

Application of Biochar for Cadmium Stabilization in Contaminated Paddy Soil

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Abstract. Cadmium contamination in rice fields near zinc mines in Mae Sot District, Tak Province has been a persistent problem for decades. The contamination covers a vast area, making several soil remediation methods, such as soil washing or excavation impractical. Phytoremediation would also take several years and interfere with farming. However, there are recent reports on the potential of biochar in cadmium stabilization which resulted in reduced cadmium uptake by rice. Therefore, in this study, several biomaterials were investigated to produce the most suitable biochar for cadmium stabilization in paddy soil in Mae Sot. Rice husk, rice straw and bagasse were selected because of their availability in Mae Sot. Cadmium adsorption efficacy of biochar made from these biomaterials were analyzed using the adsorption isotherm. The results showed that cadmium adsorption by biochar from bagasse, rice husk, and rice straw were in accordance with Freundlich adsorption isotherm equation. By comparing the distribution coefficient, the adsorption efficacy of the biochar was ranked as rice straw > bagasse > rice husk. Therefore, rice straw biochar, which had the highest cadmium adsorption efficacy, was selected for stabilization experiments. After 30 days of incubating contaminated soil with rice straw biochar, the amount of extractable Cd using CaCl₂ and EDTA were reduced significantly. The optimal application rate of rice straw biochar was 5% with the incubation period of 20 days. This warrants the next phase of this study which will be conducted in the field experiments in Mae Sot.

Keyword. Adsorption Isotherm, Cadmium, Stabilization, Biochar, Paddy, Mae Sot District

1 Introduction

Cadmium contamination in rice fields near zinc mines in Mae Sot District, Tak Province was reported by the International Water Management Institute (IWMI) and the Pollution Control Department (PCD). [1, 2]. According to the reports, the contamination covered a large area of paddy field downstream from the mines (approximately 6 square kilometres) as shown in **Fig. 1** and **2**. Cadmium concentration in paddy soil and rice grains in the contaminated area were between 0.5 to 284 mg/Kg of soil and 0.05 to 7.7 mg/Kg of rice, respectively. These contaminations pose a health risk to human because harvested rice contained cadmium that exceeded CODEX standard of 0.2 mg Cd / Kg of rice. Besides, there is also contamination in other agricultural products such as soybeans, mung beans, corn and sugarcane. [3]. Cadmium contamination could cause respiratory and circulatory disorders, including an orthopedic disorder known as Itai-Itai. [1, 4]. The contamination in soils also affected soil fertility and agricultural productivity. Hence, it is imperative to remediate the contaminated area with appropriate and effective methods.

There are several methods for remediation of heavy metals in contaminated soil. Excavation can quickly restore soil that is contaminated with a wide variety of contaminants. However, this method is limited by the cost

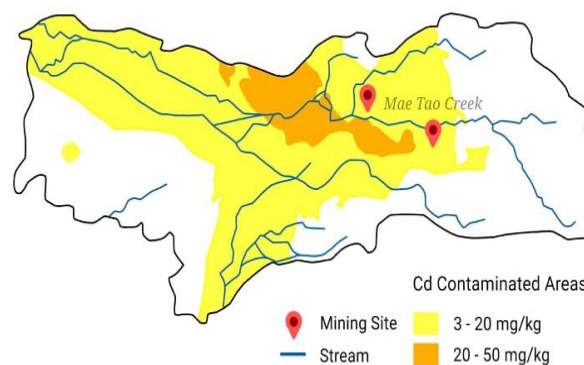


Fig. 1. Contaminated area in Mae Sot District, Tak Province [2].

of excavation, transportation, and disposal, therefore not suitable for a large contaminated area such as Mae Sot. Soil washing, which leaches contaminants from the soil with chemicals, can be done quickly but is also limited by the amount chemicals required and their effects on soil's fertility and pH. This method can subsequently affect soil organisms and its suitability for agriculture. Biological method such as phytoremediation is relatively safe, but limited by slow plant growth and uptake [5]. Thus, this

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method would take several years to reduce the contaminant concentration to acceptable level.



Fig. 2. Cadmium contamination in rice fields in Phra That Pha Deang Sub-district, Mae Sot District, Tak Province.

