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Biosorption of Cadmium(II) from Aqueous Solution by Fruiting Body of *Agaricus blazei* Murill

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Fungal organisms can remove heavy metals from aqueous solutions. The aim of this study was to investigate the removal of cadmium by the fruiting body of *Agaricus blazei* Murill (AbM). Batch experiments were carried out to investigate the effect of pH, biosorbent dose, contact time and initial cadmium concentration on biosorption efficiency. The desired pH, biosorbent dose and contact time for the removal of cadmium was found to be 6, 2 g/L and 180 min, respectively. The percent removal of cadmium was found to increase with the increase in biosorbent dosage and contact time and the adsorption capacity was found to increase with the increase in initial cadmium concentration. The fitness of the biosorption data for Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption models was investigated. It was found that biosorption of cadmium onto the biomass of *Agaricus blazei* Murill was better suitable to Langmuir than Freundlich and D-R adsorption model. For four kinetics models, the kinetics of cadmium adsorption was very well described by the pseudo-second-order kinetic model ($R^2 > 0.99$) and the liquid film diffusion process is the rate-limiting step occurring during biosorption of cadmium. The thermodynamic parameters showed the exothermic and spontaneous nature of the biosorption of cadmium onto *Agaricus blazei* Murill.

Keywords: Adsorption, Sorption kinetics, Sorption isotherms, Thermodynamic parameters, Cadmium, *Agaricus blazei* Murill.

INTRODUCTION

Cadmium, like other heavy metals, is introduced into natural waters by industrial and domestic wastewater discharges. It is non-biodegradable and tends to accumulate in living organisms, causing significant threats to both the environment and public health, such as poisonous rice with high concentration of cadmium in Taiwan Province of China[1,2]. Many laws and rules are set up to restrict this pollutant releasing into environment to pollute the air, soil and water in China.

Biosorption, which encompasses heavy metal uptake by live or dead microorganisms, is an emerging technology for heavy metal pollution control[3]. A variety of biomaterials and microorganisms have been explored by researchers for heavy metal biosorption and bioaccumulation including fungi[4], yeast[5], algae[6] and mosses[7] but mushrooms, which belong to the category of macrofungi, are yet to be thoroughly investigated[8].

Mushrooms have unquestionable tendency to accumulate heavy metals, such as mercury, lead, cadmium, selenium and, to a lesser extent, cobalt, nickel and chromium[9]. As shown in our previous research[10], the cadmium content in washed fresh *Agaricus blazei* Murill was 10.27 mg/kg DW, which was the common cadmium levels for *Agaricus blazei* Murill. Fruit bodies of macrofungi (mushrooms) are also considered ideal for the purpose of evaluation as biosorbents, because it has been demonstrated that many fungal species exhibit high biosorptive potentials[11,12]. Some genera can specifically accumulate certain metals: lawn-decomposing species, mainly Agaricales and especially the genus Agaricus, have a strong affinity for copper, silver and cadmium[8,9].

The objectives of this study were to evaluate the uptake capability of cadmium from aqueous solutions by the fruiting body of *Agaricus blazei* Murill, to examine the applicability of known kinetic, adsorption isotherm models, thermodynamic parameters and the physicochemical properties that might influence the adsorption.

EXPERIMENTAL

Biosorbent: Fresh *Agaricus blazei* Murill were provided from the Mu-Shui-Hua fresh market in Kunming during May 2012. Fruiting bodies were cleaned from soil and substrate with a stainless knife and washed with tap water and then deionized water for three times and dried at 60 °C until reaching a constant weight. The sample was then powdered. Particles of size smaller than 250 μm were obtained by passing the milled materials through a plastic sieve for the experiment.

Cadmium solutions and analytical methods: Stock solution of cadmium (2 g/L) was prepared by dissolving 4.0633 g of $CdCl_2 \cdot 2.5H_2O$ in 1 L deionized water. The stock solution was used to prepare dilute solutions of different working concentrations. All reagents were ultrapure or analytical grade.

The concentration of cadmium sorbed on the biomass was calculated by the difference of the initial concentration of cadmium added and the final concentration of cadmium in the solution. The concentration of cadmium in the biosorption medium was determined using atomic fluorescence spectroscopy.

Batch biosorption experiments: Some modification was made on the basis of previous study[13]. The batch biosorption experiments of *Agaricus blazei* Murill were carried out as a function of pH (from pH 2 to 7, which was adjusted with 0.1 N HCl or 0.1 N NaOH at the beginning of the experiment), biosorbent dosage (from 0.5 to 5 g/L), contact time (from 10 to 360 min) of the biosorbent in solution and initial concentrations of cadmium (from 10 to 100 mg/L). Controls were performed without the biomass addition. For each treatment with the biosorbent, 0.0125 g biomass was added into a 50 mL conical flask containing 25 mL of a solution. The flasks were shaken at 150 rpm and 25 °C for the entire reaction time. The metal solutions were filtered after the desired contact time. Aqueous cadmium concentrations before and after biosorption were measured using atomic fluorescence spectroscopy. All experiments were carried out in triplicate throughout the experiments. Adsorption efficiency was expressed as a percentage of adsorbed metal compared to initial metal concentration, whereas adsorption capacity was expressed as amount of cadmium adsorbed per mass unit of *Agaricus blazei* Murill using the following equations, respectively:

$$\text{Cadmium removal efficiency } (\%) = \frac{(C_i - C)}{C_i} \times 100 \quad (1)$$

$$Q(\text{mg/g}) = \frac{(C_i - C)V}{m} \quad (2)$$

where C_i and C are the initial and residual concentrations of cadmium in mg/L, Q (mg/g) is the adsorption capacity, V (L) is the volume of cadmium solution and m (g) is the adsorbent mass.

