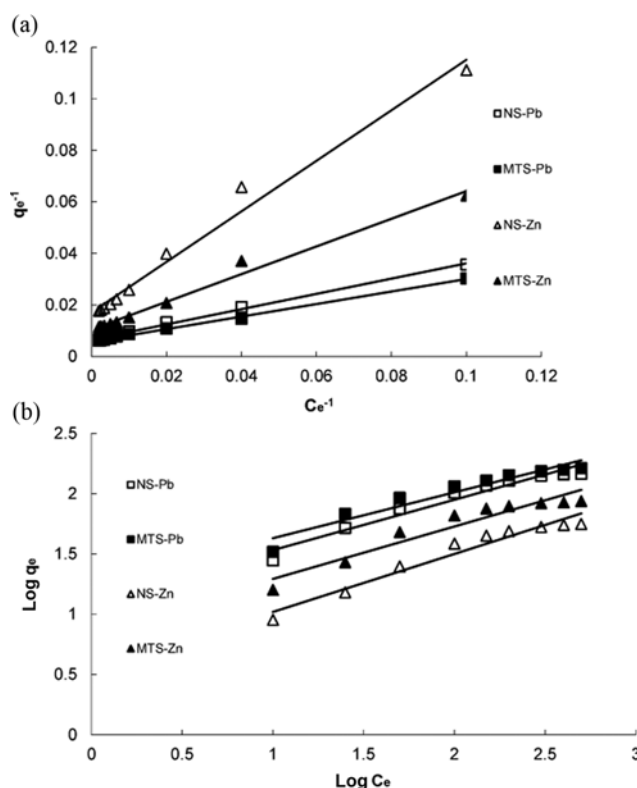


Fig. 5. (a) Langmuir biosorption isotherm (initial concentration of metal ions: 500 mg L^{-1} , biosorbent dosage: 0.2 g , pH 5.0 for Zn^{2+} , pH 6.0 for Pb^{2+} , contact time: 120 min), (b) Freundlich biosorption isotherm (initial concentration of metal ions: 500 mg L^{-1} , biosorbent dosage: 0.2 g , pH 5.0 for Zn^{2+} , pH 6.0 for Pb^{2+} , contact time: 120 min). (Yun Wu)

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor called the equilibrium parameter, R_L , which is used to predict that the adsorption system is either unfavorable ($R_L > 1$) or linear ($R_L = 1$) or favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [20]. It is defined by:

$$R_L = \frac{1}{1 + b C_0} \quad (6)$$

Fig. 5 shows that biosorption follows both Langmuir and Freundlich isotherms, and also demonstrates that the biosorption increased with an increase in equilibrium concentration of the adsorbate. The isotherm parameters are reported in Table 2. The R^2 indicate that Freundlich model is not able to describe the relationship between the amount of metal ions adsorbed by the stipe and its equilibrium

Table 2. The Langmuir and Freundlich isotherm models constants and correlation coefficients for biosorption of Zn^{2+} and Pb^{2+} ions on NS and MTS

Metal ions	Stipe forms	Langmuir isotherm model			Freundlich isotherm model		
		q_m (mg g^{-1})	$b \times 10$ (L mg^{-1})	R^2	n	K_f (mg g^{-1})	R^2
Zn^{2+}	NS	58.14	0.176	0.984	2.080	3.45	0.952
	MTS	95.24	0.196	0.987	2.296	7.19	0.919
Pb^{2+}	NS	151.51	0.223	0.997	2.396	13.05	0.950
	MTS	172.41	0.239	0.998	2.620	17.75	0.928

concentration in the solution, adequately. However, the Langmuir model best fits the equilibrium data since it presents higher R^2 values. The maximum Zn^{2+} adsorption capacities on NS and MTS obtained from the Langmuir model are 58.14 and 95.24 $mg\ g^{-1}$, respectively; while the maximum Pb^{2+} adsorption capacities are 151.51 and 172.41 $mg\ g^{-1}$, respectively. The difference of biosorption capacity not only comes from different adsorbents, but from the nature of different heavy metals. Pb^{2+} possesses strong affinity for carboxylic moieties onto the adsorbent, and studies revealed that biomaterial has sufficient carboxylic groups in the cellulose, which is also the important part of the plant's cell wall [39]. Table 2 also shows that n is greater than unity, indicating that both metal ions were effectively adsorbed by the biosorbents.

