Adsorption of cadmium onto illite modified by *Bacillus mucilaginosus*

Yanwu Pei[1,a], Zilong Song[1,b], Liying Qin[1,c], Xiaxia Zhou[1,d], Yajie Guo[1.e], Min Wu[1.f], Jianchao Hao[1,g], Xianzhi Lu[1,h]

[1]College of Agronomy and Resources ＆Environment; Tianjin Engineering Research Center of Agricultural Ecological ＆ Remediation; Tianjin Agricultural University, Tianjin 300384, China;

[a]email:1415645334@qq.com,[b]email:2905169757@qq.com,[c]email:13672117519@qq.com,[d]email: 2210553867@qq.com,[e]email:524034354@qq.com,[f]email:1597137633@qq.com,[g]email:qqhjc1980 @163.com, corresponding author, [h]email:nxylxz@163.com

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ABSTRACT: *Bacillus mucilaginosus* was cultured in the medium containing illite, then the culture was burned in muffle to prepare adsorption material modified by microorganism. The biological modified illite (BMI) was used to adsorb cadmium ions at different conditions. The result showed that BMI had significantly improved Cd adsorption potential compared to original illite; BMI had a good adsorption in the neutral environment; adsorption isotherms of Cd onto BMI followed Langmuir equation and adsorption kinetic of Cd on BMI followed pseudo-second order kinetic equation. Fast adsorption of BMI and its environmental friendly implied that the BMI has good prospects for application in practice.

INTRODUCITON

Heavy metals-contaminated soil has become global environmental concern, heavy metals pose a potential threat to soil ecosystem for its concealment, irreversibility and persistence. Heavy metals will migrate from soil to plants and animals along the food chain, so people was biggest victims because human is at the top of food chain [1]. It was reported that one fifth of cultivated soil was contaminated by heavy metal and cultivated soil of 25 districts in 11 province was contaminated by Cd[2,3]. Guangzhou revealed that 44.4% of rice and rice products contained Cd and the concentration exceeded standard in 2013[4]. Cd not only accumulated in the liver and kidney, but also bond with protein containing some functional groups such as hydroxyl, amino and sulfydryl which inhibited activity of enzyme and induce some disease such as Itai-itai disease[5,6]. At present, some methods were used to repair Cd-contaminated soil. Soil replacement decreased the Cd concentration of soil and seems to be most efficient, yet cost-prohibitive [7]. Soil washing is using some reagent to dissolve Cd in the soil and Cd in soil was removed by collecting solution containing Cd. However, this method might cause second pollution, soil nutrient loss and damage of soil structure [8,9]. Phytoremediation is the most effective method to decrease concentration of heavy metals, but it cost a long time [10,11]. The situ immobilization of heavy metals could inhibit migration of heavy metals from soil to plant, so development of passivator was focused at present [12,13]. In order to prevent second pollution, it is important to develop environmental-friendly materials. This paper chose *Bacillus mucilaginosus* to modify illite which improved Cd adsorption of original illite. Adsorption capacity of Cd onto biological modified illite (BMI) in the solution was evaluated in the lab, the objective of this research is providing basis for practical application of BMI in Cd-contaminated soil.

MATERIALS AND METHODS

Materials

Bacillus mucilaginosus was chosen to modified illite and modified method was showed as follows: The bacterium was inoculated in a 200 mL medium (1 L medium containing 10.0 g sucrose, 0.3 g yeast extract, 0.5 g $(NH_4)_2SO_4$, 1.0 g K_2HPO_4, 1.0 g $MgSO_4·7H_2O$, and 0.5 g $CaCO_3$ in distilled water) and incubated at 30 °C on a shaker (140 rpm) for 3 d. The resultant culture served as start culture and was inoculated at 10 % volume into 500 mL nitrogen-free medium (1 L medium containing 5 g sucrose, 1.25 g $Na_2HPO_4·12H_2O$, 0.5 g $MgSO_4·7H_2O$, 0.1 g $CaCO_3$, 5.0 mg $FeCl_3$, and 50 g illite in distilled water) and incubated at 30°C on a shaker (140 rpm) for 7 d. The culture was dried in drying oven and the solid was calcined at 400 °C in Muffle furnace for 2 h, cooled in the air, then the solid and hydrogen peroxide were mixed uniformly and calcined at 200 °C in Muffle furnace, at last the solid was ground into 100 mesh and it was used as BMI.

Experimental Design

Adsorption of Cd onto different materials

Aqueous Cd solution (50 mL, 20 mg/L) was added to five 100 mL flasks and 0.2 g of different adsorption materials were placed to them, respectively. Three replications were performed. Each mixture was shaken at 30°C and 140 rpm for 40 min. Then, the solutions were filtered and the filtrate was used for Cd analysis.