Adsorption isotherm models: Adsorption isotherms are important to describe the adsorption mechanism of a solute on adsorbent surface thus aid in optimizing the design of a specific adsorption process. In the present study, the equilibrium data obtained for cadmium removal using *Agaricus blazei* Murill was tested with three isotherm models available in the literature to reveal the best fitting isotherm. Adopted isotherm models were Langmuir, Freundlich and D-R isotherm equations. Isotherm coefficients and correlation coefficients (R^2) were computed from linearized equations of these isotherms in Microsoft Excel 2003.

Langmuir isotherm is applicable for monomolecular layer adsorption. This isotherm is described as a homogeneous one assuming that all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site. The Langmuir isotherm is used to obtain a maximum adsorption capacity produced from the complete monolayer coverage of adsorbent surface. The linear form can be represented as given by eqn. 3[14].

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (3)$$

where K_L (L/mg) is the biosorption equilibrium constant related to the apparent energy of adsorption, Q_m (mg/g) is the theoretical monolayer capacity and Q_e (mg/g) is the amount adsorbed on unit mass of the adsorbent when the equilibrium concentration is C_e in mg/L.

The plot of C_e/Q_e *vs.* C_e should yield a straight line if Langmuir isotherm is obeyed by the adsorption equilibrium. Q_m and K_L values will be calculated from the slope and intercept of the graphed line, respectively. A further analysis of the Langmuir equation can be made using a dimensionless equilibrium parameter, the separation factor R_L as given by eqn. 4:

$$R_L = \frac{1}{1 + K_L C} \quad (4)$$

For a favorable adsorption, the value of R_L should lie between 0 and 1; $R_L > 1$ represents an unfavorable adsorption, $R_L = 1$ represents linear adsorption, whereas $R_L = 0$ translates into irreversible adsorption[15].

Freundlich isotherm describes that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in the solution is not constant at different concentrations. For many systems, the heat of adsorption decreases in magnitude with increasing the extent of adsorption. This has been well taken care of by the Freundlich isotherm, previously considered to be an empirical isotherm. The linear form can be represented as given by eqn. 5[16]. Where K_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) and n are the Freundlich equilibrium constants related to adsorption capacity and biosorption intensity which can be determined from the plot of $\ln Q_e$ *vs.* $\ln C_e$.

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (5)$$

Values of n in the range from 1 to 10 indicate favorable biosorption[17]; the smaller the value of 1/n, the more heterogeneous[18]. Freundlich isotherm model is widely used but does not provide the information on the monolayer adsorption capacity.

Dubinin and Radushkevich have proposed another isotherm which can be used to analyze the equilibrium data. It is not based on the assumption of homogeneous surface or constant adsorption potential, but it is applied to estimate the mean free energy of adsorption (E). The linear form of D-R equation is given by eqn. 6[19].

$$\ln Q_e = \ln Q_m - K_D \varepsilon^2 \quad (6)$$

where Q_m (mg/g) is the maximum adsorption capacity, K_D (mol^2 kJ^{-2}) is the activity coefficient which relates to the adsorption energy and ε (J/mol) calculated as eqn. 7 is the polanyi potential. The mean free energy of biosorption, E (kJ/mol), is calculated as eqn. 8:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

$$E = \frac{1}{\sqrt{-2K_D}} \quad (8)$$

If the value of E is between 1 and 16 kJ/mol, then physical adsorption prevails and if the value is more than 16 kJ/mol, then chemisorption prevails[15].

Adsorption kinetic models: The process of pollutant removal from an aqueous phase by any adsorbent can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process. The study of adsorption kinetics is desirable as it provides information about the dynamics of the adsorption process in terms of the order and the rate constant which are of significance in designing and modeling an efficient adsorption operation. Various adsorption kinetic models have been used in the literature to describe the adsorption of metal ions[15,20-21].

Four kinetic models, namely, the pseudo first-order model, the pseudo second-order model, the intra-particle diffusion model and the liquid film diffusion model, were used to characterize the biosorption kinetics of cadmium by *Agaricus blazei* Murill.

The integration form of the pseudo first-order model is as follows[22]:

$$\ln (Q_e - Q_t) = \ln Q_e - K_1 t \tag{9}$$

where K_1 (min^{-1}) is the rate constant of the pseudo-first-order biosorption, Q_e (mg/g) is the equilibrium biosorption capacity and Q_t (mg/g) is the concentration of metal ion on the surface of the biosorbent at time *t* (min). The rate constant and the equilibrium biosorption capacity can be determined from the plot of ln (Q_e-Q_t) *vs.* *t*.

The integration form of the pseudo second-order model is eqn. 10[22,23]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{10}$$

where K_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo second-order biosorption. The values of K_2 and Q_e can be determined from the plot of t/Q_t *vs.* t.