Cadmium stabilization using clay minerals or biochar have been shown in several research for their potential for treating heavy metal-contaminated soil [4, 6, 7]. Treated clay minerals were shown to adsorb heavy metals effectively from aqueous solution and immobilize heavy metals in contaminated soil [8, 9]. Application of wheat straw derived biochar was shown to reduce the bioavailability of Cd and Pb in paddy soil and limit Cd uptake by rice [7, 10]. Bamboo and rice straw biochar decreased the amount of extractable heavy metals (Cd, Cu, Pb and Zn). [11]. Acacia biochar decreased the accumulation of As and Mn in Napier grass grown in contaminated mine tailing. [12]. Moreover, rice straw biochar was shown to reduce the accumulation of Cd, Zn, Mn and Ni in roots, stems and seeds of wheat. [13].

However, unlike clay minerals, biochar can be produced from various agricultural wastes by pyrolysis process. It can also be used as a soil amendment material because of its high organic carbon, the ability to retain minerals, and its water holding capacities [14]. Rice straw and bamboo biochar were found to increase the growth and yield of wheat and rice, respectively [13, 15]. Moreover, pine pellet biochar was shown to increase the growth of cucumber plug seedling in both stem and root. [16]. Therefore, biochar can be applied to contaminated soil to decrease heavy metal uptake by crops while increasing the growth and yield of the crops. This allows farmers to grow crops while remediating the soil, making this method highly suitable for solving the cadmium contamination problem in Mae Sot.

Biochar is black carbon which is very stable and can be retained in the soil for a long time. It has a large surface area with numerous functional groups which are able to adsorb heavy metals. Biochars produced from different biomass and pyrolysis temperature have different physical and chemical properties, as shown in the Table 1. The mechanisms of biochar adsorption include electrostatic attraction, ion exchange, complexation and co-precipitation at the surface of biochar as shown in Fig. 3.

Plant uptake generally requires Cd to be in the exchangeable form such as Cd^{2+} , thus Cd could be stabilized by reducing the amount of exchangeable Cd by means of biochar adsorption. Additional factors include physical and chemical properties of biochar which are greatly influenced by the production temperature, the application rate of biochar in the soil, and the pH of the soil [17].

Table 1. Properties of different biochars.

Type of Biochar	Pyrolysis Temp (°C)	pH	Surface area (m ² /g)	CEC (cmol/kg)	Ref
Bagasse	450	6.5	3.04	17.58	[12]
Napier grass	450	9.86	11.68	18.61	
Acacia wood	450	9.13	25.55	23.83	
Bamboo	750	9.5	907.4	15	[11]
Rice straw	500	10	36.7	45	
Rice Husk	700	8.5	25.161	-	[18]
Empty fruit bunch	700	9.4	1.89	-	
Populus wood	500-550	8.2	15	-	[19]
Carozo corn	400-500	10.3	22.3	-	
Sewage sludge	500-550	8.7	31.4	-	
Scots pine	450	8.56	9.16	3.41	[20]
Scots pine	700	8.52	10.4	2.40	
Silver birch	450	8.69	5.92	5.09	
Silver birch	700	9.27	7.17	5.71	

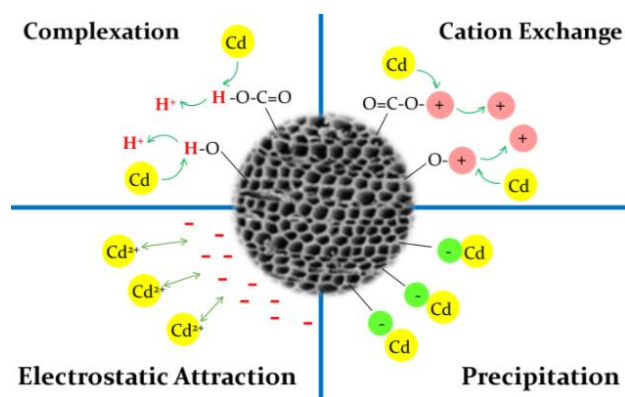


Fig. 3. Biochar - Heavy metals adsorption mechanism.

