Immobilization of cadmium (Cd\textsuperscript{2+}) in contaminated soil using biochar derived from *Calophyllum inophyllum* (bitaog) seed husks

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Abstract. Many heavy metals such as cadmium found in contaminated soil naturally leach out and seep in groundwater through time. Natural leaching is further accelerated in acidic conditions specifically with acid rain. This study investigated the effectiveness of biochar derived from *Calophyllum inophyllum* (Bitaog) seed husks as an immobilizing agent through a simulated acid rain leaching test (equivalent to 100 years of acid rain) using artificially contaminated soil. Furthermore, magnetization and phosphoric acid treatment were utilized to produce modified biochar where Thermo-gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) analyses revealed that the modifications led to the enhancement of physiochemical properties such as fixed carbon content, surface morphology, and surface chemistry respectively. Walkley-Black Loss on Ignition test showed that all the biochar amendment increased the organic matter content of soil making it attractive for in-soil applications. Adsorption kinetic and isotherm models were used to describe the adsorption mechanism of cadmium onto the soil amended with modified and unmodified biochar where experimental results showed that the adsorption best fitted the pseudo-second order kinetic and Langmuir isotherm models. The leaching test results showed that the soil amended with magnetic and phosphoric acid modified biochar were not suitable as immobilizing agents especially in highly acidic conditions. Whereas the unmodified biochar significantly reduced leached cadmium concentration by 40.02% than in unamended soil as shown by the AAS results. Bitaog derived biochar was affirmed to be potentially effective for the long-term immobilization of cadmium in contaminated soil while may simultaneously increase soil fertility.

1. Introduction

Heavy metal pollution has become a significant global environmental problem that has worsened through rapid industrialization and exploitation of the earth’s resources. Heavy metals are persistent environmental pollutants that are transferred to different organisms via food chain and pose several health hazards to animal and human health such as affecting the hormone system, biological functions and the growth of different body tissues. Exposure to different heavy metals is ceaseless and is even increasing in some countries. Anthropogenic activities like mining, waste disposal and the use of metal containing compounds for industrial and agricultural purposes are some of the main contributors of heavy metal pollutants. Air, water, and soil are the major environmental compartments, which are affected by heavy metal pollution. Cadmium (Cd), is one of the naturally occurring heavy metals that has been widely distributed to various environment and thus pose high risks due to its toxicity [1-3]. The contamination and accumulation of Cd is a non-reversible process, having an estimated half-life in soil which varies from 15 to 1100 years. Cadmium is transferred into the food chain through different ways of inputs from the atmosphere, land, and water resources. Due to the biopersistence of cadmium, it stays inside the organism that has absorbed it for many years. In humans, exposure and intake of cadmium, even in small concentrations, causes renal dysfunctions, rhinitis, emphysema, lung diseases, and other chronic disorders [1-4].
Biochar is defined as a carbon-rich solid product produced by pyrolysis of biomass in the absence of oxygen created for safe and potentially beneficial storage in soil. Biochar has exhibited a greater potential in treating contaminated soils as it contains mesoporous structures that has a variety of functional groups present. These functional groups especially the O-containing compounds such as carboxylic and hydroxyl groups can adsorb heavy metals via surface complexation or electrostatic attraction [5,6]. Most of the time, the ability of biochar to adsorb heavy metals is mainly due to electrostatic interaction between the metal cations and carbon negative surface charge as well as due to ion exchange between the biochar surface protons and metallic cations. However, the effectiveness of applying biochar to contaminated soils depend on the soil and biochar properties, soil conditions, type of element to be adsorbed or immobilized, and the source of feedstock. The source of raw material used in this research is from *Calophyllum inophyllum* (Bitaog) seed husks that is considered one of the agricultural wastes that are abundant in the Philippines [7,8].

2. Materials and Methods

2.1. Materials and Reagents

Bitaog seed husk feedstocks were obtained from Batangas, Philippines. Soil samples were acquired from the University of Santo Tomas Botanical Garden. Analytical grade Cadmium Chloride was used to prepare 1000 ppm of Cd²⁺ stock solution used throughout the experiment. Phosphoric acid (85% w/w Ortho) and iron chloride hexahydrate were used for the modification of biochar. Synthetic acid rainwater (equivalent to 100 years of acid rain) was prepared using chloride compounds such as sodium chloride, potassium chloride, calcium chloride, magnesium chloride, and ammonium chloride.

