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Bi-metal biosorption using *Pleurotus ostreatus* spent mushroom substrate (PSMS) as a biosorbent: isotherm, kinetic, thermodynamic studies and mechanism

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ABSTRACT

The bi-metal biosorption of *Pleurotus ostreatus* spent mushroom substrate (PSMS), a novel agriculture waste from solid substrate fermentation for mushroom production, was explored in this study. The biosorption of Cu(II) and Ni(II) in bi-metal solution using PSMS were examined under batch biosorption technique. Determination of metal biosorption was evaluated through isotherm, kinetic and thermodynamic studies in order to elucidate the mechanisms of metal biosorption. Metal biosorption results were well corresponded to Langmuir and Freundlich isotherms. The maximum uptakes were 3.54 mg/g Cu(II) and 1.85 mg/g Ni(II) for bi-metal solution. However, this PSMS biosorbent has higher selectivity to Ni(II) when compared to Cu(II). The mean energy indicated that chemisorption involved in metals biosorption. Biosorption data were superbly fitted to pseudo-second-order kinetic when compared to pseudo-first-order kinetic. The results from the pseudo-second-order kinetic also implied that chemisorption plays a major role in biosorption process. Thermodynamic parameters showed that biosorption reaction was spontaneous and exothermic. Furthermore, a weaker and reversible bond formed after biosorption, which provided evidence that chemisorption is one of the mechanisms in biosorption. The ion exchange mechanism was evaluated through ICP-OES metals concentration and pH observation. In conclusion, the high metal biosorption uptake of PSMS indicates that it is a potential biosorbent for metal removal from waste streams. The findings revealed that both chemisorption and ion exchange were the two main mechanisms involved in spontaneous exothermic reversible metal biosorption process. This piece of information provides insight into application of biosorption of PSMC in real wastewater sample.

Keywords: Bi-metal biosorption; Cu(II); Mechanisms; Ni(II); *Pleurotus ostreatus* spent mushroom substrate

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1. Introduction

Metal pollution is an environmental issue of global concern due to industrialization and development. Current metal removal technologies have limitations of technical constraints, high chemical consumption, incur high cost, and generate secondary toxic waste. Furthermore, these technologies are not effective for low concentration of metal removal in range of 1–100 mg/L and petrochemical or mineral based materials are not environmental friendly [1]. Therefore, these limitations have driven to alternative technology for metal removal in order to improve cost effectiveness and environmental friendly concepts.

Biosorption defined as a physico–chemical process that involving binding between substances from solution and functional groups on the surface of biosorbent [2,3]. Biosorption has been highlighted as a green alternative technology for metal removal. It offers advantages of easily and abundantly available, economic especially for low metal concentration, minimum secondary products as well as recovery of metal from biosorbent and reusability of biosorbent can be easily achieved [4–6].

Most of experimental design in batch biosorption studies provide fundamental knowledge of biosorption performance under influence of physical and chemical factors such as initial pH, contact time, initial metal concentration, particle size of biosorbent, dosage of biosorbent, and temperature [7,8]. However, there is a lack of investigation on bi-metal and selectivity studies which reflect better in real status of industrial wastewater.

Pleurotus ostreatus spent mushroom substrate (PSMS) is a commercial agricultural waste. Although different potential fungal based biosorbent has been investigated, very little is known of such biosorbent in bi-metal removal. This study reports on the potential of PSMS biosorbent as biosorbent for removal of Cu (II) and Ni(II) in bi-metal solution. In addition, biosorption maximum uptake, mechanisms and selectivity for bi-metal solution are also investigated.

2. Material and methods

2.1. Biosorbent and metal solution preparation

Sample of PSMS was collected from C & C Mushroom Cultivation Farm Sdn. Bhd., Gerisek, Johor. It was sterilized and dried at a temperature of 60˚C. After that, the sample was ground to particles of size 710 μm and washed with ultrapure water to remove contaminants. Finally, the dried sample was kept in drying cabinet as biosorbent.

Cu(II) and Ni(II) solution were prepared by using ultrapure water. Copper (II) sulphate anhydrous salt (CuSO4) (Merck, Germany) and Ni(II) nitrate hexahydrate salt ($Ni(NO_3)_2·6H_2O$) (Merck, Germany) were used for metal solution.

