Research article

The Impact of Organic and Chemical Organic Fertilizers on the Efficiency of Cadmium Mobility Reduction by Potassium Hydroxide Modified Biochar

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Abstract

Keywords

acid soil;
modified biochar;
cadmium;
crude oil;
DTPA;
organic fertilizers;
sequential extraction

The aim of this study was to investigate the impact of organic and chemical organic fertilizers on the translocation of cadmium in crude oil-contaminated soil treated with potassium hydroxide-modified biochar (KOH-biochar). The soil sample was collected from Chonburi Province. The soil was characterized as moderately acidic sandy loam with relatively low organic matter, medium salinity, medium cation exchange capacity, and high nutrient levels. The concentration of cadmium in the soil fell within the acceptable range for agricultural use. The KOH-biochar exhibited strong alkalinity, a high carbon/nitrogen (C/N) ratio, and an oxygen/carbon (O/C) ratio. Crude oil was slightly acidic, with high organic matter content and low sulfur and cadmium concentrations. The synthetic soil created in this study composed of 5% crude oil, and 100 mg/kg of cadmium. KOH-biochar, organic and chemical organic fertilizers were applied to this synthetic soil. Subsequently, the soil was subjected to extraction with 0.005 M diethylenetriamine pentaacetate (DTPA), and a sequential extraction method was employed to determine six different forms of cadmium in the soil samples. Cadmium concentrations in the extracts were measured using a graphite furnace atomic absorption spectrophotometer. The findings revealed that fertilizers effectively slowed down the movement of cadmium. Fertilizer application led to the transformation of cadmium from unstable forms to more stable forms within the soil. Fertilizer with the highest organic matter content and pH showed the least cadmium mobility. Increased nitrogen and phosphorus content in the fertilizer resulted in slightly higher cadmium mobility within the soil. Conversely, higher potassium content in the fertilizer led to slightly reduced cadmium mobility in the soil.

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1. Introduction

Contamination of soil with crude oil can result from various incidents including underground reservoir leaks, underground pipeline leaks, and accidents during land oil transportation. In 2022, Thailand's crude oil production reached approximately 28.87 million barrels, involving the drilling of 353 production wells. Among these wells, 82 were located onshore, and 281 were situated in the Gulf of Thailand. Additionally, there were 16 appraisal wells in 2022, 8 of which were onshore and 8 offshore [1]. Chonburi, a province that hosts both oil wells and pipelines for transporting crude oil to refineries, faces an elevated risk of oil seepage into the ground. Furthermore, Chonburi Province boasts numerous industrial estates, including Hemaraj Chonburi Industrial Estate, Amata Nakorn Industrial Estate, Pinthong Industrial Estate, Laem Chabang Industrial Estate, Asia Clean Industrial Estate Chonburi, Yamato Industrial Estate, Ban Bueng Industrial Estate, WHA Chonburi Industrial Estate, and Rojana Industrial Estate [2].

Cadmium (Cd) finds widespread use across various industries such as metal plating, pigment manufacturing, alloy production, and the battery sector [3]. However, the release of cadmium from these industrial processes can lead to water and soil contamination. When plants grow in cadmium-contaminated soil, they tend to absorb cadmium into their seeds, stems, and roots [4-6]. This poses a risk to humans who consume cadmium-contaminated plants as cadmium and its compounds are known for their high toxicity. Exposure to cadmium can result in detrimental effects on various bodily systems including the cardiovascular, gastrointestinal, reproductive, neurological, renal, and respiratory systems, and is also associated with an increased risk of cancer [7].

To mitigate the impact of cadmium contamination and enhance soil quality, biochar is utilized. Biochar has demonstrated an ability to reduce the uptake of heavy metals by plants, offering a promising approach to address this environmental concern [8-11]. Numerous researchers have sought to enhance the quality of biochar through various methods including treatments with steam, alkaline solution, oxidizing agents, acidic solution, metal oxides, and clay minerals. Among these approaches, modifying biochar with potassium hydroxide has emerged as an effective, uncomplicated, and cost-efficient method. Alkali modification is primarily aimed at enhancing surface area, pore volume, and the presence of oxygen-containing functional groups, as evidenced by numerous studies using SEM and FTIR analyses. Researchers have utilized potassium hydroxide-modified biochar to treat wastewater contaminated with various substances, establishing superior treatment efficiency compared to unmodified biochar [12-14]. Furthermore, potassium hydroxide-modified biochar has demonstrated effectiveness in mitigating the mobility of heavy metals within soil [15]. The mechanisms underlying the elimination of contaminants from soil and wastewater by modified biochar primarily involve complex formation, electrostatic behavior, ion exchange, and hydrogen bonding [16].