Based on the effect of separation factor R_L values ($0 < R_L < 1$) (Table 3) and adsorption capacities of different adsorbent (Table 4), NS and MTS are favorable and effective biosorbents for Zn^{2+} and Pb^{2+} .

Table 3. R_L values based on Langmuir equation for biosorption of Zn^{2+} and Pb^{2+} ions on NS and MTS

Initial metal concentration ($mg\ L^{-1}$)	R_L values			
	NS- Zn^{2+}	MTS- Zn^{2+}	NS- Pb^{2+}	MTS- Pb^{2+}
10	0.8503	0.8361	0.8177	0.8071
25	0.6944	0.6711	0.6421	0.6260
50	0.5319	0.5051	0.4728	0.4556
100	0.3623	0.3378	0.3096	0.2950
150	0.2747	0.2538	0.2301	0.2181
200	0.2212	0.2033	0.1832	0.1730
300	0.1592	0.1453	0.1300	0.1224
400	0.1244	0.1131	0.1008	0.0947
500	0.1020	0.0926	0.0823	0.0772

Table 4. The metal biosorption capacities ($mg\ g^{-1}$) of different biosorbents for Zn^{2+} and Pb^{2+}

Materials	Zn^{2+}	Pb^{2+}	References
Sugar beet pulp	17.80	73.76	[40]
Pleurotus platypus	-	27.00	[41]
Agaricus bisporus	-	33.78	[41]
Pseudomonas putida	-	36.00	[42]
NaOH-spent grain	-	35.50	[43]
NaOH- olive tree pruning	-	16.40	[44]
H_2SO_4 -peanut husk	-	29.14	[45]
Keratin colloidal solution	-	43.30	[46]
Rice husk	-	108.00	[47]
Lentinus edodes pellets	33.70	-	[48]
Cashew nut shell	24.98	-	[49]
Padina sp.	52.95	-	[50]
Fontinalis antipyretica	14.70	-	[51]
Penicillium digitatum	9.70	-	[52]
NaOH-agave bagasse	20.26	-	[53]
Wheat straw	3.25	-	[54]
Coir	8.60	-	[55]
NS	58.14	151.51	in this work
MTS	95.24	172.41	in this work

CONCLUSIONS

The single component biosorption equilibriums of Pb^{2+} and Zn^{2+} ions are experimentally studied using NS and MTS of *Flammulina velutipes* at 27 °C. The effects of parameters like pH, contact time and initial metal ion concentration during the biosorption process are noted. The desired pH value for biosorption is 6.0 for Zn^{2+} and 5.0 for Pb^{2+} for the stipe under study. Longer contact time and higher initial metal ion concentration resulted in higher removal of Zn^{2+} and Pb^{2+} . The biosorption followed pseudo-second order model, but the intra-particle diffusion was not the rate-limiting step for the sorption of both metals. The Zn^{2+} and Pb^{2+} biosorption data is better fitted to Langmuir isotherm model.

The results show that the stipe of *Flammulina velutipes* is an efficient biosorbent for removal of Zn^{2+} and Pb^{2+} ions from aqueous solution; the values of q_{max} were 58.14 and 151.51 $mg\ g^{-1}$ for Zn^{2+} and Pb^{2+} sorption on NS. Higher values of q_{max} , 95.24 $mg\ g^{-1}$ for Zn^{2+} and 172.41 $mg\ g^{-1}$ for Pb^{2+} , indicate the higher suitability of MTS to remove both metal ions. The difference in sorption capacities is mostly due to the porous structure on the surface and the additional available binding sites in the cell wall composition produced by the microwave treatment.

Based on the results of the biosorption study, the discarded stipe of *Flammulina velutipes* may be recycled as an efficient adsorbent for the removal of Zn^{2+} and Pb^{2+} from aqueous solution. Further research is in progress to elucidate the mechanism involved during the biosorption process.

ABBREVIATIONS

NS : native stipe
MTS : microwave treated stipe
SEM : scanning electronic microscopy

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