2.2. Biosorption study

An amount of 0.7 g PSMS biosorbent was weighed and added into 50 mL of 50 mg/L in total bi-metal solution in a ratio of 1:1 for Cu(II) and Ni(II) [9]. The constant initial pH at unadjusted pH condition of 4.58 ± 0.05 was measured prior to experiment. Samples in bi-metal concentration of 10–250 mg/L were agitated at 125 rpm for 60 min in an orbital incubator shaker set at 25 ± 1˚C for isotherm study. Samples were then filtered and the filtrates were analyzed using ICP-OES (7300DV, Perkin Elmer, USA). All samples were prepared in duplicates. An average data was used for data analysis and low standard deviation of 2 was neglected in the graph. The similar experimental design was repeated by changing the agitation time from 60 min to 0.5, 1, 3, 5, 10, 15, 30, 45, 60, 90, and 120 min in kinetic study. The initial and final pH after biosorption for kinetic study were measured using pH meter (744, Metrohm, Switzerland). For thermodynamic study, the experimental design was repeated with a temperature of 5, 15, and 35˚C.

2.3. Data evaluation of existing mathematical model

The results from isotherm study were fitted to linearized Langmuir and Freundlich equations as shown in Eqs. (1) and (2), mean while the mean energy of biosorption through the Dubinin–Radushkevich constant as Eq. (3).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b\, q_{\max}} \tag{1}$$

$$\ln q_e = \ln K_F + \frac{1}{n \ln q_e} \tag{2}$$

$$E = (-2\,K)^{-1/2} \tag{3}$$

where q_e—equilibrium metal biosorption uptake (mg/g), $q_{\max}$—maximum metal biosorption uptake (mg/g), C_e—metal concentration at equilibrium (mg/L), b—Langmuir constant, K_F and n—Freundlich constant, E—mean free energy (kJ/mol), K—constant related to the mean free energy of biosorption per mol of biosorbent (mol^2/J^2).

The experimental data for kinetic bi-metal study was used to fit the pseudo-first-order kinetic and pseudo-second-order kinetic equations (Eqs. (4) and (5)).

$$\log\,(q_e - q_t) = \log q_e - \frac{k_1\,t}{2.303} \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{2k_2\,q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e and q_t—metal biosorption uptake at equilibrium and at time (mg/g), t—time (min), k_1 and k_2—constant of pseudo-first-order and second-order kinetic.

The obtained thermodynamic results were evaluated by thermodynamic equations using Eqs. (6) and (7). Thermodynamic parameters of Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated.

$$\log K_c = -\frac{\Delta H}{2.303\mathrm{RT}} + \frac{\Delta S}{2.303R} \tag{6}$$

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

where K_c (L/g) is the distribution coefficient, q_e (mg/g) and C_e (mg/L) are the biosorption capacity and metal concentration at equilibrium, respectively, T is temperature in Kelvin and R is the gas constant. ΔG is free energy (kJ/mol). ΔH and ΔS were obtained from the slope and intercept of the plots of log K_c vs. $1/T$.

3. Results and discussion

3.1. Isotherm study: Langmuir and Freundlich models

The Langmuir isotherm model is the most common model applied to calculate the amount of monolayer biosorption on the surface of biosorbent. Fig. 1 shows Cu(II) and Ni(II) in bi-metal solution were well fitted to the Langmuir isotherm plot with a correlation coefficient of 0.9589 and 0.9601, respectively. Results revealed that bi-metal biosorption occurred in a single layer on the surface of biosorbent, involving interaction of metal ions with functional groups of biosorbent. The calculated maximum uptake of metal ($q_{\max}$) was found to be at 3.54 mg/g for Cu(II) and 1.85 mg/g for Ni(II). The Cu(II) has a higher maximum uptake capacity than Ni(II) in bi-metal solution. This indicated that metal with higher atomic number, standard atomic weight and atomic radius exhibit a better uptake capacity. Zakhama et al. [10] and Kleinübing et al. [11] reported that the maximum uptake of Cu(II) is higher than Ni(II).