Fertilizer plays a pivotal role in crop cultivation, and it can potentially influence the effectiveness of biochar in reducing the mobility of cadmium. Therefore, the objective of this research was to investigate the effectiveness of potassium hydroxide-modified biochar (KOH-biochar) in mitigating cadmium mobility in soils contaminated with cadmium and crude oil. This study also delved into the impact of fertilizers on the reduction of cadmium mobility in these soils.

2. Materials and Methods

2.1 Preparation of potassium hydroxide modified biochar (KOH-biochar), fertilizers and synthetic soil

In the research conducted, rice straw was gathered from agricultural areas within Chonburi Province. The collected straw was then cut into small pieces, subjected to multiple washes with clean water, sun-dried, and further dried in an oven at 105°C for a duration of 24 h. Subsequently, the production of biochar involved passing the dried rice straw through a pyrolysis process at 400°C for a span of 4 h. After pyrolysis, the resulting biochar was ground and sieved through a 35-mesh sieve. To modify the biochar, 500 g of it were immersed in a 2 M KOH solution, and the mixture was heated at 65°C for a 24-h period. Following this, the mixture was filtered, rinsed repeatedly with distilled water, and then dried in an oven at 105°C for 24 h [17].

For this research, a total of three organic fertilizers (cow manure, bat manure, earthworm manure) and five chemical organic fertilizer formulas were employed. Each was represented by its nitrogen-phosphorus-potassium (N-P-K) ratio as follows: 10-10-10, 5-5-5, 10-0-0, 0-0-10, and 0-0-20. The fertilizers chosen for this investigation were widely used in Thailand for various crops and plants, encompassing field crops, garden plants, ornamentals, and a variety of vegetables. Their varied compositions in nitrogen (N), phosphorus (P), and potassium (K) content were considered pivotal in analyzing how different levels of N, P, and K influenced the cadmium fixation process in soil. All fertilizers underwent a crushing process and were sieved through a No. 20 sieve to prepare them for experimentation.

A soil sample was procured from an undisturbed area located in Panthong District, Chonburi Province, at a depth of 0-30 cm (coordinates: N13°26'40.6" E101°01'48.4"). Equal amounts of soil samples were collected at nine locations around the area and the samples were mixed together to obtain soil samples representative of the area. This soil sample was subjected to a series of preparatory steps, which included sun-drying, grinding using a stone mortar, sieving through a 20-mesh sieve, and subsequent oven-drying at 105°C for a period of 24 h.

2.2 Physical and chemical characterization of soil, fertilizers and KOH-biochar

The soil's particle distribution was assessed by the hydrometer method, specifically the ASTM No. 1.152H standard. For determining the soil sample acidity or alkalinity, a pH meter (Consort model C860) was employed, while electrical conductivity (EC) was measured using a conductivity meter (Memmert model UM400). Other soil properties, including cation exchange capacity (CEC) (utilizing the ammonium acetate method), organic matter (OM) (determined via Walkley-Black titrations), total nitrogen (measured using the Kjeldahl method), available phosphorus (analyzed through the Bray II method), and available potassium (extracted with ammonium acetate), were assessed following the methods specified by the Land Development Department [18].

Cadmium concentrations in all soil samples were determined through acid digestion ($HClO_4$/HNO_3) and analyzed using a graphite furnace atomic absorption spectrophotometer (GFAAS: Perkin Elmer model PinAAcle 900z) [19]. The ash content of the biochar was determined in accordance with the ASTM D1762-84 method [20]. To investigate the biochar's surface properties and functional groups, a scanning electron microscope (SEM: Leo model 1455 VP) and a Fourier-transform infrared spectrometer (FTIR: Perkin Elmer model Spectrum GX) were employed. Additionally, a CHNS/O analyzer (Thermo quest model Flash smart) was utilized to determine the composition of the KOH-biochar.

2.3 Experimental method

Synthetic soil (SS) was created by combining the soil collected from Chonburi Province with cadmium concentration of 100 mg/kg and 5% crude oil. Subsequently, synthetic soil with biochar (SSB) was formulated by mixing the synthetic soil (SS) with 5% KOH-biochar. Both the synthetic soil (SS) and synthetic soil with biochar (SSB) were left to settle at room temperature for a period of two weeks. Afterward, the synthetic soil with biochar (SSB) was treated with 8% fertilizer and allowed to sit at room temperature for an additional two weeks. After this incubation period, extraction was carried out using a 0.005 M diethylenetriamine pentaacetate (DTPA) solution [21]. The concentration of cadmium in the extract was then determined by employing a graphite furnace atomic absorption spectrophotometer. In addition to the above, a sequential extraction procedure was performed to assess the cadmium concentration in six distinct fractions, which were the water-soluble, exchangeable, carbonate-bound, Fe-Mn oxide-bound, organically bound, and residual fractions [22, 23].