The adsorbate are most likely transported from the bulk of the solution into the solid phase through an intra-particle diffusion process, which often is the rate-limiting step in many adsorption processes[24]. The intra-particle diffusion model is given in eqn. 11[25]:

$$Q_t = K_{id} t^{0.5} \tag{11}$$

where K_{id} is the rate constant of the intra-particle diffusion estimated from plotting Q_t *vs.* $t^{0.5}$.

The significant feature of this expression is that the linear plots of Q_t *vs.* $t^{0.5}$ should pass through the origin (zero intercept). Thus the intra-particle diffusion model can be easily tested through the above plots provided they have zero intercept, which indicates a controlling influence for the diffusion process on the kinetics[26].

When the flow of the adsorbate through the liquid film surrounding the adsorbent particles is the slowest process determining kinetics of the rate processes, the liquid film diffusion model could be the appropriate way to characterize the kinetics[26]. The liquid film diffusion model is given in eqn. 12[27].

$$\ln (1-F) = -K_{fd} t \tag{12}$$

where F is the fractional attainment of equilibrium (Q_t/Q_e) and k_{fd} (min^{-1}) is the film diffusion rate coefficient. A linear plot of -ln (1-F) *vs.* t with zero intercept suggests that the kinetics of the adsorption process is controlled by diffusion through the liquid film[26].

In order to determine the thermodynamic parameters, experiments were carried out at different temperature 293-303 K for cadmium biosorption. The free energy change (ΔG°) of the sorption reaction is given as eqn. 13[28,29].

$$\Delta G^\circ = -RT \ln K \tag{13}$$

where T is the temperature (K), R is the gas constant (8.314 J mol^{-1} K^{-1}), K (Q_e/C_e) is the distribution coefficient.

The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{14}$$

The values of enthalpy (ΔH°) and entropy change (ΔS°) can be obtained from the slope of the plot of ΔG° *vs.* T.

RESULTS AND DISCUSSION

It was found from blank and control studies that the adsorption of cadmium onto the walls of the conical flasks was negligible and the mushrooms did not leach any metal into the aqueous solutions.

Factors affecting efficiency of metal adsorption

Effect of pH: Hydrogen ion concentration in the adsorption is considered as one of the most important parameters that influence the adsorption behaviour of metal ions in aqueous solutions[30]. It affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction[8,31]. To avoid the precipitation in alkaline condition, the biosorption of cadmium was carried out in acid condition in this study.

As shown in Fig. 1, only little cadmium adsorption was observed at strong acid condition (pH = 2). With the increase of pH in the solution, higher removal of cadmium was occurred. This pH dependency of biosorption efficiency could be explained in terms of pH_{zpc} (zero point of charge) of the adsorbent, at which the adsorbent is neutral[21]. When the pH is below pH_{zpc}, protons occupy most of the biosorption sites on the biosorbent surface and less cadmium ions could be sorbed because of electric repulsion with protons on biosorbent. With the pH values increased (from 2 to 6), biosorbent surfaces

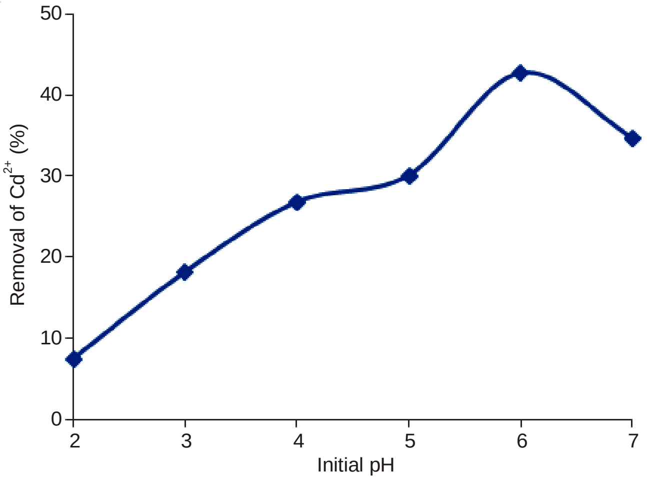

Fig. 1. Effect of initial pH on Cd^{2+} biosorption capacity of *Agaricus blazei* Murill

contained more negatively charged and the biosorption of metal ions (positive charge) increased and reached equilibrium at pH_{zpc} (pH = 6). Decrease in biosorption at higher pH_{zpc} (pH > 6) is due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, as a consequence, the retention would decrease again.

Effect of dosage: The percent removal obtained for cadmium with the initial pH 6 at different adsorbent doses, as well as metals adsorbed per adsorbent unit biomass (biosorption capacity) is shown in Fig. 2.

It is apparent that the removal (%) of cadmium ions increases with increasing adsorbent dosage (from 0.5 to 2 g/L) due to the greater availability of surface area and thus active sites. However, once adsorbent dosage exceed 2 g/L, the contribution of additional adsorbent will be insignificant. About 66.7 % of cadmium removal was achieved from a 20 mg/L cadmium solution at pH 6 in the presence of 2 g/L adsorbent. On the other hand, the adsorption capacity, the amount adsorbed per unit mass of adsorbent, decreases mainly due to unsaturation of adsorption sites through the adsorption reaction[32]. Another reason may be due to the particle interaction, such as aggregation, resulting from high sorbent concentration[33,34]. Such aggregation would lead to decreases in total surface area of the sorbent and an increase in diffusion path length[26,32,35].