The purpose of this research is to study the efficacy of biochar made from different types of agricultural wastes in stabilizing cadmium in paddy soil. Bagasse, rice husk, and rice straw were used to produce biochar because of their availability in Mae Sot District, Tak Province. The ability of biochar to adsorb and reduce exchangeable cadmium in paddy soil was tested in lab-scale experiments. Biochar with the highest efficacy for cadmium adsorption and stabilization from this study will be applied in a field experiment in Mae Sot to provide the most effective and practical remediation method for rice farmers in the area.

2 Experimental Methods

2.1. Soil and biochar preparation

Cadmium contaminated soil samples and rice straw were obtained from a paddy field in Mae Tao Sub-district, Mae Sot District, Tak Province as shown in **Fig. 4**. Bagasse biochar (BB), rice husk biochar (RHB), and rice straw biochar (RSB) were produced by pyrolysis process at 450 °C for 4 hours. The process was conducted in a 200-liter steel furnace at Huai Sai Royal Development Study Center as seen in **Fig. 5**. Biochar was then ground and sifted to 250 µm. The pH of paddy soil and biochar were determined according to the USEPA Method 9045D by mixing soil or biochar with water at 1:1 ratio. The pH of the supernatant was then measured with a Mettler Toledo F20 pH meter. The pH of Cd-contaminated paddy soil, uncontaminated paddy soil, BB, RHB, and RSB were determined to be 7.50, 5.23, 9.31, 7.80, and 10.15, respectively.

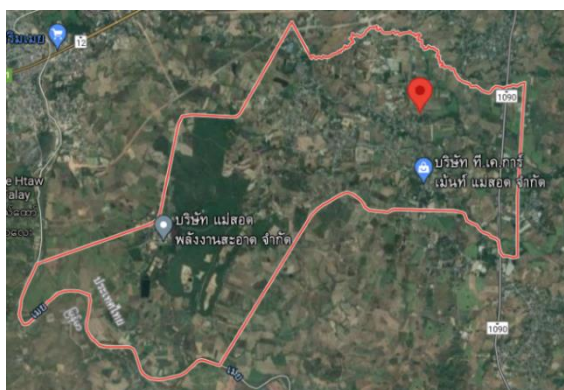


Fig. 4. The location of the sampling site in Mae Tao Sub-district, Mae Sot District, Tak Province. The red line outlines the boundary of Mae Tao Sub-district.



Fig. 5. Biochar steel furnace.

2.2 Cadmium adsorption

To study the efficacy of cadmium adsorption on biochar, 1 g of uncontaminated paddy soil sample was added to 20 mL of cadmium solution (prepared from cadmium chloride dissolved in 0.01M CaCl₂) at 5 concentrations: 10, 15, 20, 25 and 30 mg/L. To compare the effect of

biochar concentration, the concentration of biochar added to each vial was varied at 0, 10, 20 and 100% of soil sample. The mixtures were shaken at 120 rpm for a period of 24 hours. The supernatant was then filtered with No.42 Whatman filter. Cadmium concentration and pH of the supernatant were determined by Atomic Absorption Spectroscopy (Agilent 240FS) and pH meter, respectively. The amount of adsorbed cadmium was determined using Equation (1).

$$q_e = \left(\frac{(C_0 - C_e) \times V}{W} \right) \quad (1)$$

where q_e is the amount of Cd adsorbed by biochar, C_0 and C_e are the initial and equilibrium concentration of Cd in the supernatant, respectively [21]. Adsorption isotherm was plotted between q_e and C_e .

2.3 Cadmium extraction

To study the stabilization effect of biochar on cadmium-contaminated soil, biochar with the highest efficacy for cadmium adsorption was incubated with 200 g of contaminated paddy soils for 30 days with water saturation. The amount of biochar was varied at 5 and 7 % (w/w). Soil samples were collected at 0, 10, 20 and 30 days. Cd was extracted by adding 2 g of soil in 15 mL of 0.01M CaCl₂ and 15 ml of 0.05M EDTA and shaken at 120 rpm for a period of 24 hours [11, 14]. The concentration of extracted Cd was determined with Atomic Absorption Spectroscopy.

3 Results and Discussion

3.1 Cadmium adsorption isotherm

The cadmium adsorption isotherms of paddy soil, BB, RHB, and RSB at concentration of 10, 20 and 100% are shown in **Fig. 6-9**. Least-square linear and non-linear regression were used to fit the adsorption isotherms with linear and Freundlich adsorption models, respectively. The goodness of fit of the experimental data to the adsorption models were compared using the standard error of the estimate (SE). The parameters of the adsorption models are shown in Table 2.