The sequential extraction procedure can be summerized as follows:

Fraction 1 (F1): Water-soluble fraction

One gram of soil underwent a 2-h extraction with 20 mL of deionized water.

Fraction 2 (F2): Exchangeable fraction

The residue from F1 underwent a 1-h extraction with 20 mL of 1M $MgCl_2$ at pH 7.

Fraction 3 (F3): Carbonate-bound fraction

The residue from F2 underwent a 4-h extraction with 20 mL of 1 M NH_4OAc at pH 5.

Fraction 4 (F4): Fe-Mn oxide-bound fraction

The residue from F3 underwent a 5.5-h extraction at 96°C with 50 mL of 0.04 M $NH_2OH.HCl$ in 25% HOAc.

Fraction 5 (F5): Organically bound fraction

The residue from F4 underwent a multi-step extraction: first, 2 h at 85°C with 7.5 mL of 0.02 M HNO_3 and 12.5 mL of 30% H_2O_2. Then, an additional volume of 7.5 mL of 30% H_2O_2 adjusted to a pH of 2.0 was added, with maintenance of agitation at a temperature of 85°C for another 3 h. After cooling, 12.5 mL of 3.2 M NH_4OAc in 20% HNO_3 was added, and the sample was shaken for 30 min.

Fraction 6 (F6): Residual fraction

The residue from F5 was digested for 2 h with 7 mL of 10 M HCl and 2.3 mL of 15.8 M HNO_3.

After each extraction, solid/liquid separation was achieved by centrifugation at 5,000 rpm for 15 min. The supernatant was collected and diluted to 50 mL with 2% (v/v) HNO_3 before analysis for cadmium. Additionally, the residue from all fractions was washed with 20 mL of deionized water, followed by 15 min of centrifugation before the subsequent extraction step.

2.4 Statistical analysis

Each set of experiments was conducted in triplicate to ensure consistency and reliability. The experimental data were analyzed to calculate both the mean and the standard deviation. To evaluate the statistical significance at a 95% confidence level, a one-way analysis of variance (ANOVA) was employed. Statistical analysis was performed using SPSS version 23 to determine any significant differences between various groups of data. A stepwise linear regression program was utilized to examine the relationship between the chemical attributes of fertilizers and the movement of cadmium. The dependent variable in this analysis was the cadmium concentration found in the DTPA-extracted samples. The independent variables taken into account were pH, electrical conductivity, organic matter, total nitrogen, available potassium, and available phosphorus.

3. Results and Discussion

3.1 Characteristic of soil, fertilizers and KOH-biochar

The characteristics of the undisturbed soil collected from Chonburi Province and KOH-biochar were presented in Table 1 and Table 2, respectively. Analysis of the undisturbed soil from Chonburi Province revealed a classification as moderately acidic sandy loam [18]. As per soil analysis guidelines, the soil's organic matter content fell within the 0.5-1.0% low range, salinity ranged from 4-8 dS/m (medium range), and CEC ranged from 10-15 cmol/kg (medium range). The available phosphorus was notably high, exceeding 45 mg/kg, while available potassium was also high, surpassing 120 mg/kg. In acidic soils, heavy metals tend to demonstrate increased mobility [24]. As per the soil quality standards set by the National Environment Board, the permissible concentration of cadmium in soil for agricultural use should not exceed 762 mg/kg [25]. In this specific soil, the concentration of cadmium fell within acceptable limits.

However, after the introduction of crude oil and cadmium, the synthesized soil showed a rise in organic matter content, reaching 6.78%, and an increase in cadmium concentration to 100.82 mg/kg. The crude oil itself exhibited a slightly acidic pH of 5.36, containing organic matter at 89.62±7.57%, sulfur (S) at 0.03%, and cadmium at 0.19±0.01 mg/kg. In a study by Appenteng *et al.* [26], crude oil was reported to contain sulfur at approximately 0.2%, with no detectable levels of cadmium.