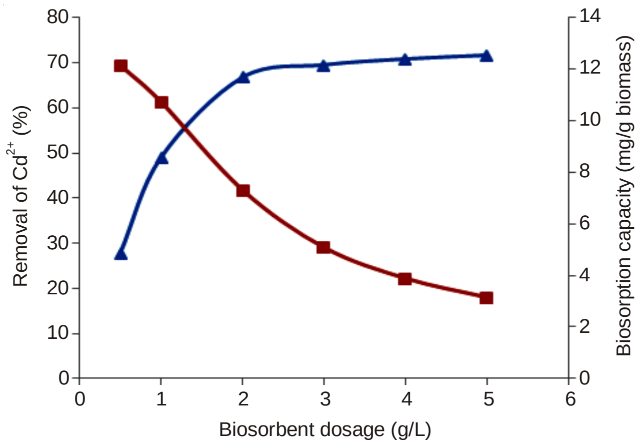

Fig. 2. Effect of biosorbent dosage on Cd^{2+} biosorption capacity of *Agaricus blazei* Murill

Effect of contact time: The effect of contact time on cadmium adsorption on *Agaricus blazei* Murill is investigated to study the rate of cadmium removal (Fig. 3). The plot reveals that the rate of the removal percentage of cadmium is higher at the beginning. It is evident from Fig. 3 that time is an important parameter for the adsorption of cadmium on *Agaricus blazei* Murill. The rate of metal removal is higher in the beginning due to the larger surface area of the *Agaricus blazei* Murill being available for metal adsorption[21,28]. As the surface available active sites of adsorbent gets exhausted and then the uptake rate is controlled by the rate at which the metal is transported from the exterior to the interior sites of the adsorbent particles.

The rate of adsorption decreases in later stages probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent. Cadmium removal attained equilibrium after approximately 180 min stirring. It does not seem to be much benefit from a stirring time longer than 180 min. Therefore, 180 min was chosen as contact time for further experiments in order to ensure the equilibrium of adsorption.

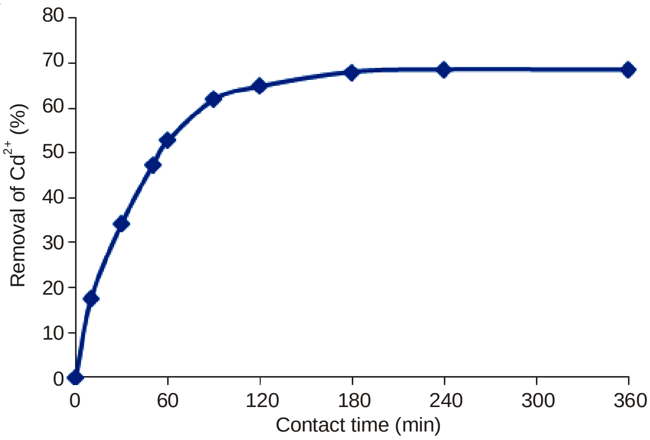

Fig. 3. Effect of contact time on Cd^{2+} biosorption capacity of *Agaricus blazei* Murill

Effect of initial cadmium concentration: The initial concentration of the cadmium in the solution remarkably influenced the equilibrium uptake of cadmium. In Fig. 4, it was noted that initial concentration increased the sorption of cadmium as is generally expected due to equilibrium process. The adsorption capacity was found to increase (from 3.81 to 14.39 mg/g) with the increase in initial cadmium concentrations (from 10 to 100 mg/L). This increase in uptake capacity of *Agaricus blazei* Murill with the increase in initial metal concentrations is due to higher availability of metal ions for the sorption. Moreover, higher initial concentration provides increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phase resulting in higher probability of collision between metal ions and sorbents[8,36].

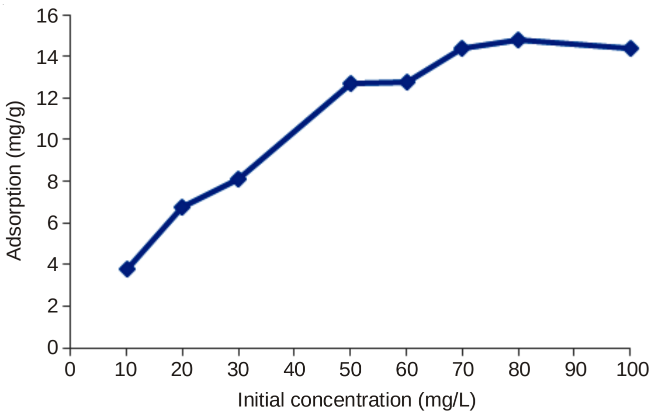

Fig. 4. Effect of initial concentration of Cd^{2+} on Cd^{2+} biosorption capacity of *Agaricus blazei* Murill

Biosorption isotherm models: Adsorption isotherm models are usually used to fit the adsorption data in order to obtain a linear regression data to predict the maximum adsorption capacity of the adsorbent. The adsorption isotherm for the metal ions onto *Agaricus blazei* Murill were shown in Figs. 5 to 7.

