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Mn(II) Ions Biosorption from Aqueous Solution using *Pleurotus* Spent Mushroom Compost under Batch Experiment

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Abstract. The *Pleurotus* spent mushroom compost was selected as biosorbent to sorption Mn(II) ions. The Mn(II) ions biosorption was investigated under batch experiments. The influences of pH, contact time and initial Mn(II) concentration were also investigated. The optimum Mn(II) ions biosorption was achieved at pH 6, 20 minutes of contact time and 10 mg/L of initial Mn(II) concentration using 1.0 g biosorbent dosage. The Mn(II) ions biosorption experimental data were best described by the Langmuir isotherm model and pseudo-second order kinetic model. As conclusion, the *Pleurotus* spent mushroom compost can be used to sorption the Mn(II) ions from the aqueous solution.

Introduction

Biosorption has been highlighted as a low-cost treatment technology with possibility for biosorbent regeneration, metals recovery and minimizing toxic sludge production [1]. Biosorption is the passive uptake of pollutants by dead or inactive biological materials [2]. The biosorption process mechanisms may involve ion exchange, chemisorption, physical adsorption, complexation, precipitation and chelation [3, 4]. However, the mechanisms responsible for heavy metals uptake will differ according to the functional group of biosorbent. Various agricultural waste as potential biosorbent for heavy metals removal have been investigated including corn chaff [5], tea-waste [6], rice husk [7], peanut shell [8], pre-treated orange peel [9], green tomato husk [10], rubber tree sawdust [11] and neem sawdust [12]. Factors that influence the selection of biosorbent include easily available in large quantities, economical and high uptake capacity [13].

In this study, the *Pleurotus* spent mushroom compost have been selected as a biosorbent for Mn(II) ions biosorption. It is an abundant agricultural waste material from mushroom farms. In Malaysia, about 24 tons per month of spent mushroom compost are disposed in the municipal solid waste landfill [14]. The aim of the study is to evaluate the performance of Mn(II) ions biosorption using *Pleurotus* spent mushroom compost under batch experiments through parameters such as pH, contact time and initial Mn(II) concentration. The sorption equilibrium of Mn(II) ions were determined using the Langmuir isotherm model, whereas kinetic data were analysed using a pseudo-second order kinetic model.

Materials and Methods

Preparation of Biosorbent. The *Pleurotus* spent mushroom compost sample was obtained from a mushroom production at Muar, Johor state, Malaysia. The sample was sterilised using autoclave (Hirayama, HVE-50) at 121°C for 15 minutes and kept in an oven at 60ºC. The dried sample was crushed into powder and sieved to less than 710 μm particle size.

Biosorption Study. About 1.1430 g of Manganese(II) Nitrate Tetrahydrate ($Mn(NO_3)_2.4H_2O$) was dissolved with 250 mL ultrapure water to produce 1000 mg/L Mn(II) stock solution. Biosorption batch experiments were conducted by adding 1.0 g of biosorbent into 50 mL of Mn(II) ions. Then, the mixture were shaken at a speed of 125 rpm and temperature of 25± 1ºC. The influences of pH (pH 2 to 7), contact time (1 to 90 minutes) and initial Mn(II) concentration (10 to 200 mg/L) were investigated. The final effluents were filtered and analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (Perkin Elmer, 7300DV).

Biosorption Performance. The Mn(II) ions biosorption was calculated based on the following equation;

$$\text{Mn(II) Biosorption (\%)} = \frac{C_o - C_f}{C_0} \times 100\% \tag{1}$$

Where, C_o is the initial Mn(II) ions concentration (mg/L), C_f is the final Mn(II) ions concentration (mg/L). The sorption equilibrium of Mn(II) ions were determined by using the linearized Langmuir isotherm model.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{2}$$

Where, q_e is the Mn(II) ions uptake at equilibrium (mg/g), q_{max} is the maximum biosorption capacity (mg/g), C_e is the Mn(II) ions concentration at equilibrium (mg/L) and b is the Langmuir constant (L/mg). The kinetic data for Mn(II) ions biosorption were analysed using linearized pseudo-second order model.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

Where, q_t is the Mn(II) ions uptake at time (mg/g), t is time (minute) and k_2 is the rate constant of pseudo-second order (g/mg/min).

Results and Discussion

Biosorption Studies. The effect of pH on the biosorption of Mn(II) ions by *Pleurotus* spent mushroom compost is presented in Fig.1. The contact time and initial Mn(II) concentration were held constant at 60 minutes and 50 mg/L respectively. The Mn(II) ions biosorption was increased from 4.8% to 49.3% with increasing pH values from pH 2 to 7. At low pH, high H^+ concentration caused protonation of the biosorbent active binding sites. The charge repulsion occurred and thus, reduces Mn(II) ions biosorption [15, 16]. As the pH increased, the biosorbent active binding sites were deprotonated and the charge attraction occurred between the active binding sites and Mn(II) ions. Therefore, the increase of pH value resulted in an increase of Mn(II) ions biosorption. The Mn(II) ions biosorption was rapidly increased as the pH values increased from 2 to 5. However, no changes were observed between pH 5 to 7. Therefore, the subsequent experiments were conducted at pH 6 because it is closer to the Mn(II) solution pH value. Similar pH trend also have been reported in Mn(II) ions biosorption study by Ma et.al [17].