Carbon and oxygen were identified as the predominant elements in the KOH-biochar (Table 2). The high C/N ratio and O/C ratio observed in this study suggested a slow rate of organic matter degradation by microbes, indicating strong hydrophilicity and polarity. Moreover, the low H/C ratio indicated a pronounced aromatic nature and a robust biochar structure [27, 28]. It is important to note that the biochar was alkaline in nature. The application of substantial quantities of biochar to the soil had the potential to reduce the mobility of cadmium within the soil. Since the cadmium content in KOH-biochar was significantly lower than in the synthetic soil, the addition of KOH-biochar did not lead to a significant increase in the Cd content of the soil. The ash content analyzed was consistent with findings from other researchers [29].

Table 1. Soil characteristics

Parameter	Value	Parameter	Value
Sand (%)	76.32±3.62	OM (%)	0.57±0.08
Silt (%)	23.46±3.61	Total N (%)	0.27±0.01
Clay (%)	0.22±0.007	Avail P (mg/kg)	57.50±2.30
pH	5.61±0.01	Avail K (mg/kg)	200.80±7.50
EC (dS/m)	7.99±0.07	Cd (mg/kg)	0.24±0.01
CEC (cmol/kg)	12.66±0.05		

Table 2. KOH-biochar characteristics

Parameter	Value	Parameter	Value
C (%)	33.05±3.07	O/C	0.98
H (%)	2.52±0.20	H/C	0.08
N (%)	0.69±0.19	pH	8.97±0.03
O (%)	32.26±5.56	EC (dS/m)	17.13±0.12
S (%)	0.22±0.02	Ash (%)	8.54±0.43
C/N	48	Cd (mg/kg)	0.07±0.01

Figure 1 and Figure 2 indicate the scanning electron microscope (SEM) image and Fourier-Transform Infrared (FTIR) spectrum of biochar and KOH-biochar samples. As shown in Figure 1, the elimination of ash, tar particles, and corrosion resulting from the KOH treatment hydrolysis reactions led to a wider pore structure in the KOH-biochar. This larger pore width makes it a preferable option as a soil amendment compared to untreated biochar. These larger pores allow for improved permeability, facilitating the penetration and absorption of water, nutrients, and heavy metals [30].

The FTIR spectrum in Figure 2 displays bands at 3,102 cm^{-1} and 3,235 cm^{-1}, corresponding to -OH stretching. The increased -OH absorption around 3,235 cm^{-1} during hydrothermal carbonization appears linked to KOH modification, which catalyzed the breakdown of lignin ether linkages [17]. Bands at 1,578 cm^{-1} and 1,595 cm^{-1} indicate aromatic -C=C ring stretching. The enhancement of these bands reflected the formation of carboxylic C, ketones, esters, anhydrides and/or aromatic components, and occurrence of strong dehydration reaction and carbonization. Another strong peak, observed at 1,373 cm^{-1}, emerged after the treatment with KOH, indicating an increased presence of alkyl C-O groups, potentially due to the formation of new ether or alcohol functional groups [31]. Bands at 1,010 cm^{-1} and 1,096 cm^{-1} correspond to aliphatic ether -C-O stretching, with the decline in C–O stretching vibrations at 1,096 cm^{-1} after heating indicating decomposition of cellulose, hemicellulose, and lignin. Additionally, the strong peak at 2,357 cm^{-1} pointed to the formation of CO_2. The chemical characteristics of all fertilizers are depicted in Figure 3.

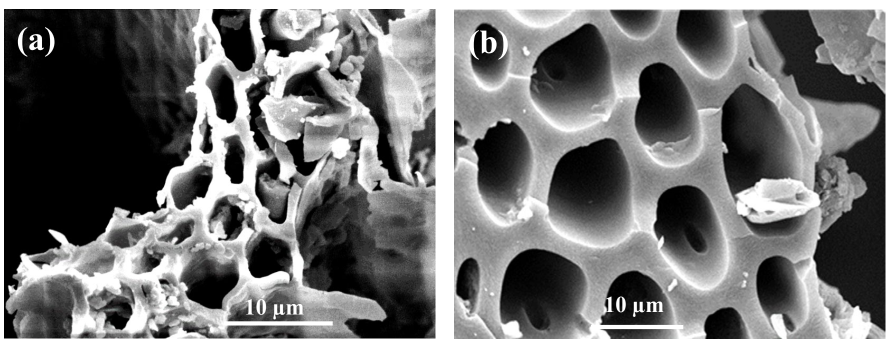

Figure 1. SEM images of (a) biochar and (b) KOH-biochar at magnification 10,000 times