Variation in Cd removal with adsorbent dosage

Aqueous Cd solution (50 mL, 20 mg/L) was added to five 100 mL flasks and 0.1 g, 0.2 g, 0.4 g, 0.6 g, and 0.8 g of BMI were added to them, respectively. Three replications were performed. Each mixture was shaken at 30°C and 140 rpm for 40 min. Then, the solutions were filtered and the filtrate was used for Cd analysis.

Variation in Cd removal with pH

Aqueous Cd solution (50 mL, 20 mg/L) was added to 100 mL flasks. Aqueous hydrochloric acid and potassium hydroxide were used to adjust the pH of each solution(2.02，3.01，4.09，4.94，6.08，7.12，7.98). Then, BMI (0.1 g) was added to each flask and the subsequent operations were same with above.

Adsorption isotherms

Aqueous Cd solutions having different concentrations (5, 10, 20, 30, 40, and 50 mg/L) were added to 100 cm^3 flasks and BMI (0.2 g) were added to each. The mixtures were shaken at 30°C and 140 rpm for 40 min. The solutions were filtered and the filtrates were used for Cd analysis. Three replications were carried out. Two models, involving the Langmuir and the Freundlich isotherms, were used to estimate the adsorptive capacity and adsorption equilibrium constant. The Langmuir and Freundlich isotherms could be expressed respectively in the forms:

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \quad , \quad \ln q_e = K_F + \frac{1}{n}\ln c_e$$

where c_e was the equilibrium concentration of the Cd (mg/L), q_e was the equilibrium amount of Cd adsorbed per unit mass of adsorbent (mg/g), q_m was the adsorption capacity (mg/g), n was a constant, and K_L and K_F were the Langmuir and Freundlich adsorption constants.

Adsorption kinetics

Aqueous Cd solution (500mL, 20 mg/L) and BMI (2 g) were placed in a 1L flask. The mixture was shaken at 30°C and 140 rpm for 40 min. Samples (10 cm^3) were subsequently collected at fixed time intervals (5，10，15，20，40，60 and 80min) to determine the change in the Cd concentration. The pseudo-second order kinetic model was written in the form:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{kq_e^2}$$

where q_e and q_t were the amounts (mg/g) of Cd adsorbed at equilibrium and at time t, respectively, and k was the pseudo-second order rate constant.

Statistical Analysis

Data are expressed as the means ± the standard errors (SD). Error bars in the figures represent ± SD of triplicate samples. Control groups are the same in all cases.

RESULTS AND DISCUSSIONS

Adsorption of Cd onto different materials

Adsorption of Cd onto different materials was showed in Figure1. Cd removal of I_1 was lowest among five materials (63.27%). Cd removal of I_2 (64.33%) was similar with I_1, suggesting that direct calcination did not improve adsorption of Cd onto original illite. Organism in the culture was transformed into activated carbon in the process of calcination and the activated carbon existed in the pores of illite, hydrogen peroxide could oxidize carbon into carbon dioxide and released into air. Cd removal of I_5 was higher than I_4 showed that activated carbon produced in the process of calcination did not improve adsorption capacity of original illite. Adsorption of Cd onto I_5 is highest because the interaction between microbes and minerals improved adsorption capacity of Cd onto illite. Cd removal of I_3 was higher than that of I_1, but lower than that of I_5, the reason was that culture produced by *B.mucilaginosus* contained illite and the illite in the culture was modified to improve it's adsorption of Cd. This result also proved that modification mechanism was the interaction between microbes and minerals.
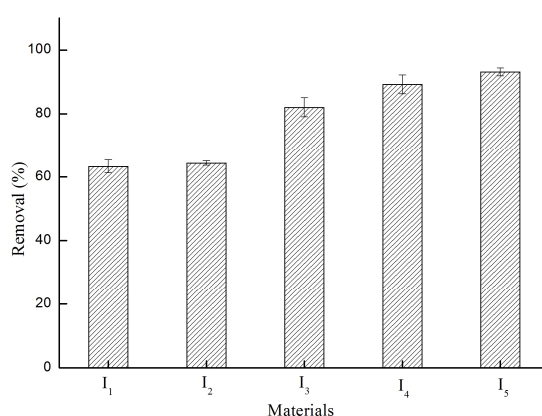