The influence of contact time on the Mn(II) ions biosorption is presented in Fig. 2. The pH and initial Mn(II) concentration were held constant at pH 6 and 50 mg/L respectively. The biosorption of Mn(II) ions rapidly occurred during the first 10 minutes of contact time, followed by an equilibrium phase after 20 minutes. The Mn(II) ions biosorption increased from 33% to 47% following the increase in contact time from 1 to 90 minutes. At the first phase (within 1 to 10 minutes), the biosorption process occurred rapidly because of large surface area and more biosorbent active binding sites were available for Mn(II) ions biosorption [15]. However, the biosorption process was slowed down and reach an equilibrium phase when the surface of the active binding sites were gradually occupied. Therefore, the further experiment was conducted at 20 minutes contact time.

The influence of initial Mn(II) concentration on the Mn(II) ions biosorption by *Pleurotus* spent mushroom compost is shown in Fig. 3. The pH and contact time were held constant at pH 6 and 20 minutes respectively. The Mn(II) ions biosorption was reduced from 73% to 24% with increasing the initial Mn(II) concentrations from 10 mg/L to 200 mg/L. This was due to at high concentrations, the number of active binding sites for biosorption process to occur is less compared to the number of Mn(II) ions present and thus reduced the Mn(II) ions biosorption. In addition, the initial concentration also provides a driving force to solve the mass transfer resistance in the Mn(II) ions biosorption [16].

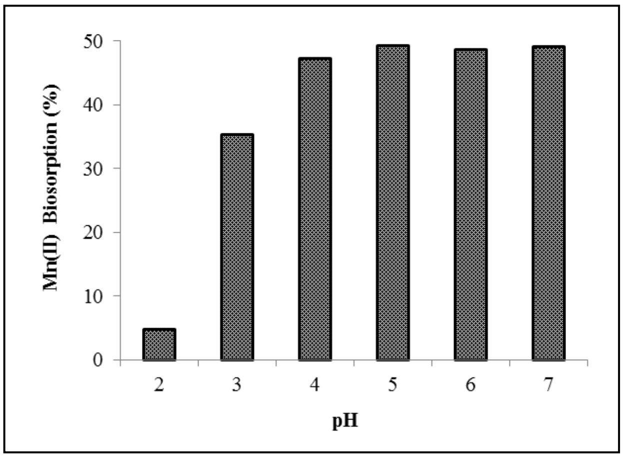

Fig. 1: Effect of pH on the Mn(II) ions biosorption (Mn(II) concentration: 50 mg/L; biosorbent dosage: 1.0 g; agitation speed: 125 rpm; temperature: 25ºC; contact time: 60 minutes)

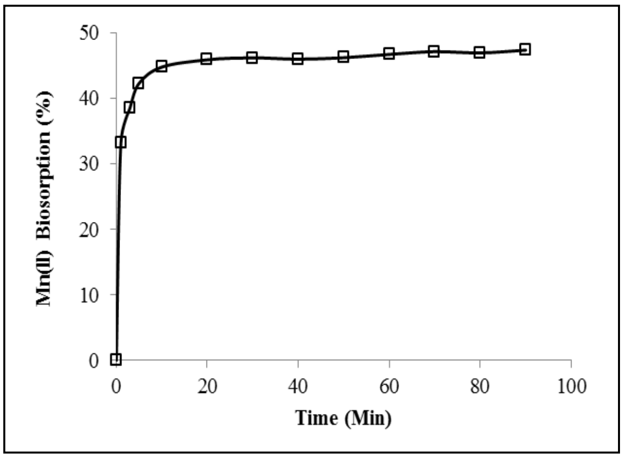

Fig. 2: Effect of contact time on the Mn(II) ions biosorption (Mn(II) concentration: 50 mg/L; pH: 6; biosorbent dosage: 1.0 g; agitation speed: 125 rpm; temperature: 25ºC)