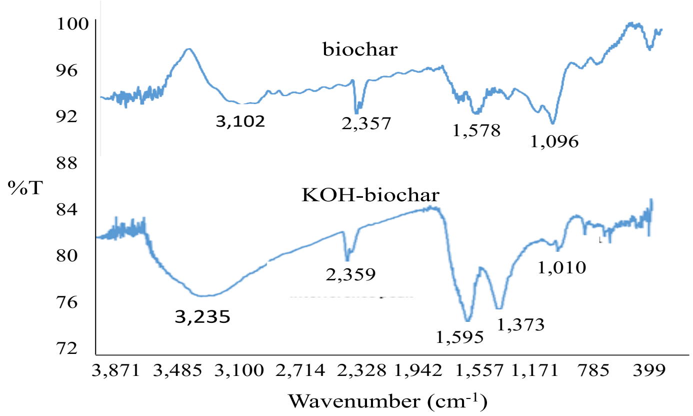

Figure 2. FTIR spectra of biochar and KOH-biochar

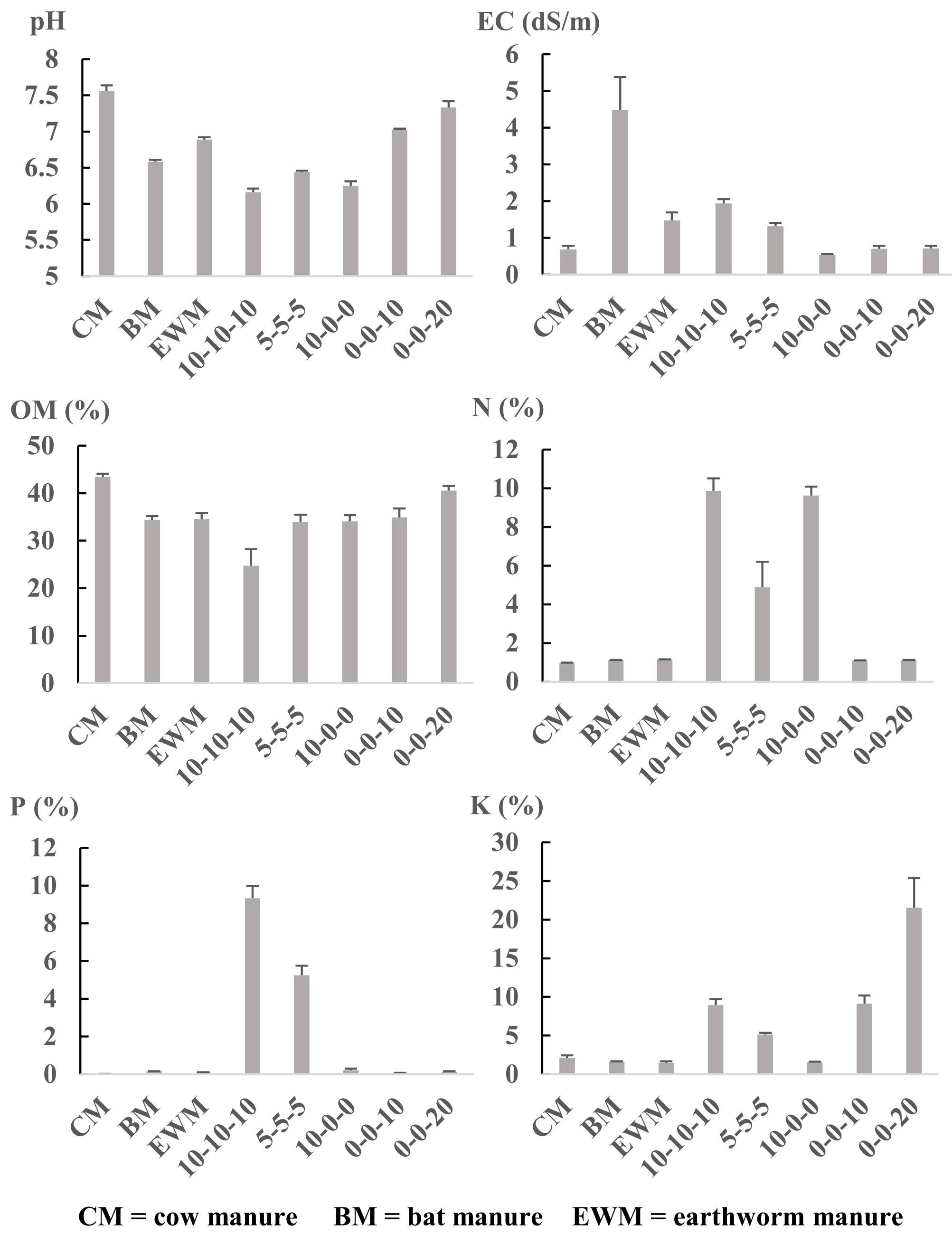

Figure 3. Characteristics of fertilizers

The organic fertilizers used in this study were cow manure (CM), bat manure (BM), and earthworm manure (EWM). Additionally, five chemical organic fertilizers with different nutrient compositions (10-10-10, 5-5-5, 10-0-0, 0-0-10, 0-0-20) were employed. These chemical organic fertilizers were created by blending organic materials with inorganic substances to achieve specific N-P-K (nitrogen-phosphorus-potassium) ratios. The pH values of the fertilizers used in the study ranged from 6.16 to 7.56, surpassing the pH of the soil. Among these, cow manure exhibited the highest pH and the highest percentage of organic matter. The 10-10-10 formula contained roughly 10% of each nutrient (N, P, K) and had the lowest organic matter content. On the other hand, the 0-0-20 formula had the second-highest pH and organic matter values, and the highest potassium content. Electrical conductivity is intricately tied to soil salinity levels, and from Figure 3, it is evident that bat manure contributed to the highest salinity. Introducing this fertilizer may elevate soil salinity, potentially impacting cadmium mobility and uptake by plants [32]. Moreover, increased salinity could adversely affect the yield of salinity-sensitive crops [33]. The cadmium concentrations in all samples were detailed in Table 3.

As depicted in Table 3, the cadmium concentration in the synthetic soil exceeded that typically found in natural environments but still remained within the acceptable limit for agricultural use (acceptable limit: cadmium <762 mg/kg) [34]. In contrast, the cadmium content in KOH-biochar was significantly lower than that in the synthetic soil, remaining below the allowed threshold for soil application (maximum allowed thresholds range: cadmium 1.4 to 39 mg/kg) [35]. Therefore, the addition of KOH-biochar did not result in a significant increase in cadmium content within the soil. Furthermore, the concentration of cadmium in all the studied fertilizers remained below the standard value for agricultural use (standard value: cadmium <10 mg/kg) [36].