Figure 1. Adsorption of Cd onto different materials

Note: I_1 , original illite; I_2, original illite was calcined at 400 °C in Muffle furnace; I_3, the mixture of original illite and culture was calcined at 400 °C in Muffle furnace; I_4, illite modified by *B.mucilaginosus* was calcined at 400 °C in Muffle furnace; I_5, BMI.
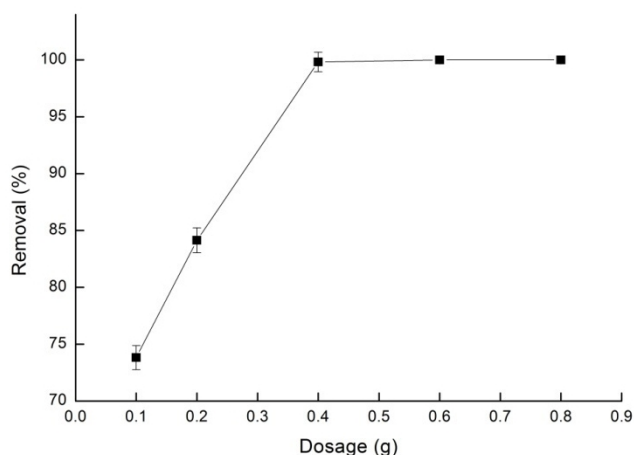
Variation in Cd removal with adsorbent dosage

Figure 2. Variation in Cd removal with adsorbent dosage

The variation in the Cd removal efficiency with dosage was shown in Figure 2. When the dosage was 0.1 g, the Cd removal efficiency from an aqueous solution (50 mL, 20 mg/L) was 87.46%. Doubling the dosage to 0.2 g increased the removal efficiency to more than 89.90%. Cd removal was about 100% when the dosage was above 0.4g. Therefore, the dosage was set to 4g of adsorbent in 1 L of solution (20 mg/L) in subsequent experiments. As the above result showed, Cd removal did not reveal a linear increasing trend with the increase of dosage which might have a relationship with adsorption equilibrium. Initial Cd concentration was 20 mg/L, so Cd concentration decreased with the increase of dosage of BMI and adsorption rate also decreased at the same time.

The variation in Cd removal with pH

A change in pH might have a significant influence on the adsorption potential and thus we determine the optimum pH required for practical use. The change in Cd removal efficiency with pH was shown in Figure 3.
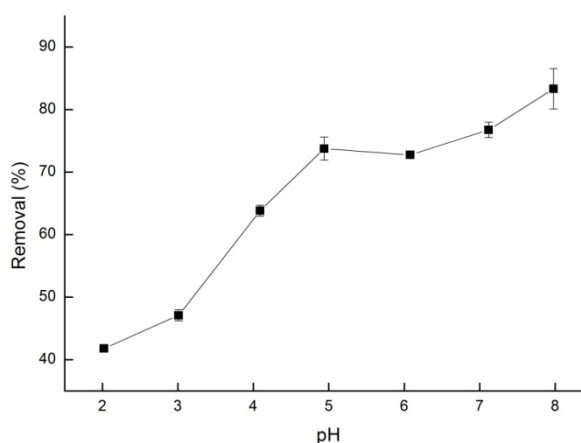

Figure 3. The variation in Cd removal with pH

Cd removal increased with the increase of pH. The removal of Cd was low when the pH was lower than 4.94. BMI charged negative, the ion strength of H^+ was higher than that Cd^+ in the acid environment, so H^+ would bind with BMI by charge neutralization and inhibit combination between BMI and Cd^+. Cd removal was higher than 70.00% when the pH was between 4.94 and 7.98, suggesting than BMI had a good adsorption in the neutral environment. When the pH was higher than 7.98, Cd^+ bond with OH^{1-} and precipitated in the bottom of water, so higher Cd removal in alkaline environment did not show BMI had a good adsorption.

Adsorption isotherms

The data obtained from adsorption isotherms were analysed by the Langmuir and Freundlich models. The Langmuir and Freundlich isotherms obtained using BMI were $c_e/q_e=0.209c_e+0.041$ ($R^2=0.9979$) and $\ln q_e=1.2269+0.127\ln c_e$ ($R^2=0.9910$) respectively, so adsorption isotherms of Cd onto BMI followed Langmuir equation. The adsorption capacity of BMI was 4.78mg/g which was higher than original illite (1.09 mg/g).

