



## Research Article

## The Influence of Chemical Fertilizers on the Effectiveness of Biochar in Mitigating Cadmium Mobility in Soil

Chompoonut Chaiyaraksa\*, Navapat Sangworn

*Environmental Chemistry Program, Department of Chemistry, School of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand*

\*Correspondence Email: Chompoonut.ch@kmitl.ac.th

### Abstract

The focus of this study was to explore how various fertilizers influence the movement of cadmium in soil treated with biochar. The research utilized a strong acid sandy loam soil from Chanthaburi Province, naturally rich in organic matter with moderate cation exchange capacity and low nitrogen, potassium, phosphorus, sulfate, salinity and chloride levels. The soil was purposely contaminated with 50 mgkg<sup>-1</sup> of cadmium and treated with biochar derived from water hyacinth through pyrolysis at 450°C for an hour. This biochar displayed moderate alkalinity, high organic matter, phosphorus, potassium, and cation exchange capacity, but low nitrogen content. Analytical techniques like Scanning Electron Microscopy and Fourier-Transform Infrared Spectroscopy were employed to study the surface characteristics of the biochar. The cadmium adding soil was blended with 10% biochar and various chemical fertilizers at a 0.04% ratio. Diethylenetriamine pentaacetate (DTPA) extraction was used to assess the bioavailability of cadmium to plants in the soil, while sequential extraction was conducted to identify the different forms of cadmium present in the soil. The study revealed distinct effects of different fertilizers on cadmium mobility. Fertilizers like 46-0-0 and 0-3-0 caused a transformation of cadmium from stable to less stable forms, increasing the bioavailability of cadmium to plants. Conversely, fertilizers such as 15-15-15, 0-0-50, 0-0-60, and 0-52-34 shifted cadmium from less stable to more stable forms, resulting in decreased cadmium extracted by DTPA. Other fertilizers showed no significant impact on cadmium mobility in the soil. A stepwise linear regression analysis highlighted that nitrogen content, potassium content, and electrical conductivity were influential factors affecting cadmium mobility.

### ARTICLE HISTORY

Received: 17 Nov. 2023

Accepted: 7 Mar. 2024

Published: 27 Mar. 2024

### KEYWORDS

Acid soil;  
Biochar;  
Cadmium;  
Fertilizers;  
Sequential extraction

### Introduction

Chanthaburi Province is renowned for its agricultural prowess, with a focus on cultivating a variety of fruits such as durian, mangosteen, rambutan, sala, rakam, longkong, longan, and santol. Fruits are a vital economic crop for the region. To optimize crop growth and yield, the use of chemical fertilizers and herbicides is common practice. Additionally, the cultivation process involves the use of equipment and materials that can introduce various heavy metals. An associated activity is the burning of agricultural waste, further contributing to the accu-

mulation of chemicals in the soil. Some of these substances have low degradability, resulting in their long-term persistence in the soil. Heavy metals, including copper, zinc, cadmium, and lead, have been found to accumulate in the soil due to these agricultural practices. Plants growing in these contaminated soils can absorb these heavy metals, which then become distributed throughout various plant parts. Consequently, these heavy metals can enter the human food chain, posing risks to the health of animals, plants, and humans [1–2]. Cadmium, in particular, is a hazardous element, with high-level exposure

causing lung damage and potential fatality. Chronic exposure to low levels of cadmium, found in air, food, water, and tobacco smoke, may lead to kidney disease and weakened bones [3]. Cadmium is also classified as a carcinogen [4]. Furthermore, cadmium toxicity can detrimentally affect plant health, impacting chlorophyll biosynthesis, photosynthesis, water regulation, and hormonal and nutritional balance [5].

Biochar, an organic material produced through slow pyrolysis, has emerged as a promising solution for mitigating heavy metal contamination in agricultural soils [6]. Researchers have found that biochar possesses high porosity, negatively charged surfaces, and a strong capacity for adsorbing positively charged ions. Introducing biochar to soils has been shown to reduce the uptake of heavy metals by plants [7–9]. Biochar, an economical and efficient adsorbent, can be derived from diverse biomass sources like agricultural waste, sewage sludge, crop residues, manures, forestry byproducts, and various solid waste materials. Determining the optimal material is challenging since the production of biochar at varying temperatures, heating rates, and durations yields differing performance outcomes [10]. Crucial factors in material selection for biochar production include accessibility, cost-effectiveness, minimal local environmental impact, and high carbon content. Water hyacinth, a fast-spreading weed that is rich in carbon content (comprising 20% cellulose, 48% hemicellulose, and 3.5% lignin), serves as an attractive organic material for biochar production [11].

Farmers in the region commonly rely on chemical fertilizers to enhance plant growth. Cadmium can be found in some fertilizers, such as mineral phosphate fertilizers. Its concentration varying based on the phosphate rock type (apatite and phosphorite), commonly comprising phosphate dioxide ( $P_2O_5$ ), lime, clay, gypsum, dolomite, silica, and an array of other minerals, including heavy metals and metalloids like cadmium, lead, and arsenic [12]. The application of certain fertilizers has the potential to elevate cadmium levels in the soil. The chemical properties of these fertilizers can have varying effects on the concentration and mobility of heavy metals in the soil. Some fertilizers may facilitate the movement of heavy metals within the soil, potentially increasing their uptake by plants, while others may have the opposite effect. This issue is interesting to study further.