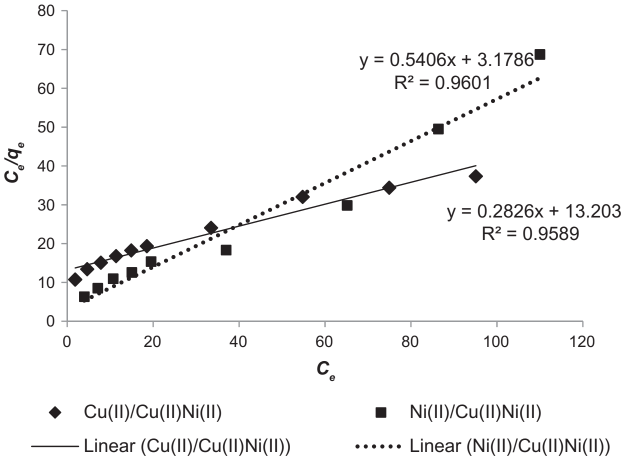

Fig. 1. Langmuir isotherm plot for Cu(II) and Ni(II) biosorption in bi-metal solution.

The calculated Langmuir constant (b) for Cu(II) and Ni(II) were 0.0214 and 0.1701 L/mg, respectively. This result inferred that the parameter b for Ni(II) is approximately one order of magnitude higher than Cu (II) in bi-metal solution. The PSMS biosorbent has higher selectivity affinity to Ni(II) compared to Cu(II). Such desirable circumstance leads to effective treatment of the target metal in industrial wastewater. Study by Mekewi et al. [12] supported result of this study where the rate constants sequence Ni(II) was higher than Cu(II).

The linear Freundlich plot for bi-metal biosorption is shown in Fig. 2. The coefficient correlation of Cu(II) ($r^2 = 0.9946$) was higher than Ni(II) ($r^2 = 0.8765$). This is attributed to the higher uptake capacity of Cu(II) when compared to Ni(II). Values of Freundlich

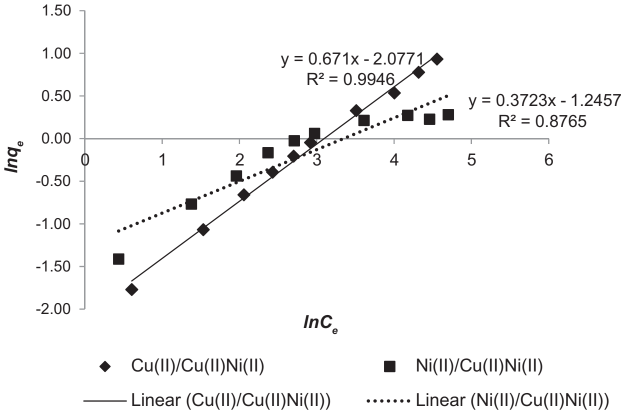

Fig. 2. Freundlich isotherm plot for Cu(II) and Ni(II) biosorption in bi-metal solution.

constant (n) were 1.49 and 2.69 for Cu(II) and Ni(II) in bi-metal solution, respectively. Since the value of $1/n$ is less than 1, this indicates that a relatively stronger bond between metal ions and functional groups of surface biosorbent formed and biosorption mechanism occurred.

The mean biosorption energy is used to predict the physical adsorption in the range of 1–8 kJ/mol and the chemisorption is more than 8 kJ/mol [13]. The calculated mean energy of biosorption for Cu(II) and Ni(II) were 21–24 kJ/mol, respectively. This indicated that the biosorption process is predominant on the chemisorption process.

3.2. Kinetic study: pseudo-first-order and second-order kinetic model

Figs. 3a and 3b show Cu(II) and Ni(II) biosorption in bi-metal solution were excellently fitted to pseudo-second-order kinetic compared to pseudo-first-order kinetic with a high correlation coefficient. The calculated q_e values of pseudo-second-order kinetic were in excellent agreement with the actual experimental values which inferred that the validity of this model for biosorption (Table 1). The pseudo-second-order kinetic model also corresponded to chemisorption, involving the valency force through the sharing of electrons. In addition, such results also indicated that chemisorption is the rate-limiting factor in biosorption process. Table 1 lists the parameters of kinetic models with other recent studies.