Adsorption kinetics

The variation in Cd concentration with time was showed in Figure 4. Adsorption of Cd onto BMI was divided into two stages. The first stage was fast adsorption, the Cd concentration decreased from 20.87mg/L to 3.76 mg/L in the first minute and Cd removal was 81.96%. This result showed than adsorption of Cd onto BMI might be physical adsorption. The second stage was slow adsorption, the concentration of Cd decreased from 3.76 to 1.45mg/L and Cd removal was just 11.09%. This adsorption might be induced by chemical adsorption and internal diffusion. The batch kinetic studies indicated that Cd adsorption onto BMI reaches equilibrium very quickly (less than 5 min). The adsorption process was explained by the fact that the adsorption of Cd onto BMI involves a combination of physical and chemical adsorption.
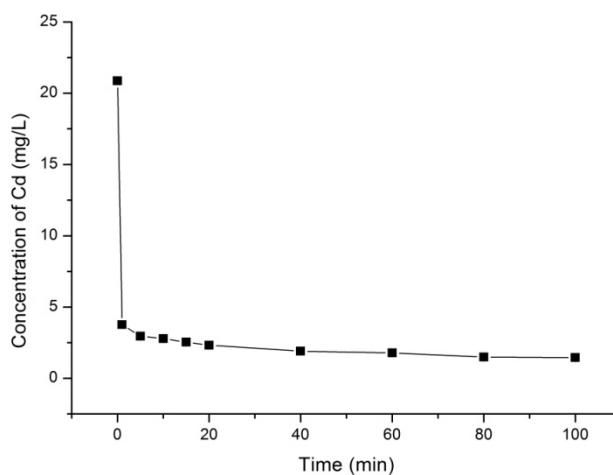

Fig 4. The variation in Cd concentration with time

Fitting the kinetic data to various mechanistic models, it appeared that a pseudo-second order kinetic equation best fited the adsorption data ($t/q_t=0.205t+0.149$（$R^2=0.996$）) between 1 and 100min.The amounts of Cd adsorbed at equilibrium (q_e) and pseudo-second order rate constant (k) were 4.88 mg/g and 0.28 g·mg^{-1}·min^{-1}. The pseudo-second order rate constant (k) was small which proved slow adsorption between 1 and 100min. The best adsorption time was 40min and Cd removal was 90.91%.

CONCLUSIONS

BMI had significantly improved Cd adsorption potential compared to original illite; BMI had a good adsorption in the neutral environment; adsorption isotherms of Cd onto BMI followed Langmuir equation and the maximum adsorption capacity was 4.78 mg/g; adsorption kinetic of Cd on BMI followed pseudo-second order kinetic equation and the amounts of Cd adsorbed at equilibrium (q_e) was 4.88 mg/g. Fast adsorption of BMI and it's environmental friendly implied that the BMI has good prospects for application in practice.

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REFERENCES

[1] RA Wuana，FE Okieimen. 2011 Heavy metals in contaminated soils: A review of sources, chemistry, Risks and best available strategies for remediation, ISRN Ecology, 2012:1-20.

[2] H Z Zhang, Y M Luo, H B Zhang, and etal. 2010 Study on soil environmental quality guidelines and standards Ⅴ. modeling of cadmium uptake in soil-crop systems for human food safety in china. ACTA Pedologica Sinica, 47(4): 628-638.

[3] X L Cao, Z Z Luo, DY Huang, etal. 2013 Effects of Cd-contaminated rice straw incorporation on transformation of Cd forms in soils. Journal of Agro-Environment Science, 32(9):1786-1792.

[4]http://www.gzfda.gov.cn/business/htmlfiles/gzfda/jdxw/201305/90190.html.2013.05.16.

[5] M MStorelli, and G. Barone. 2013 Toxic Metals (Hg, Pb, and Cd) in Commercially Important Demersal Fish from Mediterranean Sea: Contamination Levels and Dietary Exposure Assessment. Journal of Food Science, 8(2): 362-366

[6] M M Storelli, G Barone, G Cuttone, et al. 2010Occurrence of toxic metals (Hg, Cd and Pb) in fresh and canned tuna: Public health implications Food and Chemical Toxicology , 48(11): 3167-3170.

[7] Y B Zhu, L B Zhou, H Lin. 2010 Key technologies for compiling report of land reclamation plan for projects of metal mine. Nonferrous Metals, 62(2): 103-107.

[8] D Voglar, D Lestan. 2013 Pilot-scale washing of Pb, Zn and Cd contaminated soil using EDTA and process water recycling. Chemosphere, 91(1):76-82.

[9] D Voglar, D Lestan. 2014 Chelant soil-washing technology for metal-contaminated soil. Environmental Technolgoy, 35(11):1389-1400

[10] H Ali, E Khan, MA Sajad. 2013 Phytoremediation of heavy metals-Concepts and applications. Chemosphere,91(7):869-881.

[11] Y Ma, M Rajkumar, Y Luo, et al. 2013 Phytoextraction of heavy metal polluted soils using Sedum plumbizincicola inoculated with metal mobilizing Phyllobacterium myrsinacearum RC6b. Chemosphere,93(7):1386-1392.

[12] Usman A, Kuzyakov Y, Stahr K. 2005 Effect of clay minerals on immobilization of heavy metals and microbial activity in a sewage sludge-contaminated soil. Journal of Soils and Sediments, 5(4):245-252.

[13] Y Sun, G Sun, Y Xu, etal. 2013 Assessment of sepiolite for immobilization of cadmium-contaminated soils. Geoderma,193:149-155.