Soil comprises air, water, inorganic components (such as sand, silt, clay, silica, alumina, and iron oxide), and organic matter (including carbohydrates, amino acids, proteins, lipids, nucleic acids, lignins, and humic substances). The mineral and organic colloidal particles of the solid phase are the most active soil components in the adsorption processes. Various factors, including soil pH, organic content, and the type and quantity of

ions and metals present, affect the soil's adsorption capacity. The adsorption mechanisms through which heavy metals from the soil solution interact with soil constituents vary, involving processes such as functional groups complexation, physical adsorption, ion exchange, and coprecipitation. These mechanisms either augment or diminish the movement of cadmium [13].

The researcher aimed to identify the specific factors within fertilizers that have the most significant impact on the mobility of cadmium in the soil amended with biochar. The experiment was designed to feed data regarding the characteristics of 10 different fertilizer types and the outcomes of cadmium extraction from the soil into a stepwise linear regression program. The program assists in forecasting which factors influence either the decrease or increase of cadmium movement within the soil amended with biochar. The findings from this experiment will provide insights into the potential effects of using specific types of fertilizers. This knowledge can be applied to better manage soil quality in the future. Additionally, different forms of cadmium were analyzed before and after through sequential extraction to elucidate the adsorption or de-sorption of cadmium following each fertilizer application.

## Materials and methods

### 1) Soil, fertilizer, and biochar preparation

The original soil sample was obtained from an undisturbed area in Chanthaburi Province, specifically at coordinates N13°50'32.1252" E101°9'5.6808, at a depth of 0–30 cm. This soil preparation process involved sun drying and subsequent grinding using a stone mortar. After grinding, the soil was sifted through a 20-mesh sieve. Following this, the soil was further dried in an oven at 105°C for 24 hours.

In this research, ten different fertilizer formulas were employed, each represented by its N-P-K (Nitrogen-Phosphorus-Potassium) ratio, as follows: 0-0-60, 0-52-34, 0-0-50, 0-3-0, 46-0-0, 16-20-0, 13-0-46, 13-13-21, 15-15-15, and 18-12-6. The fertilizers selected for this study are commonly utilized in Thailand across various crops and plants, including field crops, garden plants, ornamentals, and a range of vegetables. Their diverse compositions in terms of nitrogen (N), phosphorus (P), and potassium (K) content will be instrumental in examining how varying levels of N, P, and K contribute to the process of cadmium fixation in the soil. To prepare these fertilizers for the study, all of them, except for urea (fertilizer formula 46-0-0), underwent a process of crushing and sieving through a No. 20 sieve. This preparation ensured that the fertilizers were in a consistent and uniform form for application in the research experiments.

The water hyacinth used in the study was sourced from the Lad Krabang area in Bangkok. To prepare it for further use, the leaves and stems of the water hyacinth underwent several rounds of washing with clean water. After washing, the plant material was sun-dried and then placed in an oven at a temperature of 105°C for 24 hours. Once the water hyacinth was thoroughly dried, it underwent a pyrolysis process. During this process, the dried plant material was exposed to a temperature of 450°C for one hour. Subsequently, the pyrolyzed material was sieved through a 35-mesh sieve to ensure a consistent particle size for use in the research.

## 2) Chemical characterization of soil, fertilizer, and biochar

Soil particle distribution was assessed using the hydrometer method. Electrical conductivity (EC) was determined with a conductivity meter (Mettler model UM400) and pH levels were measured using a pH meter (Consort model C860). Chloride ion concentration was quantified using the argentometric method. Sulfate ion content was measured via the turbidimetric method. Cation exchange capacity (CEC) was determined using the Ammonium acetate method. Organic matter content was assessed through Walkley-Black titrations. Total nitrogen content was analyzed using the Kjeldahl method. Available phosphorus content was determined using the Bray II method. Available potassium content was assessed through Ammonium acetate extraction [14–15]. Additionally, the concentration of cadmium (Cd) in all samples was analyzed through acid digestion (HCl/HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) before determination using an Atomic Absorption Spectrophotometer (AAS: Perkin Elmer model Analyst 200) [16]. The soil's neutralization capability was examined through a titration method [17]. To investigate the biochar's surface properties and functional groups, Scanning Electron Microscope (SEM: Leo model 1455 VP) and Fourier-Transform Infrared Spectrometer (FTIR: Perkin Elmer model Spectrum GX) were employed.

## 3) Experimental method

Synthetic cadmium contaminated soil (SS) was produced by combining original soil with a precisely controlled cadmium concentration of 50 mg kg<sup>-1</sup>. Then, the synthetic cadmium contaminated soil with biochar (SBS) was formulated by blending the synthetic cadmium contaminated soil (SS) with 10% biochar. Both SS and SBS were left to settle at room temperature for a month. Following this, the SBS was treated with 0.04% chemical fertilizers and allowed to stand at room temperature for another two weeks. Subsequently, the soil underwent extraction using 0.005 M diethylenetriamine pentaacetate (DTPA) [18]. The concentration of cadmium in the resulting extract was assessed the AAS. To determine the cadmium

concentration in various fractions, a sequential extraction process was employed. This process aimed to analyze cadmium distribution in six fractions, including the water-soluble fraction, exchangeable fraction, carbonate-bound fraction, Fe-Mn oxide-bound fraction, organically bound fraction, and residual fraction.