Table 3. Cadmium concentration of synthetic soil, KOH-biochar, crude oil and fertilizers

Soil/Biochar/Crude Oil/Organic Fertilizer	Concentration (mg/kg)	Chemical Organic Fertilizer	Concentration (mg/kg)
Synthetic soil	100.82±2.01	10-10-10	0.11±0.20
KOH-biochar	0.07±0.01	5-5-5	0.38±0.04
Crude oil	0.19±0.01	10-0-0	0.15±0.03
Cow manure	0.16±0.01	0-0-10	0.43±0.09
Bat manure	0.18±0.01	0-0-20	0.79±0.11
Earthworm manure	0.28±0.04		

3.2 The influence of fertilizers on the mobility of cadmium

The study employed synthetic soil (SS), composed of the collected soil from Chonburi Province with an added cadmium concentration of 100 mg/kg and 5% crude oil. Subsequently, synthetic soil with biochar (SSB) was developed by combining synthetic soil (SS) with 5% KOH-biochar. Following this, 8% of each fertilizer was integrated into the synthetic soil with biochar (SSB). The evaluation of cadmium extraction from the soil samples was carried out using a 0.005 M diethylenetriaminepentaacetic (DTPA) solution. The aim of this step was to assess the soil's heavy metal bioavailability for potential uptake by plants. The addition of DTPA extraction solution creates strong complexes between heavy metals and DTPA. Heavy metals in soil come in six different forms: water-soluble, exchangeable, carbonate-bound, Fe-Mn oxide bound, organically bound, and residual forms. DTPA solution can extract heavy metals in soluble, exchangeable, and partially adsorbed forms with soil organic matter. The results and findings derived from this extraction and evaluation are depicted in Figure 4.

Figure 4 shows that the addition of 5% KOH-biochar to the soil led to a slightly reduced extraction of cadmium by DTPA. However, statistical analysis conducted at a 95% confidence level indicated that 5% KOH-biochar did not significantly impact the plant's ability to absorb cadmium. This suggests that the quantity of KOH-biochar incorporated into the soil might have been insufficient to make a noticeable difference between adding it and not adding it to the soil.

