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Biosorption of Cd^{2+} from Aqueous Solutions by Tolerant Fungus *Humicola* sp.

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ABSTRACT

Cadmiun contaminated water is a big problem in the environment. This research was carried out to estimate the removal of Cd^{2+} from an aqueous solution by biomass of *Humicola* sp.. Fungus was isolated from Mae Tao creek sediment receiving long-term contact with Cd contaminated water effluents from mine in Tak Province, Thailand. The removal ability of Cd^{2+} in *Humicola* sp. of viable and non-viable biomass as increasing Cd concentration were in the same pattern, but viable biomass showed better Cd^{2+} removal ability than non-viable biomass. Maximum Cd^{2+} biosorption of viable biomass took place at initial solution at pH 6 after 60 minutes, while the maximum adsorption of Cd^{2+} in non-viable biomass was obtained highest at pH 5 after 40 minutes. The Cd^{2+} was well adsorbed by both biomass at room temperature (30°C). Desorption experiments indicate that the desorption efficiency with 0.1 M HNO_3 solution reaches 78.95% and 86.77% in viable and non-viable biomass, respectively. The overall results show the metal adsorption properties of *Humicola* sp. can be applied in Cd^{2+} removal from industrial effluents.

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INTRODUCTION

Cadmium (Cd) is extensively used in different industrial products such as various alloys, protective plating, stabilizer for plastic and other. Furthermore, the problem of Cd contamination occurs when aqueous effluents from many industrial processes that containing dissolved heavy metals without treatment are disposed. High concentration of cadmium may have an adverse impact on the environment and can be accumulated and transferred into the sequence of food chains. The bioremoval treatment process of metals has received increasing attention in term of "Biosorption" because of its many advantages such as the ability to treat large volumes of wastewater, rapid kinetics and high selectivity in the removal and recovery of specific heavy metals. Several biomass types have been studied as potential adsorbents for heavy metals, including fungi [1], bacteria [2], algae [3] and yeast [4]. Some literatures report that many kinds of filamentous fungi are capable of removing Cd during sewage treatment, such as *Aspergillus fumigatus* [5], *Penicillium chrysogenum* [6], *Eupenicillium sp.*[7], *Rhizopus cohnii* [8].

The Mae Tao creek is known as the most worrisome site of Cadmium contamination in Thailand. Cadmium has contaminated the area because it is extracted during the production of zinc. There are many mining activities that may influence the Cd contamination throughout the environment, for instance, drilling, material transfer and removal of mine tailings and drainage. Krissanakriangkrai *et al*. [9] found that the high levels of Cd in the sediment from the Mae Tao creek was 31.67±0.61 mg kg^{-1} soil. Cadmium contaminations lead to changing of microbial community which can be used as an indicator for Cadmium contamination in sediment. In previews study on cadmium tolerance fungi isolated from polluted sites in the Mae Tao creek showed that there were 5 aquatic fungal resistant including *Humicola* sp., *Penicillium* sp., *Aspergillus* sp. 1, *Aspergillus* sp. 2 and *Alternaria* sp. Altogether, *Humicola* sp. could grow in the presence of high concentration Cd^{2+} and considered as high Cd resistance fungi [10].

There is no information on the use *Humicola* sp. for the biosorption of heavy metals. In this study was to investigate the removal of Cd^{2+} from aqueous solution by mycelium biomass of *Humicola* sp. from Mae Tao creek in Mae Sot District, Tak Province, Thailand.

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MATERIALS AND METHODS

Microorganism:

Humicola sp. was isolated from Mae Tao creek in Mae Sot District, Tak Province, Thailand. Fungal spores were obtained from a 5 days old culture grown on Potato Dextrose Agar (PDA) at 30±2℃. The spores were collected in 0.01 % tween-80 solution.