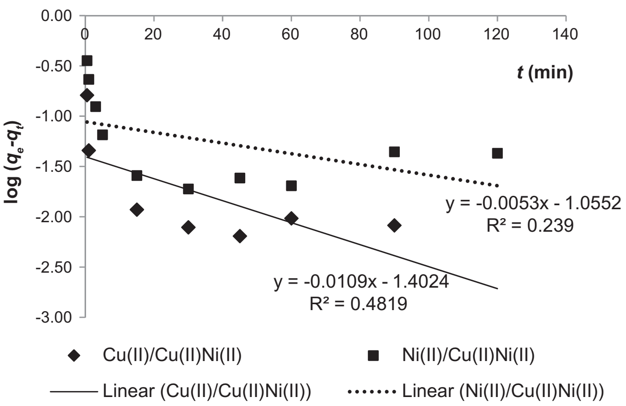

Fig. 3a. Pseudo-first-order kinetic plot for Cu(II) and Ni(II) biosorption in bi-metal solution.

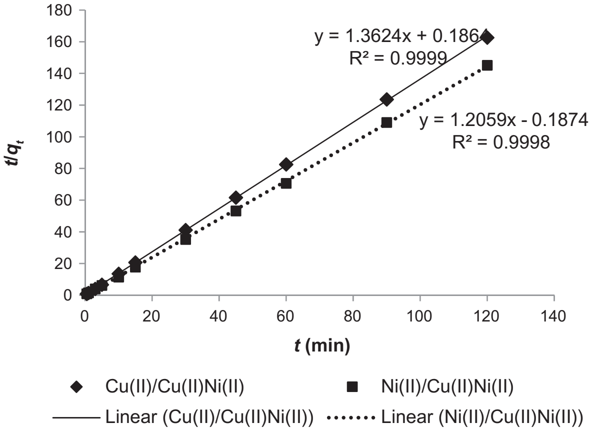

Fig. 3b. Pseudo-second-order kinetic plot for Cu(II) and Ni(II) biosorption in bi-metal solution.

3.3. Thermodynamic study

Thermodynamic parameters of free Gibb energy (ΔG), enthalpy changes (ΔH), and entropy changes (ΔS) were shown in Table 2. The negative ΔG values suggested the nature of biosorption process is spontaneous. The negative values of ΔH pointed out that metal biosorption is an exothermic reaction. The negative ΔS values represented weaker and reversible bonds were formed after the biosorption process. This implied that this PSMS biosorbent has a good potential in recovery of metal and reusability of biosorbent. Similar findings also reported by Ertugay and Bayhan [17], Aloma et al. [18], Rozaini et al. [19] and Guler and Sarioglu [20] by using fungus *Agarican biporus*, sugarcane bagasse, modified mangrove bark, and yeast *Saccharomyces cerevisiae*.

3.4. ICP-OES observation

Fig. 4 shows there was an increase in light metal ions accompanying the decrease of the Cu(II) and Ni(II) ions. During the biosorption process, light metal ions were released from the biosorbent which corresponded to the decrease of light metal ions in the bi-metal solution. Meanwhile, the biosorption of Cu(II) and Ni(II) has resulted the decrease of Cu(II) and Ni(II) concentrations. These observations suggested that the ion exchange mechanism occurred through replacement of light metal ions on PSMS biosorbent. Ca(II) and Mg(II) ions play an important function in Cu(II) and Ni(II) biosorption. On the other hand, the low concentration of Na and K ions were not significant. Similar observation also documented by Fiol et al. [21], Wahab et al. [22] and Tay et al. [23].

3.5. pH observation

The pH of Cu(II) and Ni(II) solution slightly increased during the biosorption process are shown in

Table 1
kinetic model parameters for Cu(II) and Ni(II) in bi-metal solution and comparison with other recent related studies

	Pseudo-first-order kinetic			Pseudo-second-order kinetic			
Biosorbent	q_e	K_1	R^2	q_e	K_2	R^2	Experimental data
Cu(II)							
PSMS (This study)	0.04	0.03	0.4819	0.73	4.97	0.9999	0.74
Chestnut shell [14]	1.17	0.014	0.771	4.44	0.08	0.997	4.53
Fungal *Pleurotus ostreatus* [15]	0.27	0.036	0.430	3.20	3.13	0.999	3.24
Ni(II)							
PSMS (This study)	0.09	0.01	0.2390	0.85	−3.88	0.9998	0.87
Waste pomace [16]	1.11	0.08	0.862	4.00	0.23	0.999	3.95