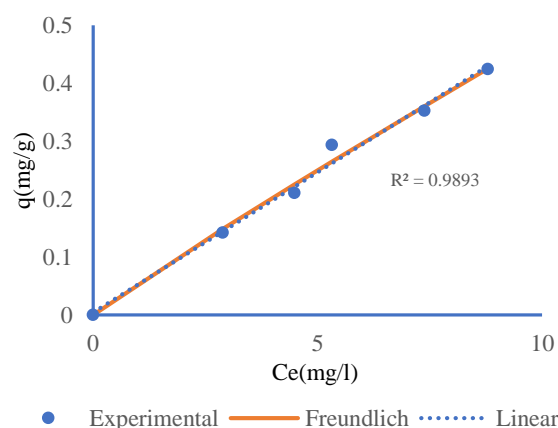
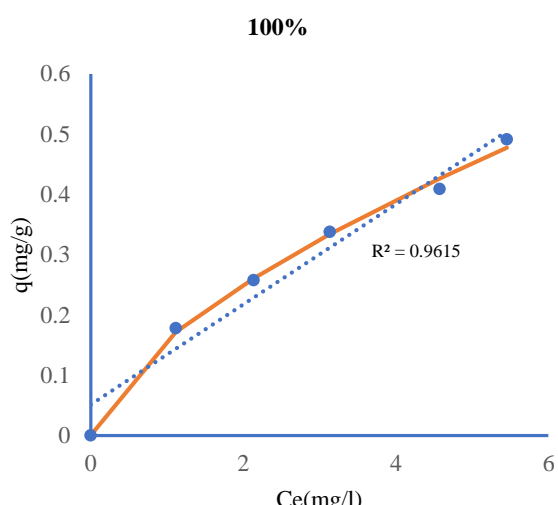
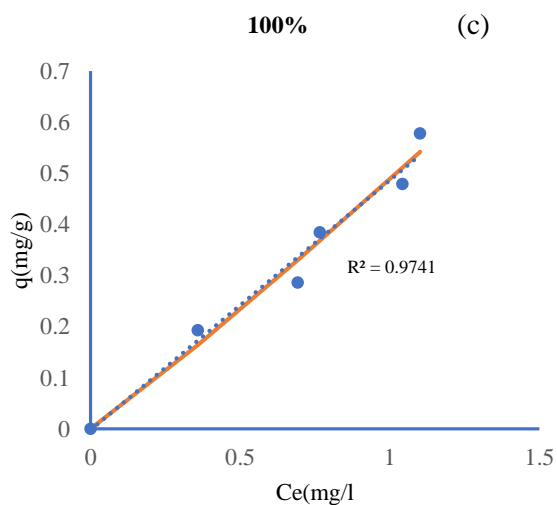
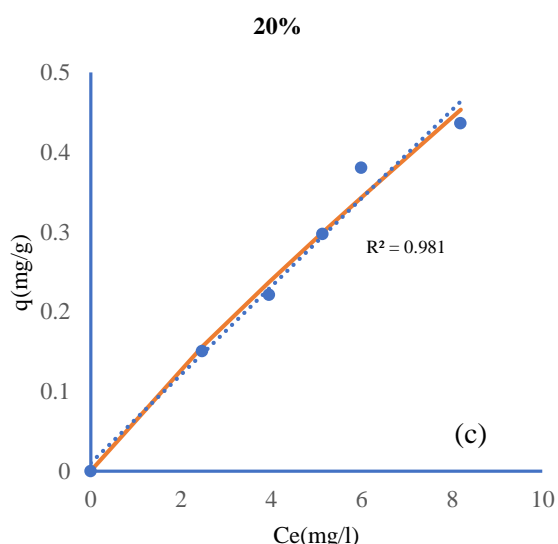