Biomass Preparation:

Humicola sp. biomass were cultivated in Potato Dextrose Broth (PDB), using the shake flask method. Spore suspension ($1x10^8$ spores) were cultivated in 250 ml erlenmeyer flask with 50 ml PDB at 30±1 ℃ with shaker at a speed of 150 rpm for 3 days. The culture grew as discrete pellicles. Harvesting of the biomass was done by filtering and washed biomass is hereafter called viable biomass, while the non-viable biomass was autoclaved at 121^{o}C for 20 minutes and then harvested by filtering through a membrane filter and dried at 80 °C in an oven for 12 hours. This was then ground, using a blender and sieved to pass through a 100 mesh sieve to obtain uniform particle size. Pellet viable biomass and non-viable biomass were used in the Cd^{2+} uptake studies.

Batch Isotherm Experiments:

Biomass were put in contact with cadmium nitrate solution in concentrations that varies from 0 to 150 mg 1^{-1}. Cd adsorption in aqueous solution before and after contact with the biomass was calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{W}$$

Where: q is the metal uptake (mg Cd g^{-1} dry wt.), *Ci* and *Cf* are the initial and final Cd^{2+} concentrations in the supernatant, respectively (mg l^{-1}), *V* is the volume of the Cd concentration (ml), and *M* is the dry weight of the biomass added (g). This definition of the uptake permits the direct calculation of the amount of metal taken up from the solution after contacting with the sorbent. The resulting values of *Cf* / *q* were plotted against *Ci* to obtain a Langmuir plot typical of the sorption behavior [11].

Effect of temperature, pH and contact time on Cd removal by fungus:

In order to evaluate the effect of temperature, pH and contact time on the Cd^{2+} uptake, the experiment was conducted in the same manner, except the temperature of Cadmium solution was changed to 30, 40, 50, 60 and 70 ^{o}C. The pH of the solution was prepared to be in the range between 3.0 and 9.0 before mixing biomass. The pH was adjusted to the required value with 0.1M NaOH or 0.1M HNO_3. The period of contact time was studied up to 180 minutes by using procedure described earlier, samples were collected every 30 minutes (30, 60, 90, 120, and 180 minutes, respectively)

Cd desorption experiments:

The 0.1M HNO_3 solution was used to elute Cd^{2+} from both biomass. Following the Cd^{2+} sorption experiments, the Cd-loaded biomass was prepared by centrifugation, washed and returned to 25 ml of the effluent 0.1 M HNO_3 for 30 minutes on a rotary shaker (125 rpm). Metal concentrations were determined after separating the biomass from eluting agent by filtration.

Atomic absorption analysis:

The samples of Cd^{2+} was measured by atomic absorption spectrophotometer (Variance spectra model AA-220 FS) by using the Flameless method of graphite system.

Statistical analysis:

All the experiments were triplicated. Mean values were used in the analysis of data by using the analysis of variance (one - way ANOVA) and Post Hoc. Duncan test ($p<0.05$).

RESULTS AND DISCUSSIONS

Uptake Mechanism of Cd by Viable and Non-viable biomass:

The removal ability of Cd in *Humicola* sp. was found to be in the same pattern for both biomass as increasing Cd concentration, however viable biomass reduced Cd^{2+} removal more than non-viable biomass. At Cd concentration of 100 mgl^{-1}, viable and non-viable biomass removed Cd of 61.77±3.25 mg Cd g^{-1} dry wt. and 47.61±2.24 mg Cd g^{-1} dry wt., respectively (Table 1). This value is better than many of fungal biomasses such as, *Rhizopus cohnii* [8], *Rhizopus nigricans*[12], *Aspergillus fumigatus* [5] *and Aspergillus niger* [13] but lower than *Penicillium chrysogenum* as observed by Xu and *et al*. [6].

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Table 1: Cadmium uptake on viable and non viable biomass of *Humicola* sp.