Langmuir isotherm: The plots of C_e/Q_e *vs.* C_e were found to be linear at different temperatures (20, 25 and 30 °C), which indicates the applicability of the Langmuir model (Fig. 5). The parameters Q_m, K_L and correlation coefficients (R^2) have been calculated and the results are represented in Table-1.

The statistical significance of the correlation coefficients was the criteria by which the fitting of the data to Langmuir isotherm were tested. It demonstrates monolayer coverage of adsorbate at the outer surface of the adsorbent (in all case $R^2 > 0.98$). The dimensionless parameter, R_L is found in the range 0.510-0.584 ($0 < R_L < 1$) which confirms favorable cadmium adsorption process using *Agaricus blazei* Murill.

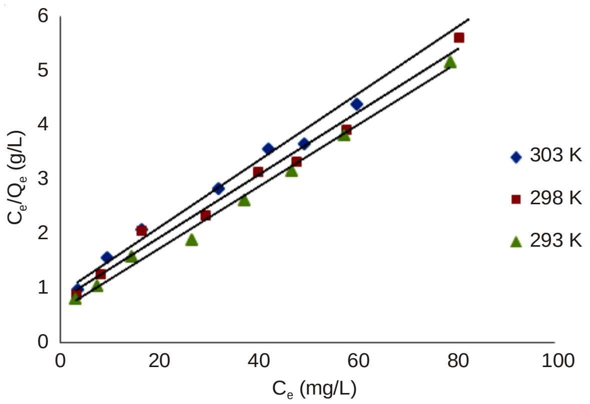

Fig. 5. Linear fitting of the Langmuir isotherm for Cd^{2+} onto *Agaricus blazei* Murill at different temperature

An important parameter, the maximum uptake (Q_m) could help us to judge the cost of biosorbent by Langmuir model simulation. From the experimental data, the relationship between Q_m and temperature was negatively correlated, the value of Q_m was found to decrease with the increase of temperature. Maximum uptake (Q_m) of cadmium was 17.73 mg/g at 20 °C, which was much greater than some other biosorbents described in Table-2. The large value of Q_m indicated that the biosorbent in this study was of vast potential to remove cadmium from aqueous solution.

Freundlich isotherm: The plots of log Q_e *vs.* log C_e, at different temperatures were found to be linear indicating the applicability of the Freundlich model (Fig. 6). The intercept of the line is roughly an indicator of the adsorption capacity and the slope is an indication of adsorption intensity[28].

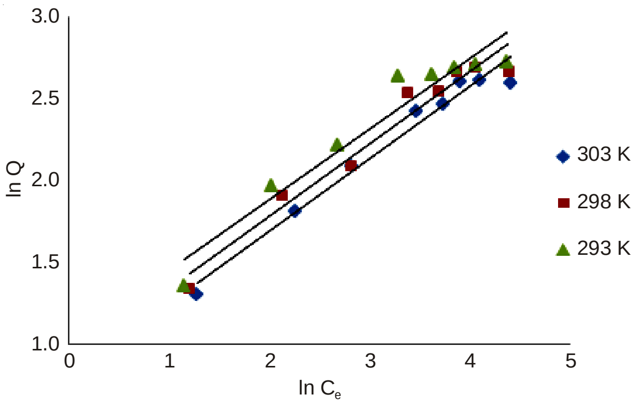

Fig. 6. Linear fitting of the Freundlich isotherm for Cd^{2+} onto *Agaricus blazei* Murill at different temperature

The Freundlich parameters and the results are represented in Table-1. The value K_f of *Agaricus blazei* Murill for cadmium at 20, 25 and 30 °C follows the order 2.788, 2.454 and 2.261. The constants, n, are ranged from 2.264 to 2.316; all of them are between 1 to 10, which indicates that the adsorption process of *Agaricus blazei* Murill for cadmium is favorable biosorption. It is found that the coefficients of determination obtained from the Freundlich isotherm model for *Agaricus blazei* Murill are lower than Langmuir isotherm model. The obtained result indicates that the equilibrium data is fitted better with the Langmuir isotherm model than with the Freundlich isotherm model.

D-R isotherm: The plot between ln Q_e and ε^2 at three temperatures of 20, 25 and 30 °C were shown in Fig. 7. The constants (Q_m and K_D) obtained for D-R isotherm model and the value of coefficient (R^2) of determination are shown in Table-1.

TABLE-1
LANGMUIR, FREUNDLICH, DUBININ-RADUSHKEVICH ISOTHERM PARAMETERS FOR Cd^{2+} WITH *Agaricus blazei* Murill

T (K)	Langmuir isotherm			Freundlich isotherm			D-R isotherm		
	Q_m (mg/g)	K_L(L/mg)	R^2	K_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	n	R^2	Q_m (mg/g)	K_D (mol^2 kJ^{-2})	R^2
293	17.73	0.096	0.9936	2.788	2.316	0.9313	13.30	-2.710×10^{-3}	0.8373
298	17.39	0.075	0.9845	2.454	2.264	0.9573	12.25	-2.850×10^{-3}	0.7814
303	16.26	0.071	0.9895	2.261	2.274	0.9712	11.38	-3.115×10^{-3}	0.7721