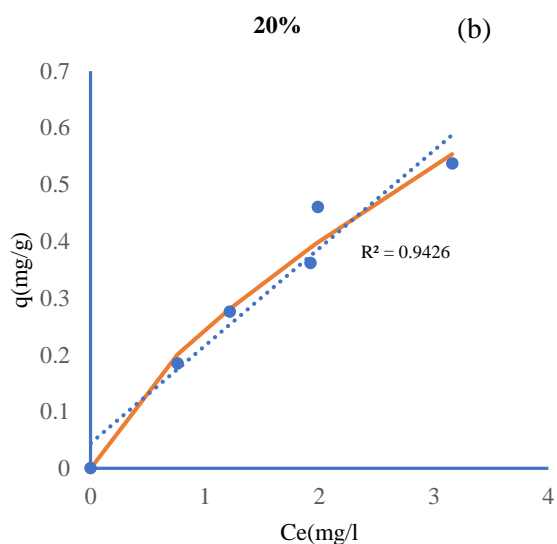
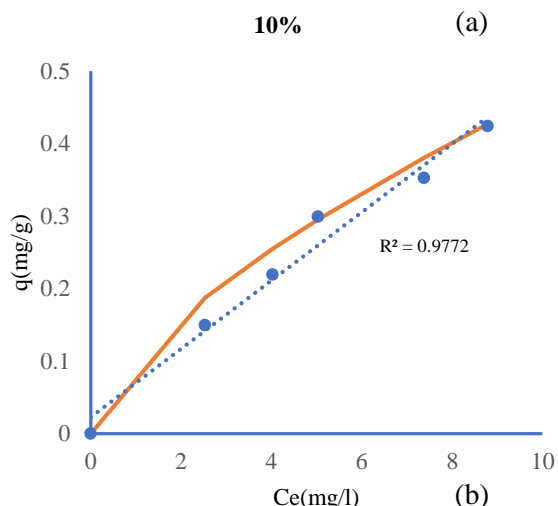
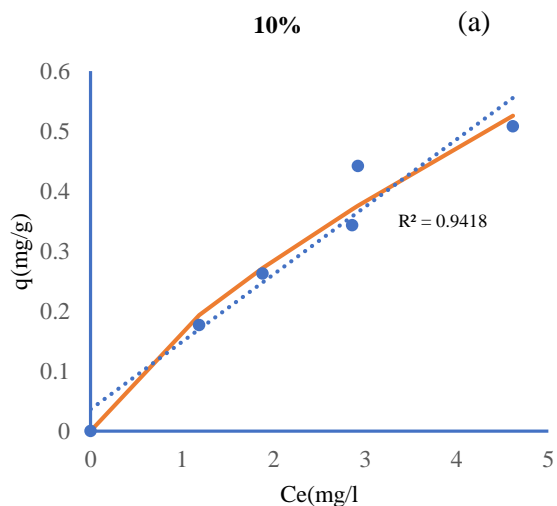


