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LANGMUIR AND FREUNDLICH ISOTHERMS FOR DESCRIBING LEAD (II) ADSORPTION ON PRETREATED MACROFUNGUS (*AGARICUS BISPORUS*)

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ABSTRACT

Studies have shown that fungal organisms possess the capacity of heavy metal removal. In the present investigation, a study in batch system was conducted using the macrofungus, *Agaricus bisporus* as biosorbent for evaluating its potentiality to adsorb lead (II) ions from aqueous solution. To improve the bioadsorption capacity, the biosorbent was pretreated with NaOH, Na_2CO_3 and $NaHCO_3$. Pretreatment with NaOH resulted in a significant improvement in bioadsorption capacity. The experimental equilibrium data were adjusted by adsorption isotherms from Langmuir and Freundlich models and their equilibrium parameters were determined. For the untreated biosobent, the Langmuir model supplied q_{max} = 28.8 mg/g and b = 0.02 L/mg and for the Freundlich model parameters are K_f = 1.7 and n =1.8. For the sodium hydroxide (NaOH) treated biomass, the parameters were q_{max} = 34.6 mg/g, b= 0.08 L/mg, K_f = 5.3 and n = 2.3. The best adjusted model to the experimental equilibrium data for both untreated and sodium hydroxide (NaOH) treated biosorbent was the Langmuir model.

INTRODUCTION

Environmental pollution, particularly water pollution by toxic heavy metals, is the result of several industrial activities, and its control has been a challenge. These heavy metals are toxic pollutants and non-biodegradable and present a cumulative effect in the food chain, threatening the human and animal health.

Conventional methods of treatments, *viz.*, precipitation, coagulation, reduction, ion exchange, membrane filtration, adsorption on activated charcoal, etc. are used in the removal of metallic ions. But these methods are normally associated with either a high cost or a low efficiency, not guaranteeing the limits of metal concentration demanded by legal standards. Biosorption is an emerging technology which has low cost in the removal/recovery of diverse heavy metals present in industrial effluents. Among the biosorbent types, which can be used in the biosorption process, fungi possess excellent metal uptake potential (Kapoor & Viraraghavan 1995). Furthermore, fungal biomasses have been subjected to physical and chemical pretreatments to enhance its performance (Kratochvil & Volesky 1998). However, there are only few reported studies on utilization of fruiting bodies of macrofungi as biosorbents in the treatment of metal laden aqueous solutions.

The metals biosorption process involves a variety of mechanisms, which can differ quantitatively and qualitatively, in agreement with the used species, the origin of the biomass and other factors (Volesky & Holan 1995). Among the employed modelling of adsorption, either at theoretical or empirically derived isotherms, the Langmuir model in monolayer and the Freundlich empirical model particularly for the biosorption, are the models which are mostly used and represent adequately the equilibrium data. The general form of Langmuir and Freundlich models, respectively, for mono-component systems are given by:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + bC_{eq}} \quad ...(1)$$

and

$$q_{eq} = K_f C_{eq}^{1/n} \quad ...(2)$$

Where q_{eq} and q_{max} are the observed uptake capacity at equilibrium and maximum uptake capacity (mg/g), C_{eq} is the equilibrium concentration (mg/L), b (L/mg) is the equilibrium constant of adsorption with relation to the affinity of the binding sites for the metals, and K_f and n are indicators of the adsorption capacity of the biomass and adsorption intensity respectively (Sag et al. 1998, Aksu & Tezer 2000).

The degree of biosorption of a metal ion on a biosorbent has been described as a function of equilibrium metal-ion concentration in solution at constant pH and temperature conditions (Volesky 1990). The objective of the present work was to adjust the experimental equilibrium data using the Langmuir and Freundlich models adsorption isotherms and to verify the performance of the pretreated biosorbent macrofungus, *Agaricus biosporus* in the lead (II) removal.

MATERIALS AND METHODS

Preparation of biosorbent: Fruiting bodies of *Agaricus bisporus* used in this study were purchased from a grocery store, which were supplied by Saptarishi Agro Industries Ltd., Pazhayanoor, Tamil Nadu. Mushrooms were washed thoroughly with deionized water to remove the dirt and impurities.

Preparation of lead solutions: The range of concentrations of the prepared metal solutions varied between 50 and 225 mg/L and prepared by diluting the lead (II) stock solution which was obtained by dissolving 1.598 g of $Pb(NO_3)_2$ in 1 litre of deionized water.

Pretreatment of biosorbent: The effect of pretreatment on biosorption of Pb (II) by *A. bisporus* was investigated. The mushrooms were chopped to pieces and subjected to pretreatments. The untreated biomass was dried at 40°C and referred to as control. Fifty g of the live biomass was pretreated with alkali such as sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3). Pretreatment methods like boiling the biomass with 500mL of 0.5N NaOH at 100°C for 15 minutes, treating the biomass with 500mL of 0.1N $NaHCO_3$ for 30 minutes and treating the biomass with 500mL of 0.05 N Na_2CO_3 for 30 minutes were carried out. The biomass after each pretreatment was washed with generous amounts of deionised water until the pH of the wash solution was near neutral range, and then dried at 40°C for overnight. The dried biomass was ground with a mortar and pestle.