## 4) Statistical analysis

Each set of experiments was conducted in three separate trials. The mean and standard deviation of the experimental data were calculated. To assess the statistical significance (at a 95% confidence level) of differences between two or more groups of data, the one-way analysis of variance (ANOVA) was employed, using SPSS version 23. A stepwise linear regression program was then applied to investigate the correlation between the chemical characteristics of fertilizers and the mobility of cadmium. In this analysis, the dependent variable was the cadmium content in the DTPA-extracted samples. The independent variables considered included pH, electrical conductivity, organic matter, total nitrogen, chloride, available potassium, available phosphorus, and sulfate.

## Results and discussion

### 1) Characteristic of soil, fertilizer, and biochar

The concentration of cadmium in all sample was shown in Table 1.

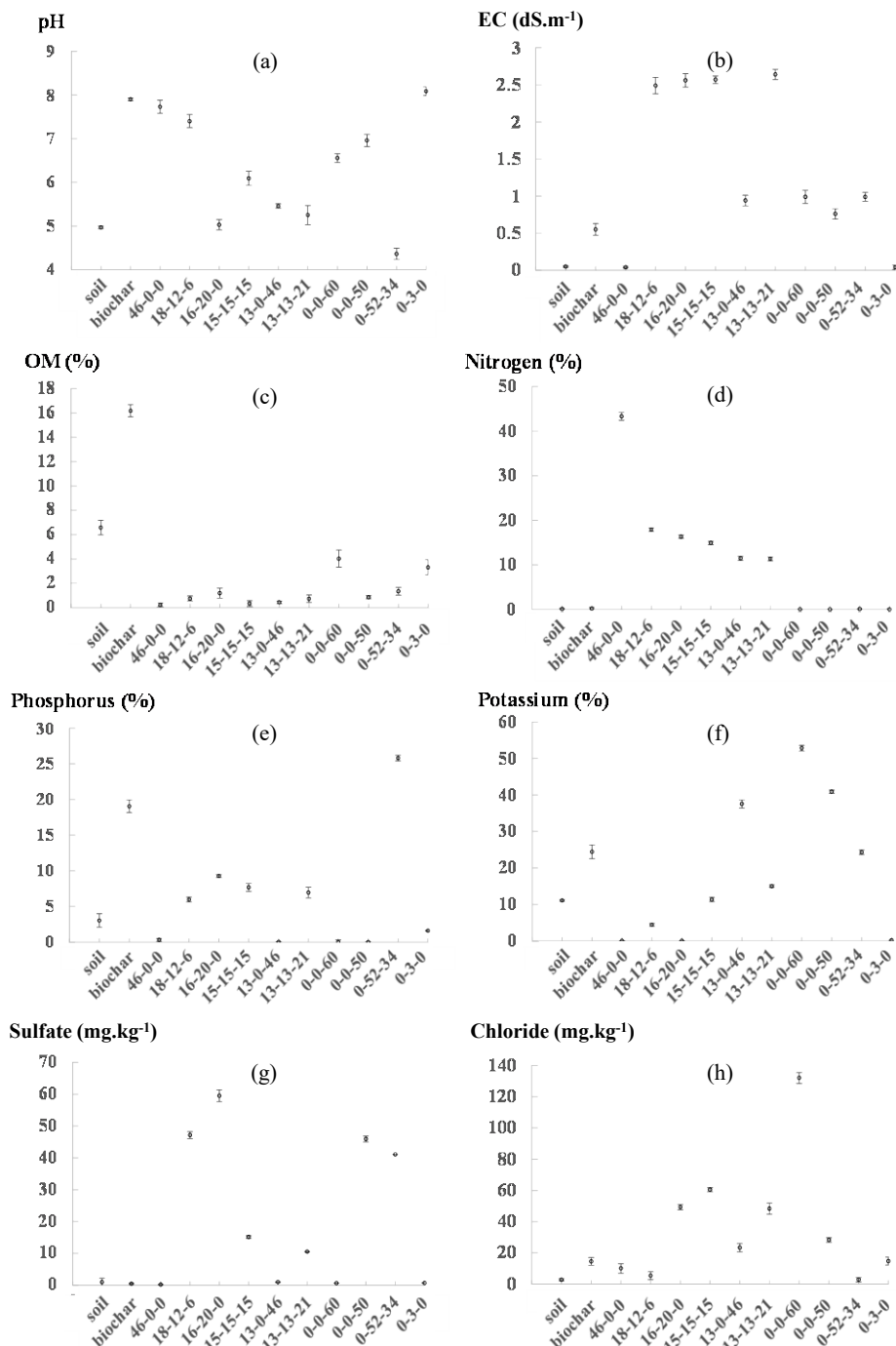
According to the data presented in Table 1, the cadmium concentration in the SS was higher than what is typically found in natural environments, but it still fell within the acceptable limit for agricultural use (the acceptable limit being Cd < 762 mg kg<sup>-1</sup>) [19]. On the other hand, the cadmium content in the biochar was lower than that in the SS and remained below the permitted threshold for soil application. These thresholds can vary, with the maximum allowed limits for cadmium in soil ranging from 1.4 to 39 mg kg<sup>-1</sup> [20]. Therefore, the addition of biochar did not lead to a significant increase in cadmium content in the soil. Furthermore, the concentration of heavy metals in all the studied fertilizers was well within the standard limits for agricultural use, with the acceptable limit for cadmium being less than 10 mg kg<sup>-1</sup> [21].