TABLE-2
CADMIUM ADSORPTION ON *Agaricus blazei* Murill IN COMPARISON WITH OTHER ADSORBENTS

Biosorbent	pH	Metal concentration (mg/L)	Cadmium adsorption capacity (mg/g)	References
Pycnoporus sanguineus	6	50-300	3.42	37
Aspergillus niger	-	10	3.74	38
Saccharomyces cerevisiae	7.2	8-30	8.17	39
Mucor roxii	5	-	8.36	40
Silver ear	-	10-100	10.73	41
Papaya wood	5	5-500	17.22	42
Calocybe indica	6	10-100	24.09	8
Agaricus blazei Murill	6	10-100	17.73	Present study

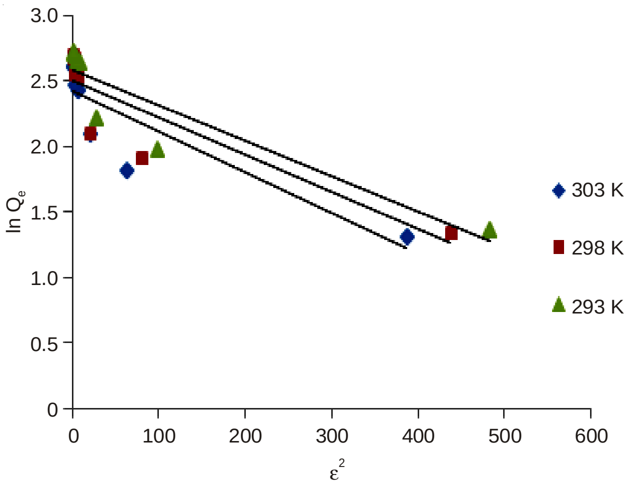

Fig. 7. Linear fitting of the D-R isotherm for Cd^{2+} onto *Agaricus blazei* Murill at different temperature

The value of coefficient of determination indicates that the D-R isotherm model does not fit well with the equilibrium experimental data as compared with the other models considered. Q_m, the maximum adsorption capacity, obtained using D-R isotherm model is 13.30 mg/g for the adsorption of cadmium by *Agaricus blazei* Murill which is less than the value of Q_m obtained using the Langmuir isotherm model (17.73 mg/g). The mean free energy of adsorption, E, is obtained as 13.58, 13.24 and 12.67 kJ/mol at 20, 25 and 30 °C, respectively. The typical E values for ion-exchange mechanisms are ranged between 1 and 16 kJ/mol, indicating that the adsorption of cadmium using *Agaricus blazei* Murill is physical adsorption[16].

Adsorption kinetics: In order to understand the kinetics of removal of cadmium using *Agaricus blazei* Murill as an adsorbent, pseudo first-order kinetics, pseudo second-order kinetics, intra-particle diffusion and liquid film diffusion models are tested with the experimental data.

Pseudo first-order kinetics: The plot of ln (Q_e-Q_t) *vs.* t is shown in Fig. 8 which represents the pseudo first-order kinetic for the removal of cadmium using *Agaricus blazei* Murill. The values of first-order rate constants, k_1 and Q_e for 20 mg/L of initial cadmium concentration and 2 g/L of adsorbent doses, are calculated and listed in Table-3. The coefficient of determination (R^2) is 0.81 which indicates that the pseudo first-order kinetic model not fit well with the experimental data of the removal of cadmium using *Agaricus blazei* Murill. The true value of Q_e obtained from experiments for 20 mg/L of initial cadmium concentrations is 6.42 mg/g which is not in agreement as expected (7.50 mg/g) with the pseudo first-order model predicted value as given in Table-3.

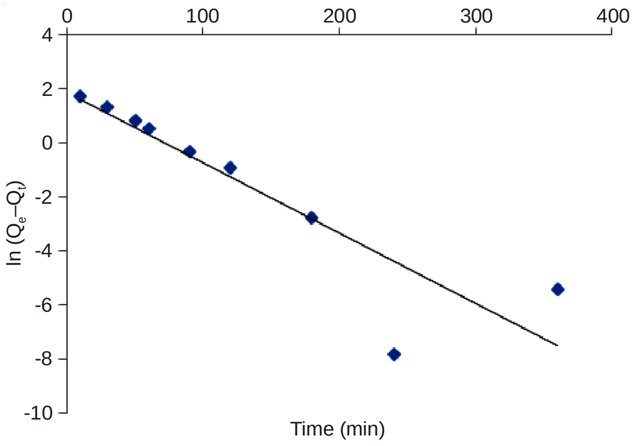

Fig. 8. Pseudo first-order kinetic model for the adsorption of Cd^{2+} onto *Agaricus blazei* Murill

Pseudo second-order kinetics: The plot of ln (Q_e-Q_t) *vs.* t is shown in Fig. 9 which represents the pseudo second-order kinetic for the removal of cadmium using *Agaricus blazei* Murill. From this plot the second-order rate constant, k_2, the estimated equilibrium capacity, Q_e and the correlation coefficient (R^2) were calculated for 20 mg/L of initial cadmium concentration as summarized in Table-3. The calculated Q_e value show a good agreement with the experimental value with R^2 values exceeding 0.99. This indicates that the pseudo second-order kinetic model describes well cadmium removal using the *Agaricus blazei* Murill.