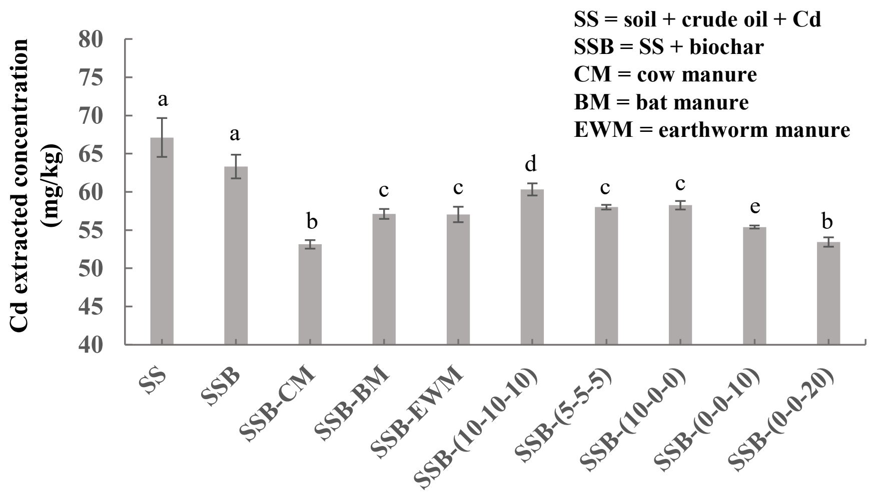

Figure 4. The concentration of extracted cadmium by DTPA

After applying both organic and chemical organic fertilizers to the synthetic soil sample with biochar (SSB), it was observed that the concentration of extracted cadmium by DTPA was lower compared to the concentration of cadmium extracted from soil without added fertilizers. The pH of all the studied fertilizers was higher than the pH of the soil. The addition of higher pH fertilizers could result in an increase in soil pH, thereby reducing the Cd concentration in the DTPA-extracted solution. Additionally, the introduction of these fertilizers led to an increase in organic matter content within the soil. Organic matter then probably played a role in forming stable organo-metallic complexes with Cd, effectively immobilizing the metal in the soil.

The addition of 10-10-10 fertilizer resulted in the smallest decrease (approximately 3%) in the cadmium extracted from the soil using DTPA compared to other types of fertilizers. The unique characteristics of the 10-10-10 fertilizer formula included having the lowest pH and organic matter content, while concurrently having the highest total nitrogen and available phosphorus values. A study by Tang *et al.* [37] found that fertilization with higher nitrogen and phosphorus content resulted in elevated concentrations of extracted Cd. The inclusion of bat manure, earthworm manure, 5-5-5, and 10-0-0 fertilizer led to a reduction of approximately 5-6% in cadmium extraction with DTPA. When 0-0-10 fertilizer was added, there was a larger reduction (about 8%) in cadmium extraction with DTPA from the soil. Cow manure and 0-0-20 fertilizer had the most significant impact, reducing cadmium removal from the soil by approximately 10%. These fertilizers exhibited the highest pH value and organic matter content. Additionally, the 0-0-20 fertilizer had the highest potassium value, which was another influential factor in reducing metal extraction from the soil. Cations with higher valence are more effective at displacing and adhering to the soil surface than those with lower valence, and in this case, potassium could replace cadmium.

The findings obtained from the DTPA extraction were subjected to analysis using a stepwise linear regression program, resulting in the formulation of equation (1).

$$y_{Cd} = 76.42 - 2.44\ \mathrm{pH} - 0.09\ \mathrm{OM} \qquad R^2 = 0.9899 \qquad (1)$$

where y_{Cd} = extracted cadmium concentration by DTPA (mg/kg)
pH = sample acidity/basicity
OM = organic matter (%)

The stepwise linear regression analysis revealed that certain factors, specifically pH and organic matter, significantly influenced the mobility of cadmium in the soil. A higher pH and organic matter content in fertilizer was associated with decreased cadmium mobility in the soil. Other factors like electrical conductivity, total nitrogen, available potassium, and available phosphorus might have exerted some influence on cadmium immobility, although their impact was considered relatively minor.

Soil is a complex matrix of detritus, comprising inorganic and organic particles. Heavy metals form diverse associations with these soil components, shaping their mobility and availability. To delve deeper into the variations in cadmium concentration across different forms, a sequential extraction method was employed. The results, depicted in Figure 5, further elucidate the intricate dynamics of cadmium's presence in various states within the soil.

The heavy metals existing in water-soluble, exchangeable, and carbonate-bound forms are considered unstable forms, whereas the stable forms are associated with Fe-Mn oxide binding, organic binding, and residual presence. As illustrated in Figure 5, the application of fertilizers led to a decrease in the cadmium content in unstable forms and its conversion into more stable forms. These findings were in line with the results presented in Figure 4. Consequently, the concentration of cadmium in stable forms increased by approximately 4.49-7.74 mg/kg.