The analysis of soil from Chanthaburi Province revealed a sandy loam composition with the following particle distribution: 81.52% sand, 0.72% silt, and 17.76% clay. The CEC value, which reflects the soil's ability to release or absorb nutrients, falls within the moderate range (15–25 cmol kg<sup>-1</sup>). This property can be influenced by various factors such as clay type, nutrient content, organic matter levels, and soil pH. In the case of the studied soil, the CEC value is moderate, and it generally falls in the range of 2–20 cmol.kg<sup>-1</sup> for most agri-

cultural soils. The biochar exhibited an acid neutralization capability (ANC) of  $4,997.90 \text{ meq kg}^{-1}$ , while Venegas et al. [17] reported ANC values of  $4,280 \text{ meq kg}^{-1}$  for municipal organic waste and  $421 \text{ meq kg}^{-1}$  for biochar derived from bark. Materials with a high ANC are ideal for use as absorbents because they can effectively raise soil pH levels. The CEC of the biochar was measured at  $26.90 \text{ cmol kg}^{-1}$ . Biochar with high CEC could reduce the movement of heavy metals [22]. The more detailed information about the characteristics of original soil, biochar and fertilizers was shown Figure 1.

**Table 1** Cadmium concentration in samples

Sample	Concentration ( $\text{mg kg}^{-1}$ )	Fertilizer	Concentration ( $\text{mg kg}^{-1}$ )
Original soil	$6.89 \pm 0.02$	0-0-50	$1.10 \pm 0.59$
SS	$49.91 \pm 0.62$	0-0-60	$0.04 \pm 0.13$
Biochar	$1.02 \pm 0.21$	0-3-0	$5.10 \pm 0.53$
		0-52-34	$1.60 \pm 0.09$
		13-0-46	$0.35 \pm 0.05$
		13-13-21	$0.23 \pm 0.07$
		15-15-15	$1.15 \pm 0.36$
		16-20-0	$10.10 \pm 0.74$
		18-12-6	$1.15 \pm 0.10$
		46-0-0	$0.65 \pm 0.05$

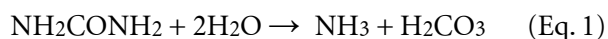


**Figure 1** Chemical properties of samples including (a) pH, (b) electrical conductivity, (c) organic matter, (d) total nitrogen, (e) available phosphorus, (f) available potassium, (g) sulfate and (h) chloride.

The soil in Chanthaburi Province was characterized by its acidity, with a pH ranging from 4.5 to 5 [14]. In acidic soils, heavy metals tend to exhibit high mobility [23–24]. The levels of salinity and chloride content were within a range that did not adversely affect plant growth. The soil's organic matter primarily consisted of humic substances, carbohydrates, proteins, and humus. The soil had a high organic matter content, exceeding 4.5%, making it suitable for plant cultivation. However, the concentrations of nitrogen, phosphorus, potassium, and sulfate in the soil were insufficient for plant growth, necessitating the use of fertilizer. In acidic soil conditions, phosphorus exists in the form of  $\text{H}_2\text{PO}_4^-$ , while in alkaline soils, it takes the form of  $\text{HPO}_4^{2-}$ .

The biochar exhibited a moderate level of alkalinity, with a pH exceeding the standard value typically recommended for biochar used in soil improvement (standard value: pH 7.5) [20]. The elevated pH of the biochar can enhance the binding of metal ions to its surface, leading to a reduction in the mobility of heavy metals [25–26]. Salinity levels in the biochar were well within acceptable limits, remaining below  $7.30 \text{ ds m}^{-1}$  [20]. The biochar contained abundant organic matter, phosphorus, and potassium, making it a valuable resource for enhancing soil fertility. However, the biochar had relatively low concentrations of nitrogen and sulfate.

The fertilizer formula 46-0-0, which is urea, has a pKb of 13.9, suggesting it should be neutral. However, urea can undergo gradual hydrolysis, producing ammonia and carbonic acid as shown in Eq. 1 [27]. The carbonic acid can then convert to carbon dioxide, making the solution more basic due to the presence of ammonia. Applying high-pH fertilizers to soils may lead to heavy metal precipitation.



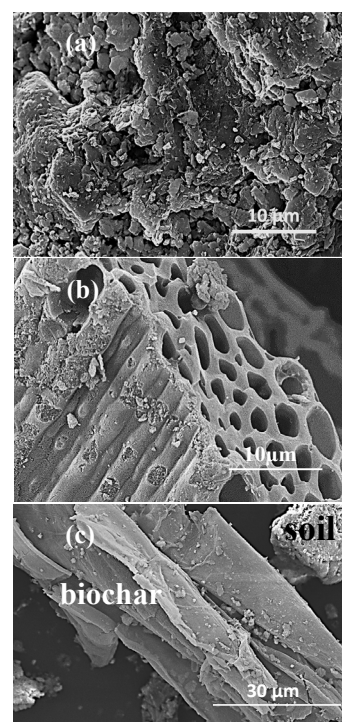
The fertilizer 18-12-6 is composed of diammonium phosphate, ammonium sulfate, and potassium chloride. Diammonium phosphate, being a salt of a weak base ( $3 < \text{pKb} < 6$ , ammonia) and a moderately strong polyprotic acid ( $\text{H}_3\text{PO}_4$ ), results in a slightly basic initial pH. This alkalinity arises from the hydrolysis reaction of the phosphate anion, generating  $\text{OH}^-$  ions. On the other hand, fertilizer 16-20-0 contains mono-ammonium phosphate (acid) and ammonium sulfate. The hydrolysis of mono-ammonium phosphate can produce phosphoric acid and ammonium hydroxide, as depicted in Eq. 2.