Fig. 6. Adsorption Isotherm of paddy soil.



● Experimental — Freundlich Linear

● Experimental — Freundlich Linear

Fig. 7. Adsorption Isotherm of BB with concentration of biochar at a) 10, b) 20 and c)100%

Fig. 8 Adsorption Isotherm of RHB with concentration of biochar at a) 10, b) 20 and c)100%

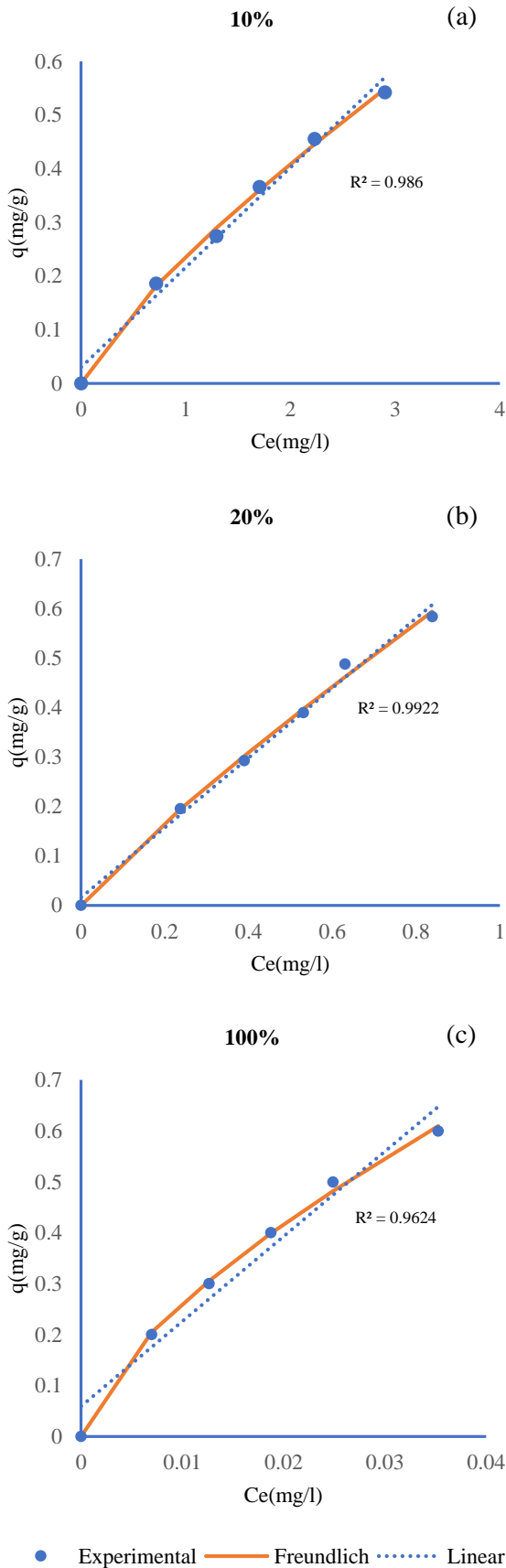


Fig. 9. Adsorption Isotherm of RSB with concentration of biochar at a) 10, b) 20 and c) 100%

Table 2. Adsorption isotherm parameters and standard error of estimate.

Biochar	conc. (%)	Linear model		Freundlich model		
		K_d	SE	K_F	1/n	SE
Paddy Soil	100	0.0484	0.018	0.055	0.944	0.017
BB	10	0.1125	0.050	0.171	0.735	0.038
	20	0.1719	0.052	0.245	0.710	0.036
	100	0.4889	0.037	0.489	1.066	0.037
RHB	10	0.0471	0.026	0.101	0.662	0.021
	20	0.0554	0.025	0.070	0.889	0.022
	100	0.083	0.038	0.160	0.645	0.012
RSB	10	0.186	0.026	0.236	0.790	0.010
	20	0.7052	0.021	0.694	0.882	0.015
	100	16.677	0.047	5.790	0.673	0.011

Table 3. The pH of paddy soil, BB, RHB and RSB.

Biochar	conc. (%)	pH
Paddy Soil	100	5.47
BB	10	6.01
	20	6.49
	100	8.59
RHB	10	5.78
	20	5.91
	100	7.53
RSB	10	6.76
	20	7.05
	100	9.90

3.2 Comparison of cadmium adsorption efficacy

Cadmium adsorption efficacy of paddy soils and biochar can be determined by comparing the constants K_d in linear adsorption isotherm or K_F in Freundlich isotherm depending on which model has the best fit. By comparing the SE, it was found that the adsorption isotherm of paddy soil and biochar fit better with Freundlich adsorption isotherm model. The K_F value showed that all types of biochar had more ability to adsorb cadmium than paddy soil. Moreover, higher concentration of biochar increased the adsorption efficacy. These results corresponded well to the results reported by Maichu et al., [14]. By comparing K_F , it was found that RSB has the highest affinity for cadmium and RHB has the lowest affinity for cadmium. Furthermore, the K_F of RSB is almost 11 times higher than BB and 36 times higher than RHB. This means that RSB has the highest efficacy for cadmium adsorption. The reason that RSB has very high cadmium adsorption efficacy could be due to its high surface area and CEC as shown in Table 1. High pH could also contribute to the precipitation of cadmium. The pH of

RSB was 9.90 as can be seen in Table 3. When RSB was mixed with soil, it raised the pH of the soil from 5.47 to 7.05. With higher pH, the CEC of the soil could have been increased as well [22]. These mechanisms have also been reported by other research. [23, 24].