Cd concentration (mg l^{-1})	Cadmium uptake (mg Cd g^{-1} dry wt.)	
	Viable biomass	Non-viable biomass
0	$0.00{\pm}0.00^{a}$	$0.00{\pm}0.00^{a}$
1	$0.88{\pm}0.07^{a}$	$0.86{\pm}0.03^{a}$
5	$4.67{\pm}0.29^{b}$	$5.08{\pm}0.63^{b}$
10	$8.79{\pm}0.64^{c}$	$10.31{\pm}0.64^{c}$
25	$20.89{\pm}1.98^{d}$	$26.02{\pm}2.07^{d}$
50	$33.36{\pm}1.95^{e}$	$39.04{\pm}2.54^{e}$
100	$61.77{\pm}3.25^{f}$	$47.61{\pm}2.24^{f}$
150	$60.84{\pm}1.25^{f}$	$47.17{\pm}2.40^{f}$

For a Cd uptake, mean concentrations followed by the same letter are not significantly different (p<0.05)

The equilibrium isotherm of Cd adsorption by the *Humicola* sp. biomass can be described by Langmuir isotherm. Figure 1 shows the isothermal adsorption equilibrium of Cd at 30±1°C and pH 7 on *Humicola* sp. mycelial. These isotherms follow the typical Langmuir adsorption pattern as shown by the linear transformation. The linearized form of Langmuir equation is represented by the following expression:

$$\frac{Ceq}{q} = \frac{Ceq}{q\text{max}} + \frac{1}{q\text{max}b}$$

Where Ceq is the equilibrium solution concentration (mg l^{-1}), q max is the amount adsorbed at equilibrium (mg g^{-1}), the Langmuir constants $q$max and b are related to adsorption capacity and energy of adsorption, respectively [14]. The linear plot between Ceq/q with Ceq shows that investigated metal ions were adsorbed by *Humicola* sp.. As compared in Table 2, the viable biomass has a greater capacity ($q$max) and binding constant (b) than non-viable biomass for Cd adsorption.

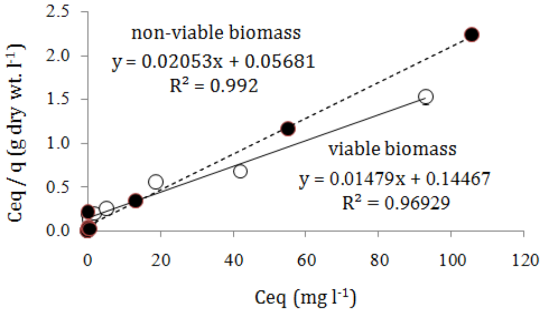

Fig. 1: Langmuir adsorption isotherm of Cd removal by *Humicola* sp., viable biomass (○,___) and non-viable biomass (●,_ _ _).

Table 2: Comparison of the Langmuir constants for Cd adsorption by *Humicola* sp. biomass.

	qmax (mg Cd g^{-1} dry wt.)	b (mg l^{-1})
Viable biomass	67.61	9.78
Non-viable biomass	48.71	2.77

Effect of contact time on Cd removal:

Viable biomass of *Humicola* sp. could also remove Cd in solution and reached the equilibrium (p<0.05) within 150 minutes, while the rate of biosorption by non-viable biomass was faster and contributed significantly (p< 0.05) to equilibrium uptake 97.91 % recovery being achieved within 120 minutes (figure 2a). Many researchers reported that the rate of absorption was observed in 2 phases, an initial phase of faster absorption then followed by the phase of slower adsorption. Initial faster uptake might be due to the availability of abundant metal species and empty metal binding sites of microbes. Slower phase might be due to saturation of metal binding site [15].

Effect of pH on Cd removal:

The pH level is one of the most important parameters on fungal biosorption of Cd^{2+} ions from aqueous solutions by *Humicola* sp.. The result shows that Cd adsorption was also very low at pH 3 and increased to pH 6 in viable biomass and pH 5 in non-viable biomass then reached the equilibrium after that (p<0.05) (Figure 2b). The low Cd biosorption at pH less than 4 has been suggested to the competition among metal ions from hydronium ions for the available biosorption sites. However, it is known that many heavy metals including Cadmium can undergo hydrolysis at different pH values, and the predominant form of the hydroxyl species depends on the pH value [16]. The predominant form of cadmium is Cd^{2+} ion between pH 4 and 6 whereas $CdOH^{+}$ is predominant between pH 7 and 9. It is likely that viable biomass preferentially adsorb monovalent $CdOH^{+}$ as same as divalent Cd^{2+}.