The pH levels of fertilizers 16-20-0, 13-0-46, and 13-13-21 fall within the 5.0–5.5 range. When acidic fertilizers are introduced to the soil, it can lead to a decrease

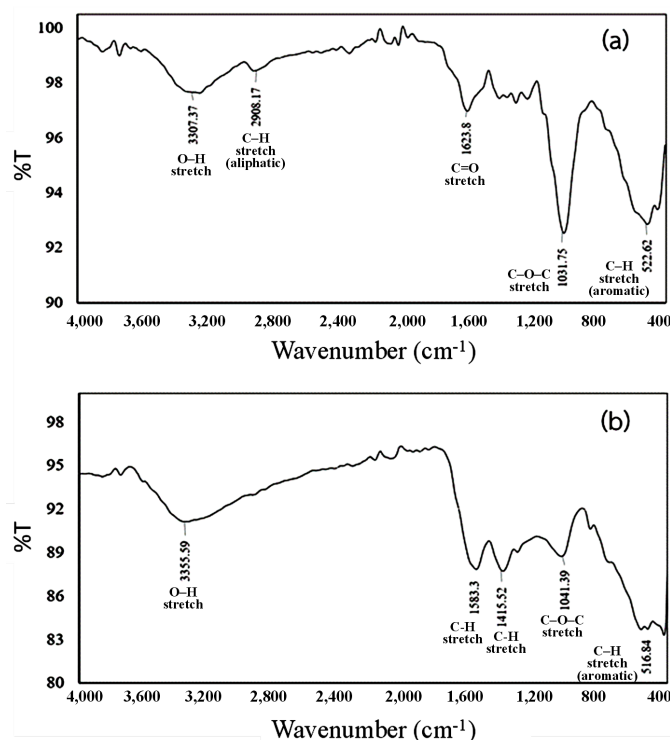
in soil pH. This shift can, in turn, enhance the mobility of heavy metals [28]. Rock phosphate (0-3-0) comprises phosphorus, silica, clay, and limestone [29]. The elevated pH of rock phosphate is attributed to the limestone it contains. The organic matter observed in rock phosphate (Figure 1(c)) originates from clay. Fertilizers 0-0-60 and 0-0-50, made up of potassium chloride and potassium sulfate, respectively, are neutral fertilizers. The highest chloride ion concentration is found in fertilizer 0-0-60 (Figure 1(h)). Fertilizer 0-52-34, containing mono-potassium phosphate (a strong acid) and potassium sulfate, exhibits a high sulfate content, as shown in Figure 1(g). Figure 1g also highlights the high sulfate content in fertilizers 18-12-6, 0-0-50, 16-20-0, and 0-52-34. Electrical conductivity is intricately tied to soil salinity levels, and from Figure 1(b), it's evident that fertilizers 13-13-21, 15-15-15, 18-12-6, and 16-20-0 contribute to higher salinity. Introducing these fertilizers may elevate soil salinity, potentially impacting cadmium mobility and uptake by plants [30]. Moreover, increased salinity could adversely affect the yield of salinity-sensitive crops [31]. The total nitrogen content (Figure 1(d)), available phosphorus (Figure 1(e)), and available potassium (Figure 1(f)) in the fertilizers show proportional relationships to their respective formulas. The use of nitrogen fertilizers has been associated with an increased uptake of heavy metals by plants [32–33].

The SEM image of soil and biochar are available in Figure 2. The FTIR spectra of biochar are available in Figure 3.



**Figure 2** SEM images of the soil sample (a) at 10,000 times magnification, the biochar sample (b) at 10,000 times magnification, and the mixed sample of soil and biochar (c) at 5,000 times magnification.





**Figure 3** FTIR spectra of (a) water hyacinth (b) biochar.

Figure 2(a) showed a soil surface that was rough and had relatively few pores. In Figure 2(b), the surface characteristics of the biochar were depicted, revealing a notably rough, layered, and extensively porous structure. This distinctive morphology is attributed to the liberation of volatile substances and the thermal breakdown of the original biomass. The substantial porosity observed in the biochar renders it particularly suitable for soil amendment applications. This is because the high porosity facilitates the infiltration and assimilation of water, nutrients, and heavy metals within its intricate network of pores, as documented in previous studies [34].

The FTIR analysis of water hyacinth, illustrated in Figure 3(a), highlighted several notable bands. These encompassed the  $3,307.37\text{ cm}^{-1}$  band (representing O–H stretching vibrations of hydrogen-bonded hydroxyl groups),  $2,908.17\text{ cm}^{-1}$  (indicating  $\text{CH}_2$  stretching vibrations in aliphatic groups),  $1,623.8\text{ cm}^{-1}$  (reflecting C=O stretching found in ketones, aldehydes, and esters),  $1,031.75\text{ cm}^{-1}$  (associated with C–O–C stretching present in cellulose and hemicellulose), and  $522.62\text{ cm}^{-1}$  (depicting C–H bonding in aromatic and heteroatomic compounds). Upon undergoing pyrolysis, the C–O–C stretching band diminished, and the  $\text{CH}_2$  stretching vibrations for aliphatic groups disappeared, as demonstrated in Figure 3(b). Conversely, the peak at  $1,522.62\text{ cm}^{-1}$  (representing CH bending vibrations in  $\text{CH}_2$  units of biopolymers) became more pronounced. These functional groups on the biochar's surface could actively engage in the adsorption of heavy metals [34].