BATCH BIOSORPTION STUDIES

For obtaining the adsorption equilibrium data and comparison of the performance of the pretreated and control biomass, the following experimental conditions were used: pH 5.0, temperature 28°C, contact time 150 minutes, rotation speed 120 rpm, volume of metal solution in each flask of 100mL, biomass concentration 0.5 g/100mL and the variation in the initial metal concentration between 50 and 225 mg/L. All the sorption experiments were performed in duplicate. At the end of the experiment, the solutions were filtered through Whatman No. 1 filter paper and supernatant solution was analysed for Pb^{2+} concentration by Varian 240-atomic absorption spectroscopy. The amount of metallic ions biosorbed per g of the biomass (Q) was calculated using the equation (Junior et al. 2004):

$$Q = \left(\frac{C_i - C_f}{m}\right) \times V$$

Where C_i is the initial concentration of the metallic ion (mg/L), C_f is the final concentration of the metallic ion (mg/L), m is the mass of the biosorbent in the reaction mixture (g) and V is the volume of the reaction mixture (L).

RESULTS AND DISCUSSION

The biosorption equilibrium of lead (II) was modelled using adsorption type-isotherms. The Langmuir and Freundlich models were applied for untreated and pretreated biosrbents. Figs.1 and 2 show the Langmuir and Freundlich plots for Pb (II) biosorption by untreated, sodium hydroxide (NaOH) treated, sodium bicarbonate ($NaHCO_3$) treated and sodium carbonate (Na_2CO_3) treated biosorbent respectively. The Langmuir constants (q_{max} and b) and Freundlich constants (K_f and n) along with coefficients of determination (R^2) were calculated from the plots and the results are presented in Table 1. As indicated from the Table 1, the coefficients of determination (R^2) of both models were close to or greater than 0.9 indicating that both models adequately describe the experimental data of this study. R^2 values of Langmuir and Freundlich isotherms for sodium hydroxide (NaOH) treated biomass were found to be higher than untreated and all other pretreated biomass.

For both, the untreated and pretreated biomass, the Langmuir adsorption isotherm presented a better adjustment for Pb(II) data biosorption in the present studied condition. However, the Freundlich model also presented a good adjustment of the experimental data in case of untreated and sodium

Table 1: Linear regression data for Langmuir and Freundlich isotherms for Pb (II) biosorption by *Agaricus bisporus*.

S.No	Biomass type	Langmuir parameters			Freundlich parameters		
		q_{max} (mg/g)	b (L/mg)	R^2	n	K_f	R^2
1.	Untreated	28.818	0.0205	0.933	1.8681	1.7092	0.911
2.	Sodium hydroxide (NaOH) pretreated biomass	34.602	0.080	0.9883	2.352	5.321	0.972
3.	Sodium bicarbonate ($NaHCO_3$) pretreated biomass	23.094	0.0105	0.9058	1.9157	1.0801	0.8273
4.	Sodium carbonate(Na_2CO_3) pretreated biomass	21.929	0.0134	0.9046	1.9657	1.1857	0.8922

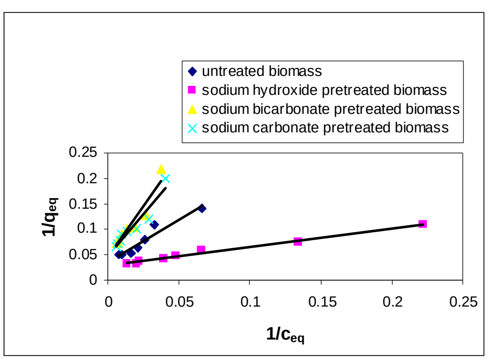

Fig.1: Langmuir adsorption isotherms of lead (II) ions on *Agaricus bisporus.*

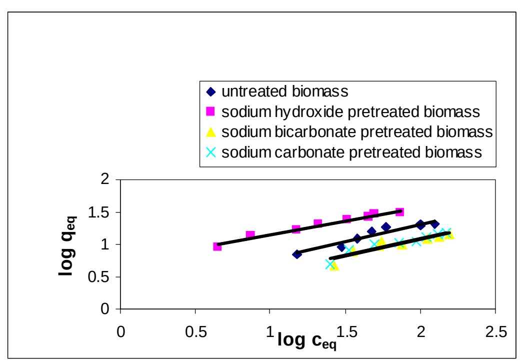

Fig.2: Freundlich adsorption isotherms of lead (II) ions on *Agaricus bisporus.*

hydroxide (NaOH) treated biomass. The maximum capacity q_{max} determined from the Langmuir isotherm defines the total capacity of the biosorbents for lead (II). The maximum sorption capacities for untreated, sodium hydroxide (NaOH) treated, sodium bicarbonate ($NaHCO_3$) treated and sodium carbonate (Na_2CO_3) treated biosorbent were found to be 28.8, 34.6, 23.0, 21.9 lead mg/g, respectively. Pretreatment of live biomass using sodium hydroxide (NaOH) increased the biosorption capacity of lead in comparison to other pretreated biosorbents. These results supported the findings of the authors Ilhan et al. (2004) who reported that sodium hydroxide significantly improved the biosorption of lead in case of *Penicilliun lanosa coeruleum*. Similar results were also reported by the authors (Ashkenazy et al. 1997) who showed that lead biosorption by *Saccharomyces uvarum* was more efficient after pretreatment with sodium hydroxide (NaOH). However, q_{max} (mg/g) value presented in Table 1 showed that pretreatment using sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) marginally reduced the biosorption capacity.

The applicability of both Langmuir and Freundlich isotherms to the lead (II) ions biosorption expresses that both monolayer adsorption and heterogenous energetic distribution of active sites on the surface of the adsorbent conditions exist under the experimental conditions employed. From all these results, it can be concluded that *Agaricus bisporus* pretreated with sodium hydroxide can be used as a potent biosorbent to remove lead (II) ions from industrial effluents.

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