Intra-particle diffusion: The possibility of intra-particle transport in the current study was explored by using the Weber-Morris equation (eqn. 10). The plot of Q_t *vs.* $t^{1/2}$ is shown in Fig. 10 for 20 mg/L of initial cadmium concentration. As shown in Table-4, the intra-particle diffusion rate constant (k_{id}) and correlation coefficient (R^2) is 0.335 mg g^{-1} $t^{-0.5}$ and 0.75, respectively. The non-zero intercepts of the plot is a clear indication that although intra-particle diffusion is slow, it is not the slowest of the rate processes that determines the overall order, thus it cannot be stated that the intra-particle diffusion process is the rate-limiting step occurring during sorption of cadmium onto *Agaricus blazei* Murill.

Liquid film diffusion: Liquid film diffusion as a model for adsorption kinetics has not received much attention. Some

TABLE-3
PSEUDO FIRST-ORDER AND PSEUDO SECOND-ORDER KINETIC MODEL RATE CONSTANT FOR THE ADSORPTION OF Cd^{2+} ONTO *Agaricus blazei* Murill

Adsorbent	Pseudo first-order kinetic			Pseudo second-order kinetic		
	Q_e (mg/g)	K_1 (min^{-1})	R^2	Q_e (mg/g)	K_2 (g mg^{-1} min^{-1})	R^2
Agaricus blazei Murill	6.42	0.0596	0.8099	8.24	0.0045	0.9964

TABLE-4
INTRA-PARTICLE AND LIQUID FILM DIFFUSION MODEL RATE CONSTANT FOR THE ADSORPTION OF Cd^{2+} ONTO *Agaricus blazei* Murill

Adsorbent	Intra-particle diffusion		Liquid film diffusion	
	K_{id} (mg g^{-1} $t^{-0.5}$)	R^2	K_{fd} (min^{-1})	R^2
Agaricus blazei Murill	0.3348	0.7500	0.0265	0.9952

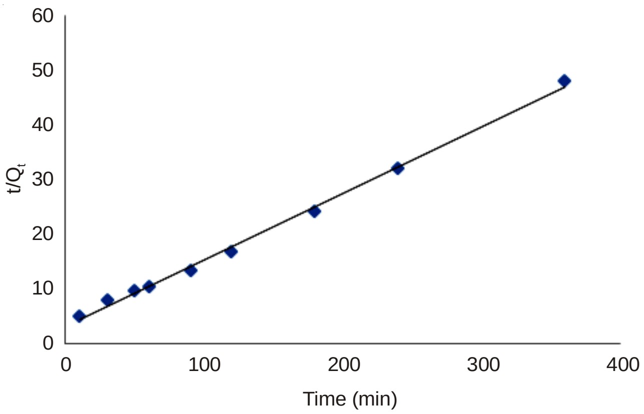

Fig. 9. Pseudo second-order kinetic model for the adsorption of Cd^{2+} onto *Agaricus blazei* Murill

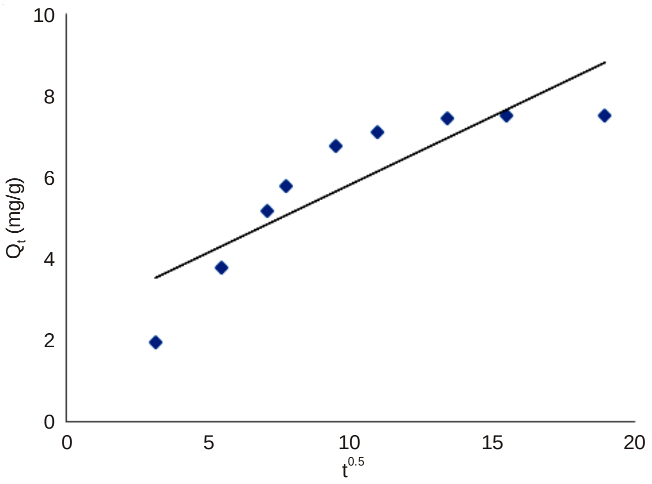

Fig. 10. Intra-particle diffusion model for the adsorption of Cd^{2+} onto *Agaricus blazei* Murill

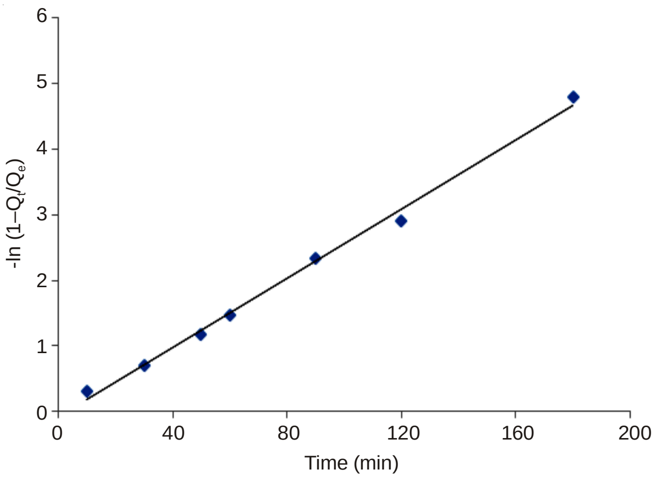

Fig. 11. Liquid film diffusion model for the adsorption of Cd^{2+} onto *Agaricus blazei* Murill