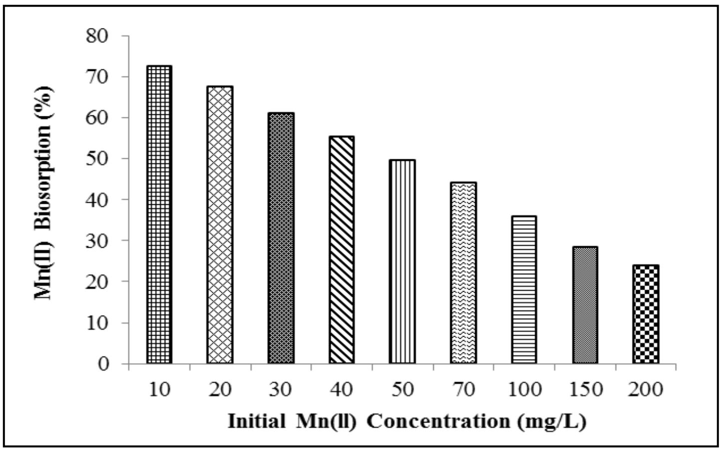

Fig. 3: The influence of initial Mn(II) concentration on the Mn(II) ions biosorption (Biosorbent dosage: 1.0 g; pH: 6; agitation speed: 125 rpm; temperature: 25ºC; contact time: 20 minutes)

Table 1: R_L values at different initial Mn(II) concentration

Conc. [mg/L]	**10**	**20**	**30**	**40**	**50**	**70**	**100**	**150**	**200**
R_L	0.6834	0.5191	0.4185	0.3505	0.3016	0.2357	0.1776	0.1258	0.0974

Isotherm and Kinetic Study. Fig. 4 shows the Langmuir isotherm plot for Mn(II) ions biosorption onto *Pleurotus* spent mushroom compost. The values of q_{max}, b and R^2 based on the plot of Langmuir isotherm model were 2.44 mg/g, 0.046 L/mg and 0.9895 respectively. The dimensionless separation factor of equilibrium, R_L, which defined by Webi and Chakravort [18] was used to predict whether the biosorption system is favourable or unfavourable and the values are shown in Table 1. The values of R_L, which was $0 < R_L < 1$ indicates that the biosorption was favourable at the conditions being studied. Fig. 5 shows the plot of pseudo-second order kinetic for Mn(II) ions biosorption onto *Pleurotus* spent mushroom compost. The values of q_e, k_2 and R^2 based on the plot of pseudo-second order kinetic model were 1.163 mg/g, 1.168 g/mg/min and 0.9999 respectively.

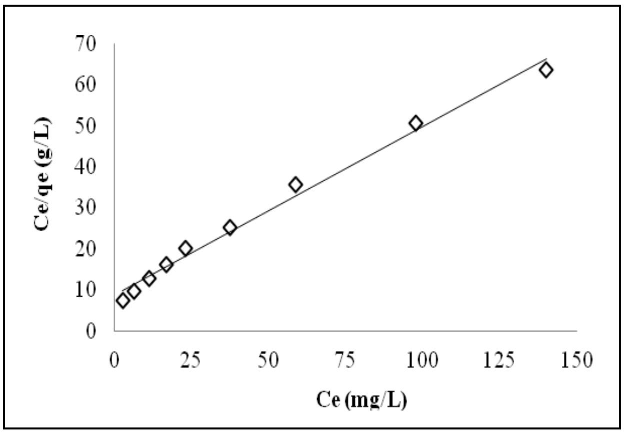

Fig. 4: Langmuir isotherm plot for Mn(II) ions biosorption onto *Pleurotus* spent mushroom compost

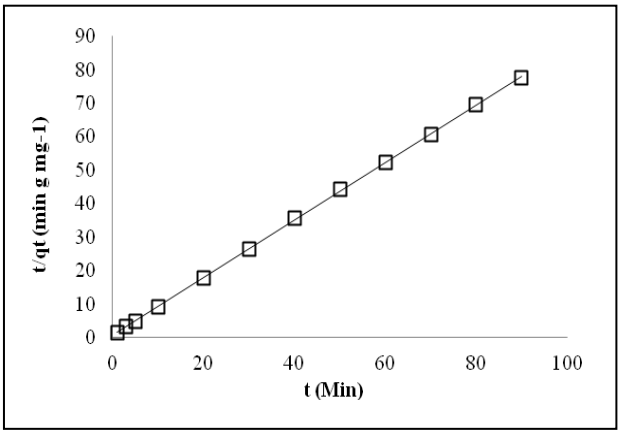

Fig. 5: Pseudo-second order kinetic plot for Mn(II) ions biosorption onto *Pleurotus* spent mushroom

Conclusion

The study demonstrates that the application of *Pleurotus* spent mushroom compost for Mn(II) ions biosorption. The performance of Mn(II) ions biosorption was strongly influenced by the pH, contact time and the initial Mn(II) concentration. The Mn(II) ions biosorption were increased with increasing the pH value and contact time. Conversely, the Mn(II) ions biosorption shows a decreasing rate as the initial Mn(II) concentration increased. The Mn(II) ions biosorption were best described by the Langmuir isotherm model with a maximum biosorption capacity of 2.44 mg/g and the kinetic data follows a pseudo-second order kinetic model.

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