## 2) The influence of fertilizers on the mobility of cadmium

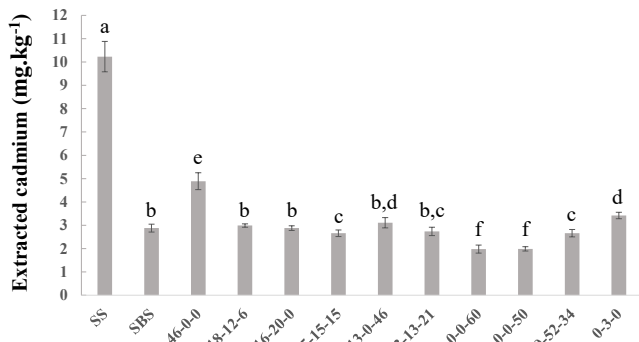
The study utilized SS made up of the original soil with an added cadmium concentration of  $50\text{ mg.kg}^{-1}$ . Subsequently, the SBS was developed, combining the original soil with the introduced cadmium and 10% biochar. Following this, ten distinct fertilizers were integrated into the SBS. The evaluation of cadmium extraction from the soil samples were carried out utilizing a  $0.005\text{ M}$  DTPA solution. This process aimed to assess the soil's heavy metal bioavailability for potential uptake by plants. The results and findings derived from this extraction and evaluation were depicted in Figure 4.

In Figure 4, biochar demonstrated a capability to decrease the movement of cadmium within the soil by about 15%. However, upon the introduction of fertilizer 46-0-0 and 0-3-0 to the synthetic soil containing biochar, there was an observed increase in the mobility of cadmium. Conversely, the application of fertilizers such as 15-15-15, 0-52-34, 0-0-60, and 0-0-50 resulted in a reduction in the mobility of cadmium. The remaining fertilizers did not significantly impact the mobility of cadmium in the soil.

The findings obtained from the DTPA extraction were subjected to analysis using a stepwise linear regression program, resulting in the formulation of Eq. 3.

$$y_{\text{Cd}} = 0.0366 N - 0.0183 K + 0.3736 \text{ EC} + 3.3748 \quad (\text{Eq. 3})$$

where,  $y_{\text{Cd}}$  = Extracted cadmium concentration by DTPA ( $\text{mg.kg}^{-1}$ ),  $N$  = Total nitrogen concentration (%),  $K$  = Available potassium concentration (%) and  $\text{EC}$  = Electrical conductivity ( $\text{ds.m}^{-1}$ ).



**Figure 4** The concentration of extracted cadmium by DTPA.

The stepwise linear regression analysis revealed that certain factors, specifically total nitrogen, available potassium, and electrical conductivity, significantly influenced the mobility of cadmium in the soil. Increased nitrogen content and higher electrical conductivity in fertilizer were linked to elevated cadmium mobility in the soil. The higher the electrical conductivity, the higher the mass transfer rate. This finding aligns with Laing et al. [30] and Hassan et al. [33]. Fertilizers containing more potassium demonstrated increased cadmium adsorption in the soil, consistent with Chen et al. [35]. Cations with higher valence displaced and adhered to the soil surface more effectively than those with lower valence. Potassium's addition facilitated the diffusion of biochar porosity, enhancing heavy metal adsorption efficiency. Other factors like sulfate, chloride, and organic matter might exert some influence on cadmium immobility, although their impact is not considered significant. For instance, cadmium can form cadmium sulfate, reducing its mobility, and the addition of fertilizer 0-0-60 with

higher organic matter, resulted in lower cadmium concentration in the extracted solution compared to when no fertilizer was added to the soil. Additionally, cations, especially transition metals, were capable of forming metal-organic complexes with organic compounds. Chloride demonstrated an adsorption effect by binding to cadmium ions, forming inner sphere complexes on the surface.

Following the application of fertilizers to the SBS, the concentration of Cd in different forms underwent alterations, as observed through a sequential extraction method. These changes in Cd concentration across various forms were depicted in Table 2.

Heavy metals found in water-soluble, exchangeable, and carbonate-bound states are acknowledged as unstable forms, whereas more stable forms include those bound to Fe-Mn oxides, organic matter, and in residual states. Table 2 showcases the impact of fertilizer applications, such as 46-0-0 and 0-3-0, in transforming cadmium from stable to less stable states, accounting for about 40% and 20%, respectively. The transition of cadmium into its less stable state is often linked to its conversion into the carbonate form due to the presence of carbonates within these fertilizers. Conversely, the use of fertilizers like 15-15-15, 0-0-50, 0-0-60, and 0-52-34 facilitated a shift of cadmium from less stable to more stable forms, representing approximately 6%, 32%, 35%, and 10%, respectively. In this context, cadmium in its less stable form was primarily converted into Fe-Mn oxide-bound and organic matter-bound forms. This conversion tendency was prominent due to the prevalence of iron oxide, manganese oxide, and a substantial organic matter content within the soil under study. These observations aligned well with the trends identified in Figure 4.