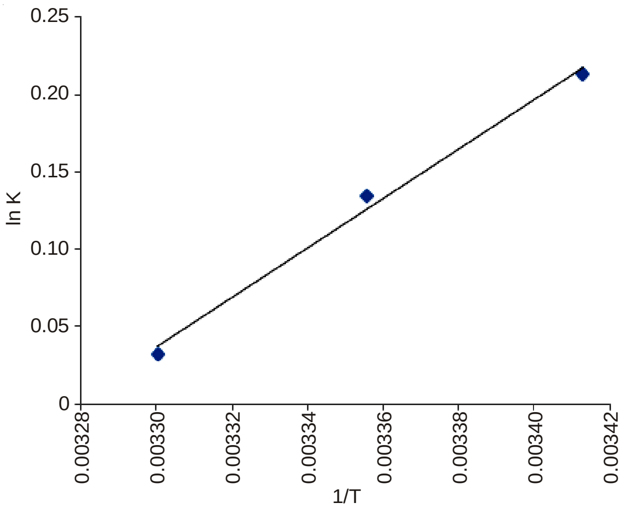

Fig.12. Plot of ln K *vs.* 1/T for the estimation of thermodynamic parameters for adsorption of Cd^{2+} onto *Agaricus blazei* Murill

TABLE-5
THERMODYNAMIC PARAMETERS OF
THE Cd^{2+} ONTO *Agaricus blazei* Murill

Temperature (K)	ΔG° (kJ/mol)	ΔS° (kJ/mol)	ΔH° (kJ/mol)
293	-0.520	-0.044	-13.341
298	-0.333	-0.044	-13.373
303	-0.082	-0.044	-13.340

reports[27,43-46] in the literature appearing during the last few years are used to discuss adsorption kinetics. Liquid film diffusion model was applied to the kinetics of adsorption of cadmium on *Agaricus blazei* Murill. The plot was linear (Fig. 11) and the line was very close to passing through origin. Thus, liquid film diffusion could not be ruled out in the adsorption processes and the kinetics is likely to be diffusion-limited. As shown in Table-4, the liquid film diffusion rate constant (K_{fd}) is low as compared with intra-particle diffusion rate constant (K_{id}), which also indicated that the liquid film diffusion process was the rate-limiting step occurring during sorption of cadmium onto *Agaricus blazei* Murill.

Thermodynamic parameters: The Gibbs free energy changes (ΔG°) for the biosorption of cadmium onto *Agaricus blazei* Murill were calculated using eqn. 12. According to eqn. 13, the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of ln K *vs.* 1/T yields, respectively (Fig. 12).

The values of ΔG°, ΔH° and ΔS° for the biosorption of cadmium on the *Agaricus blazei* Murill are given in Table-5. Negative values of ΔH° suggest the exothermic nature of the adsorption and the negative values of ΔG° indicate the spontaneous nature of the adsorption process. However, the negative value of ΔG° increased with an increase in temperature, indicating that the spontaneous nature of the biosorption and highly favorable at low temperature[28,32]. The negative value of ΔS° means a decrease in the randomness at the solid/solution interface during the biosorption process.

Conclusion

In this study, the use of *Agaricus blazei* Murill as a biosorbent was tested for removing of cadmium ions from aqueous solution. The pH, biosorbent dosage, contact time and initial metal ion concentration, were found to have an effect on the biosorption efficiency of cadmium.

The desired pH value for biosorption was found to be 6.0 and the adsorption capacity was affected by the change of pH value. Higher biosorbent dosages resulted in higher removal (%) of cadmium due to abundant availability of sorption sites and exchanging ions, but the adsorption capacity, the amount adsorbed per unit mass of adsorbent, decreased mainly due to unsaturation of adsorption sites through the adsorption reaction. The desired biosorbent dosage for cadmium sorption was 2 g/L. Cadmium removal attained equilibrium after approximately 180 min. The rate of cadmium removal is higher in the beginning and then decrease, due to the uptake rate is controlled by the rate at which the metal is transported from the exterior to the interior sites of the adsorbent particles. An increase in cadmium concentration from 10 to 100 mg/L resulted in a decrease in the percent cadmium removal from 69.6 to 26.3 % and an increase in adsorption capacity from 3.81 to 14.39 mg/g at pH of 6 and temperature of 25 °C in the presence of 2 g/L *Agaricus blazei* Murill.

The equilibrium adsorption data were tested with three isotherm models and were best fitted with the Langmuir isotherm ($R^2 > 0.98$). The kinetics of cadmium adsorption was very well described by the pseudo second-order kinetic model with R^2 values exceeding 0.99. Liquid film diffusion process was the rate-limiting step occurring during sorption of cadmium onto *Agaricus blazei* Murill compare with intra-particle diffusion. The calculated thermodynamic parameters showed the exothermic and spontaneous nature of the biosorption of cadmium onto *Agaricus blazei* Murill. Thus, it may be concluded that *Agaricus blazei* Murill exhibited the potential for application in treatment of aqueous solutions containing cadmium.

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