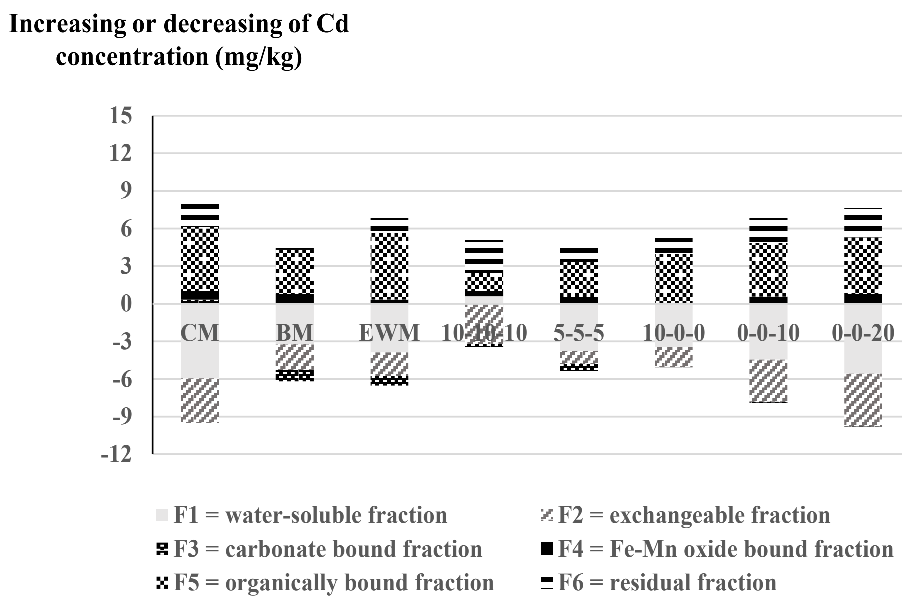

Figure 5. Increasing or decreasing of cadmium concentration in various fractions

Primarily, cadmium transitioned from water-soluble and exchangeable forms to organically bound structures due to the substantial organic content within the fertilizers derived from manure. Humic acid and fulvic acid substances found in manure, formed during composting, are known components of these fertilizers. Throughout composting, organic matter in manure undergoes humification, enhancing its aromaticity, molecular weight, and functional groups [38]. Heavy metals bind with insoluble humic substances, creating relatively immobile complexes. The carboxylic (-COOH) and phenolic (-OH) groups within humic and fulvic substances play a crucial role in forming metal-humic complexes and metal-formic complexes [39]. The stability of these complexes is influenced by soil pH and ionic strength. Of the fertilizer formulations, the 10-10-10 blend, containing the least organic matter, demonstrated lesser conversion of cadmium into organically bound structures compared to other fertilizer types upon soil addition. Additionally, there was a substantial increase in cadmium present in the residual form following fertilizer application. The residual fraction encompasses metals integrated into the crystal structures of primary and secondary minerals, representing the most stubbornly fixed forms, with minimal implications for plants and ecosystems.

4. Conclusions

In this research, the synthesized moderately acidic sandy loam soil was carried out to replicate the common occurrence of crude oil and heavy metal contamination prevalent in areas with numerous industrial operations like Chomburi Province, Thailand. Cadmium, a key industrial element, was chosen as the representative heavy metal. KOH-biochar was created specifically to serve as a soil amendment aimed at enhancing cadmium absorption. Additionally, this biochar was used to improve soil fertility for crop cultivation due to its rich organic content and high pH. However, our findings suggested that the addition of only 5% KOH-biochar did not significantly increase cadmium absorption in the soil. To potentially observe a more significant impact on cadmium mobility, future experimentation might require a higher amount of biochar. We introduced three variants of organic fertilizer and five types of organic chemical fertilizer to artificially contaminated soil to investigate their influence on cadmium mobilization in conjunction with KOH-biochar. All eight fertilizer types displayed higher pH values than the soil and were rich in organic matter. The outcomes revealed that the addition of these eight fertilizers reduced cadmium movement within the soil, as confirmed by soil extraction with DTPA. Stepwise linear regression analysis revealed that pH and organic components within the fertilizers were influential factors in cadmium bioavailability. Furthermore, sequential extraction indicated a transformation of cadmium from unstable forms—such as water-soluble and exchangeable forms—towards more stable configurations upon the addition of both organic and chemical organic fertilizers. Post-fertilizer application, cadmium in organically bound and residual forms increased. Nitrogen (N), phosphorus (P), and potassium (K) content in the fertilizers showed minimal impact on cadmium movement within the soil.

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