**Table 2** The changes in Cd concentration across various forms

Fertilizer	Water soluble	Exchangeable	Carbonate bound	Fe-Mn oxide bound	Organic bound	Residual
46-0-0	+5	+10	+25	-9	-18	-10
18-12-6	+1	-0.1	+0.5	-1	-1	-1
16-20-0	+0.5	-0.1	+0.2	-0.3	-0.5	-0.2
15-15-15	-6	-3	-2	+1	+2	+4
13-0-46	+0.5	+0.6	+0.8	-1	-2	-1
13-13-21	-0.5	-1	0	+1	-0.1	+2
0-0-60	-15	-5	-10	+10	+19	+4
0-0-50	-6	-5	-16	+10	+14	+4
0-52-34	-2	-3	-3	+5	+2	+2
0-3-0	+2	+4	+14	-9	-3	-9

Remark: - means the concentration in such form was reduced and + means the concentration in such form was increased.

## Conclusions

The inclusion of biochar led to a substantial 71.8% reduction in cadmium mobility within the soil. Fertilizers with increased nitrogen content, exemplified by 46-0-0, significantly enhanced the mobility of cadmium, causing it to transition from a more stable form to a less stable

form. Application of fertilizer with a high nitrogen content to nourish cadmium-contaminated soil, plants growing in the soil may absorb more cadmium to various part of plant. Conversely, fertilizers with high potassium content, such as 0-0-50 and 0-0-60, played a role in diminishing cadmium mobility, prompting a shift from a less stable

form to a more stable form. Furthermore, EC emerged as a critical factor influencing the immobilization of cadmium in the soil. Understanding that nitrogen-rich fertilizers can exacerbate issues in cadmium-contaminated soil enables us to manage fertilizer application more effectively. While it's unavoidable to forgo nitrogen fertilizer entirely, its addition should be prudent and based on necessity. When using mixed fertilizers, it's crucial to avoid formulas with excessive nitrogen; however, an abundance of potassium might yield positive effects.

## References

- [1] Shojaei, S., Jafarpour, A., Shojaei, S., Gyasi-Agyei, Y., Rodrigo-Comino, J. Heavy metal uptake by plants from wastewater of different pulp concentrations and contaminated soils. *Journal of Cleaner Production*, 2021, 296, 126345.
- [2] Steingr aber, L.F., Ludolphy, C., Metz, J., Kierdorf, H., Kierdorf, U. Uptake of lead and zinc from soil by blackberry plants (*Rubus fruticosus* L. agg.) and translocation from roots to leaves. *Environmental Advances*, 2022, 9, 100313.
- [3] Centers for Disease Control and Prevention, Cadmium Factsheet | National Biomonitoring Program – CDC, [Online] Available from: [https://www.cdc.gov/biomonitoring/Cadmium\\_FactSheet.html](https://www.cdc.gov/biomonitoring/Cadmium_FactSheet.html) [Accessed 8 November 2023]
- [4] Waalkes, M.P. Cadmium carcinogenesis. *Mutation Research*, 2003, 533(1–2), 107–120.
- [5] Qadir, S., Jamshied, S., Rasool, S., Ashraf, M., Akram, N.A., Ahmad, P. Modulation of plant growth and metabolism in cadmium-enriched environments. *Reviews of Environmental Contamination and Toxicology*, 2014, 229, 51–88.
- [6] Lee, Y., Eum, P.R.B., Ryu, C., Park, Y.K., Jung, J.H., Hyun, S. Characteristics of biochar produced from slow pyrolysis of *Geodae-Uksae*. *Bioresource Technology*, 2013, 130, 345–350.
- [7] Nkoh, J.N., Ajibade, F.O., Atakpa, E.O., Abdulh al Baquy, M., Mia, S., Odii, E.C., Xu, R. Reduction of heavy metal uptake from polluted soils and associated health risks through biochar amendment: A critical synthesis. *Journal of Hazardous Materials Advances*, 2022, 6, 100086.
- [8] Helaoui, S., Boughattas, I., Mkhinini, M., Chebbi, L., Elkribi-Boukhris, S., Alphonse, V., ..., Bousserhine, N. Biochar amendment alleviates heavy metal phytotoxicity of *Medicago sativa* grown in polymetallic contaminated soil: Evaluation of metal uptake, plant response and soil properties. *Plant Stress*, 2023, 10, 100212.
- [9] Bashir, S., Hussain, Q., Shaaban, M., Hu, H. Efficiency and surface characterization of different plant derived biochar for cadmium (Cd) mobility, bioaccessibility and bioavailability to Chinese cabbage in highly contaminated soil. *Chemosphere*, 2018, 211, 632–639.
- [10] Kamarudin, N.S., Dahalan, F.A., Hasan, M., An, O.S., Parmin, N.A., Ibrahim, N., ..., Wikurendra, E.A. Biochar: A review of its history, characteristics, factors that influence its yield, methods of production, application in wastewater treatment and recent development. *Biointerface Research in Applied Chemistry*, 2022, 12(6), 7914–7926.
- [11] Ajithram, A., Winowlin Jappes, J.T., Brintha, N.C. Investigation on utilization of water hyacinth aquatic plants towards various bio products – Survey. *Materials Today: Proceedings*, 2012, 45, 2040–2045.
- [12] Suci , N.A., Vivo, R.D., Rizzati, N., Capri, E. Cd content in phosphate fertilizer: Which potential risk for the environment and human health? *Current Opinion in Environmental Science & Health*, 2022, 30, 100392.
- [13] Tan, K.H. Principles of soil chemistry, 4<sup>th</sup> Editions, CRC Press, Taylor & Francis Group, Florida, USA, 2011, 1–362.
- [14] Land Development Department, A handbook for analyzation of samples of soil, water, fertilizer, plants, soil conditioners and analysis for product certification (vol. 1), W.J. Property Co., Ltd., Bangkok, Thailand, 2014, 1–184.
- [15] Land Development Department, A handbook for analyzation of samples of soil, water, fertilizer, plants, soil conditioners and analysis for product certification (Vol. 2), W.J. Property Co., Ltd., Bangkok, Thailand, 2014, 1–254.
- [16] US. EPA: Acid digestion of sediments, sludges and soil / SW-846 Method 3050b, 1996. [Online] Available from: <https://www.epa.gov/sites/default/files/2015-06/documents/epa-3050b.pdf> [Accessed 8 November 2023].
- [17] Venegas, A., Rigol, A., Vidal, M. Viability of organic wastes and biochars as amendments for the remediation of heavy metal-contaminated soils. *Chemosphere*, 2015, 119, 190–198.
- [18] Lindsay, W.L., Norvell, W.A. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Science Society of America Journal*, 1978, 42, 421–428.
- [19] Announcement of the National Environment Board No. 25. Subject: Setting soil quality standards, 2021. [Online] Available from: <https://www.pcd.go.th/laws/25162> [Accessed 8 November 2023].