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Effect of temperature on Cd removal:

The maximum value of Cd removal occurred at room temperature (30°C) in viable and non-viable biomass was 62.18±1.49 mg l^{-1} dry wt. and 48.05±0.78 mg l^{-1} dry wt., respectively. The Cd removal in both biomass were decreased after 40 °C (figure 2c). The temperature higher than 40ºC caused a change in the texture of the viable biomass and thus reduced its sorption capacity. Biomass contains more than one type of sites for metal binding, thus the effect of temperature on each site is different and contributes to overall metal uptake. The effect of temperature on biosorption also depends on the heat of sorption [17].

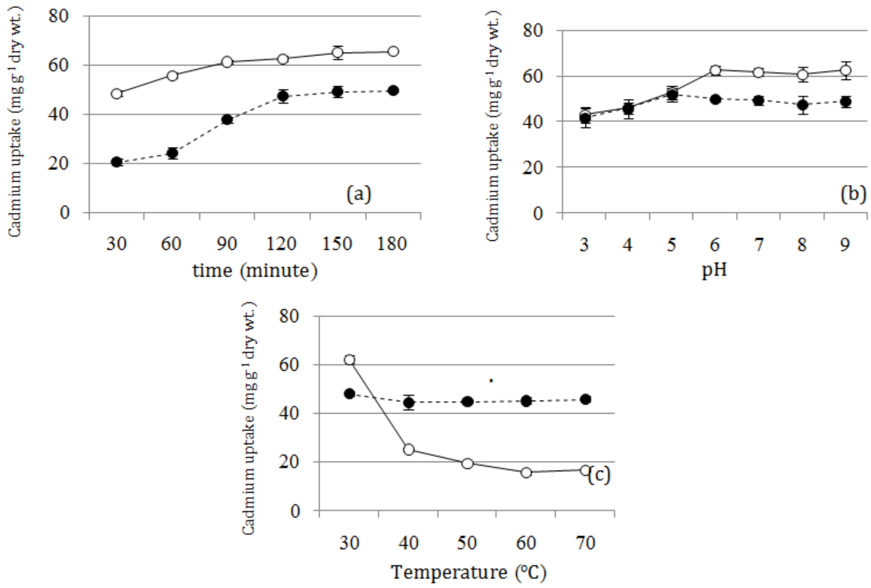

Fig. 2: Effect of contact time (a), pH (b) and temperature (c) on Cd^{2+} removal by *Humicola* sp. by —○— is viable biomass and - -●- - is non-viable biomass.

Cadmium desorption:

Desorption experiments indicate that the desorption efficiency with 0.1 M HNO_3 solution reaches 78.95% and 86.77% in viable and non-viable biomass, respectively. The decrease in lead uptake by acid desorbent might be due to the increase of the concentrations of competing hydronium ions. It is also possible that the physical structure of the biomass becomes damaged by this acid [18].

Table 2: Desorption of Cd^{2+} on biomass of *Humicola* sp. used with 0.1 M HNO_3.

Biomass	Cadmium uptake (mg Cd g^{-1} dry wt.)	Removal efficiency (%)
Viable biomass	48.77±8.35	78.95
Non-viable biomass	41.31±4.94	86.77

Summary:

The results of this research show that visible biomass of *Humicola* sp. biomass from Mae Tao creek sediment is great quantities for the removal of Cd^{2+} from aqueous solution. The adsorption process can be described by Langmuir equation. Adsorption of Cd^{2+} is fairly rapid in first 30 minutes and increased slowly to reach equilibrium in 150 minutes for viable biomass and 120 minutes for non-viable biomass. The temperature and pH are affected this process. For the desorption, 0.1 M HNO_3 showed in the highest efficiency to elute Cd^{2+} from the biomass.

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