Table 2
Thermodynamic parameters for metal biosorption utilizing PSMS biosorbent

Metal	Temperature (K)	Δ*H* (kJ/mol)	Δ*S* (kJ/mol/K)	Δ*G* (kJ/mol)	R^2
Cu(II)/Cu(II) Ni(IIT)	278	−2,532	−0.0549	−2,517	0.9957
	288			−2,516	
	298			−2,516	
	308			−2,515	
Ni(II)/Cu(II)Ni(II)	278	−159	−0.0249	−153	0.054
	288			−152	
	298			−152	
	308			−152	

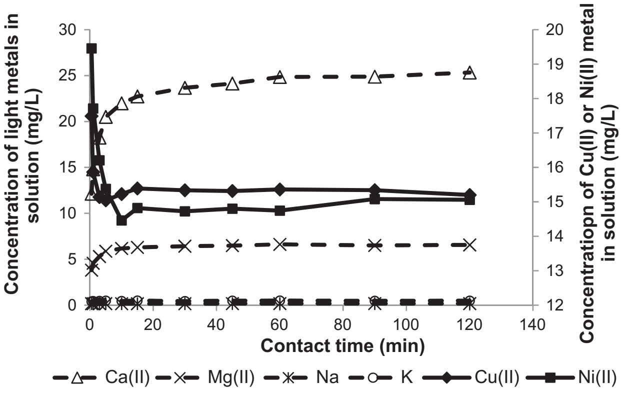

Fig. 4. ICP-OES analysis of Cu(II) and Ni(II) and light metal ions behavior.

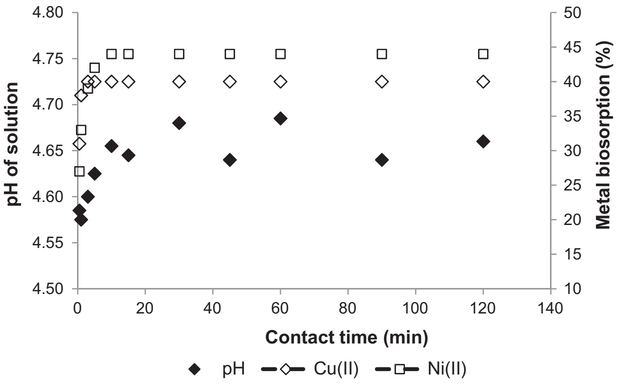

Fig. 5. Effect of contact time on pH for Cu(II) and Ni(II) biosorption.

Fig. 5. The graph shows a gradual increase of pH in the first few minutes and then gradually increased which corresponded to the Cu(II) and Ni(II) biosorption profiles. This observation may attribute to ionization of metal. Changes of metal ions species have resulted in slightly increase of solution pH. Such observation further support the ion exchange mechanism through replacement of earth alkaline metal ions and alkaline metal ions with Cu(II) or Ni(II) ions.

Generally, changes of pH solution causes changes of metal ions species may capture by hydrogen bonding mechanism along with ion exchange. The sharing of free electron pair between surface oxygen atom and metal ions implied chemisorption occurred during biosorption process. Vinodhini and Das [24] also reported the chemisorption induced hydrogen binding mechanism which is consistent with the result of this study.

4. Conclusion

PSMS has been evaluated as a biosorbent through isotherms, kinetic and thermodynamic studies. These studies also elucidate maximum uptake, selectivity, mechanisms, and nature of biosorption process. Experimental results were well fitted to Langmuir and Freundlich isotherms with maximum uptake of 3.54 mg/g for Cu(II) and 1.85 mg/g for Ni(II) in bi-metal solution. The PSMS biosorbent has higher selectivity towards Ni(II) when compared to Cu(II). The calculated mean biosorption energy suggested chemisorption mechanism. Results from kinetic study were excellently fitted to pseudo-second-order kinetic than pseudo-first-order kinetic. This also indicated that chemisorption is the rate limiting factor in biosorption process. Thermodynamic parameters revealed that biosorption process was exothermic, spontaneous and reversible. The ICP-OES and pH observation suggested ion exchange mechanism. Several mechanisms may take place simultaneously during biosorption process. This PSMS biosorbent has great potential to be developed into a green remediation technology due to high uptake capacity, selectivity as well as possibility of reusability of biosorbent, and recovery of metal from biosorbent.

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