- [20] Initiative IB: Standardized product definition and product testing guidelines for biochar that is used in soil: IBI – std – 2.1, 2015. [Online] Available from: [https://biochar-international.org/wp-content/uploads/2020/06/IBI\\_Biochar\\_Standards\\_V2.1\\_Final2.pdf](https://biochar-international.org/wp-content/uploads/2020/06/IBI_Biochar_Standards_V2.1_Final2.pdf) [Accessed 2 November 2023]
- [21] Food and Agriculture Organisation of the United Nation, Agricultural and Veterinary Products (Control of Use) Regulations, 2017. [Online] Available from: <https://www.fao.org/faolex/results/details/en/c/LEX-FAOC180012/> [Accessed 2 November 2023].
- [22] Abdel-Fattah, T.M., Mahmoud, M.E., Ahmed, S.B., Huff, M.D., Lee, J.W., Kumar, S. Biochar from woody biomass for removing metal contaminants and carbon sequestration. *Journal of Industrial and Engineering Chemistry*, 2015, 22, 103–109.
- [23] Kashem, M.A., Singh, B.R. Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. *Nutrient Cycling in Agroecosystems*, 2001, 61, 247–255.
- [24] McCauley, A., Jones, C., Jacobsen, J. Nutrient management module 8: Soil pH and organic matter, USA: Montana State University, 2009, [Online] Available from: <https://www.certifiedcropadviser.org/files/certifications/certified/education/self-study/exam-pdfs/38.pdf> [Accessed 2 November 2023].
- [25] Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environmental Pollution*, 2010, 158(6), 2282–2287.
- [26] Beesley, L., Marmiroli, M. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environmental Pollution*, 2011, 159, 474–480.
- [27] Sigurdarson, J.J., Svane, S., Karring, H. The molecular processes of urea hydrolysis in relation to ammonia emissions from agriculture. *Reviews in Environmental Science and Bio/Technology*, 2018, 17, 241–258.
- [28] Sun, L., Zhang, G., Li, X., Zhang, X., Hang, W., Tang, M., Gao, Y. Effects of biochar on the transformation of cadmium fractions in alkaline soil. *Heliyon*, 2023, 9(1), e12949.
- [29] Sadeddin, W., Abu-Eishah, S.I. Minimization of free calcium carbonate in hard and medium-hard phosphate rocks using dilute acetic acid solution. *International Journal of Mineral Processing*, 1990, 30, 113–125.
- [30] Laing, G., Vos, R., Vandecasteele, B., Lesage, E., Tack, F., Verloo, M. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. *Estuarine, Coastal and Shelf Science*, 2008, 77(4), 589–602.
- [31] United States Salinity Laboratory Staff: Chloride by titration with silver nitrate. In L.A. Richards et al. (Editors), *Diagnosis and improvement of saline and alkali soils*, Ag. Handbook 60, USDA, Washington, D.C, 1954, 98–99. [Online] Available from: [https://www.ars.usda.gov/ARSUserFiles/20360500/hb60\\_pdf/hb60complete.pdf](https://www.ars.usda.gov/ARSUserFiles/20360500/hb60_pdf/hb60complete.pdf)
- [32] Oliver, D., Schultz, J.E., Tiller, K.G., Merry, R. The effect of crop rotations and tillage practices on cadmium concentration in wheat grain. *Australian Journal of Agricultural Research*, 1993, 44, 1221–1234.
- [33] Hassan, M.J., Wang, F., Ali, S., Zhang, G. Toxic effect of cadmium on rice as affected by nitrogen fertilizer form. *Plant and Soil*, 2005, 277, 359–365.
- [34] Sahoo, S.S., Vijay, V.K., Chandra, R., Kumar, H. Production and characterization of biochar produced from slow pyrolysis of pigeon pea stalk and bamboo. *Cleaner Engineering and Technology*, 2021, 3, 100101.
- [35] Chen, S., Sun, L., Sun, T., Chao, L., Guo, G. Interaction between cadmium, lead and potassium fertilizer (K<sub>2</sub>SO<sub>4</sub>) in a soil-plant system. *Environmental Geochemistry and Health*, 2007, 29(5), 435–446.