3.3 Cadmium extraction

From the results of previous experiment, RSB, which had the highest efficacy for cadmium adsorption, was selected to be tested for cadmium stabilization efficacy. From the results shown in **Fig. 10** and **11**, it can be seen that the value of CaCl₂ extracted Cd from cadmium contaminated soil before the treatment was 1.05 ± 0.20 mg/kg. When the soil was mixed with RSB at 5 and 7 %, the amount of CaCl₂-extracted Cd was immediately reduced to 0.67 ± 0.41 and 0.49 ± 0.22 mg/kg, respectively, and further reduced to 0.18 ± 0.00 and 0.10 ± 0.01 mg/kg in 20 days. After that the amount of CaCl₂-extracted Cd remained almost unchanged. Similarly, the amount of EDTA-extracted Cd before the treatment was 9.23 ± 1.38 mg/kg. After the application of RSB at 5 and 7 %, the amount of EDTA-extracted Cd was immediately reduced to 7.47 ± 1.86 and 4.72 ± 0.19 mg/kg, respectively, and further reduced to 2.35 ± 0.20 and 2.21 ± 0.22 mg/kg in 10 days. After that the amount of EDTA-extracted Cd remained almost unchanged. These results are consistent with the results reported by Lu et al. [11] that RSB could decrease the amount of extractable Cd in soil.

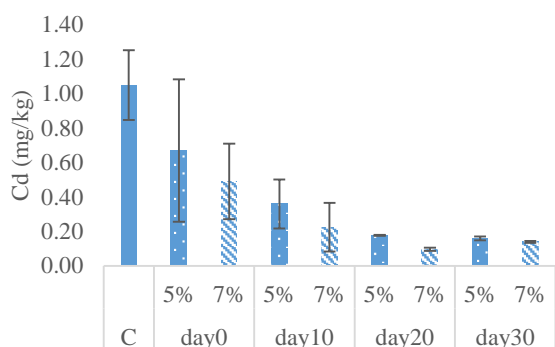


Fig. 10. Concentration of CaCl₂-extracted Cd after incubation of 30 days.

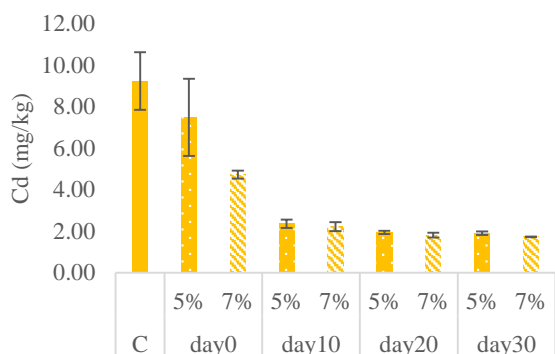


Fig. 11. Concentration of EDTA-extracted Cd after incubation of 30 days.

The concentration of CaCl₂ and EDTA-extracted Cd in the soil decreased with longer curing time. This is a result of cadmium adsorption on the biochar surface. The increase in the amount of biochar in the contaminated soil resulted in greater adsorption of cadmium because of the increase of absorption sites on biochar surface. The results at day 20 showed less adsorption rate, indicating that adsorption sites were mostly occupied or saturated. As a result, the adsorption rate decreased. However, the reduction of Cd from the soluble form in saturated soil condition could also contribute to the decrease of extractable Cd as shown in Eh-pH diagram of Cd suggested by Langmuir et al. [25].

According to the results, after incubation of 30 days, RSB at 5 and 7 % was able to reduce the amount of CaCl₂ extracted Cd by 84.84 and 90.85 % and the amount of EDTA-extracted Cd by 79.44 and 81.26 %. However, when comparing the variance, there was no difference in the results of the experiments on day 20 and 30. This means that the incubation of 10 - 20 days is adequate to achieve the maximum cadmium stabilization effect by RSB at the concentration used in this study.

4 Conclusion

Cadmium adsorption of paddy soil, BB, RHB, and RSB complied with Freundlich adsorption isotherm. The value of K_F constant in the adsorption isotherm equation showed that the efficacy of each type of biochar for Cd adsorption could be ranked as RSB > BB > RHB > paddy soil. Cadmium stabilization efficacy was indicated by the quantity of CaCl₂ and EDTA-extracted Cd. It was found that the higher application rate and longer curing time resulted in lower amount of CaCl₂ and EDTA-extracted Cd. RSB at 5% was the optimal application rate which could reduce CaCl₂ and EDTA-extracted Cd by 83.15 and 79.00 %, respectively, with an optimal incubation period of 20 days.

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