2.2. Unmodified Biochar Production (UMBC)

Dried *C. inophyllum* seed husks were milled using a Thomas-Wiley Laboratory Mill with built in 1 mm mesh for sieving. The milled biomass was then sieved using a standard testing sieve (ASTM E11 no.30) where particles less than or equal to 600 microns were collected. The biomass was then subjected to pyrolysis using a muffle furnace (Model K&K K-MF12) with pyrolytic conditions of 600°C and a residence time of 1 hour. Such conditions were determined as the optimum parameters that yielded the highest elemental carbon and fixed carbon for the *C. inophyllum* biochar [9]. The produced biochar was cooled down to room temperature, weighed, and stored in a desiccator.

2.3. Fe³⁺ Magnetization of Biochar (MBC)

The synthesis of magnetic biochar was done using a modified approach of Jiawei, et al. 2015 where the biomass was treated with 2M FeCl₃ solution. About 80 mL of 2M FeCl₃ solution was used for every 10 g of biomass. The mixture was constantly stirred for 30 minutes and underwent heat treatment at 70°C for 30 minutes. The pre-treated biomass was filtered, and oven dried at 70°C for 30 minutes and pyrolyzed at 600°C with a residence time of 1 hour. The synthesized magnetic biochar was cooled down to room temperature, weighed, and stored in a desiccator.

2.4. Phosphoric Acid (H₃PO₄) Modified Biochar (PABC)

The biomass was soaked in phosphoric acid (85% w/w Ortho) using a ratio of 1 g biomass for every 1 g of solution (1:1). The mixture was stirred and left to further impregnate for 24 hours. The treated biomass was then pyrolyzed at 600°C with a residence time of 1 hour. The produced phosphoric acid modified biochar was cooled down to room temperature, weighed, and stored in a desiccator.

2.5. Biochar Characterization
For the physical characterization, scanning electron microscopy (SEM) imaging using a Hitachi Tabletop Microscope (TM3000) was done to determine the surface morphology of the modified and unmodified biochar. The samples were examined at 800x and 2000x magnification. For the chemical characterization, the proximate analysis of the modified and unmodified biochar produced was determined via thermogravimetric analysis using a Perkin Elmer TGA 4000. Fourier transform infrared spectroscopy (FTIR) was done using Shimadzu IRPrestige-21 to identify the functional groups and analyze the surface chemistry of the modified and unmodified biochar. The pHs of the modified and unmodified biochar were determined by immersing 1 g of biochar sample in 20 g of deionized water and measuring the resulting pH using a Mettler Toledo pH meter.

2.6. Soil Sample Preparation and Contamination
The acquired soil sample was dried until minimal moisture was obtained. The soil was then sieved using mesh no.18. Other foreign solid particles present in the soil was removed. Soil samples were contaminated with Cd by mixing 50 g of soil and 150 mL of 1000 ppm Cd²⁺ solution. The mixture was subjected to rotary shaking for a total of 24 hours at a constant speed of 200 rpm. The mixture was then filtered, and the filtrate was analyzed with Atomic Absorption Spectroscopy (AAS).

2.7. Soil Characterization
About 5 g of soil was sieved with a mesh 200 Tyler standard sieve and the sand fraction was separated with silt and clay fraction. For the analysis of porosity and surface morphology of the soil, SEM imaging with a Hitachi Tabletop Microscope (TM3000) was used. Soil organic matter composition was determined via the Walkley-Black loss of weight on ignition test. About 5 g of soil was pyrolyzed at 105°C for 2 hours in a muffle furnace. The sample was cooled down to room temperature and weighed. The sample was pyrolyzed for a second time at 360°C for 2 hours, cooled down to room temperature, and weighed. The pH of the soil was analyzed by immersing 1 g of soil in 10 mL of deionized water and using a pH meter for measuring.

2.8. Adsorption Experiments
The adsorbents utilized in this experiment are soil and soil containing 5% biochar by weight. About 1 g of adsorbent was mixed with 25 mL of 100 ppm Cd²⁺ solution. The pH of Cd²⁺ solution was not adjusted. The effect of contact time on Cd²⁺ adsorption was determined by agitating the mixture using a scientific shaker at room temperature. Agitation time were set at intervals of 30 minutes for up to 3 hours. At the end of each interval, samples were withdrawn, centrifuged, and filtered. The filtrates were then subjected to AAS.

Varying Cd²⁺ solution concentrations of 50, 100, 150, 200 ppm were prepared. The adsorption system was done by mixing 20 mL of Cd²⁺ solution with a designated concentration and 1 g of adsorbent which are soil and soil containing 5% biochar. After 1 hour of agitation, samples were withdrawn, centrifuged, and filtered. The filtrates were then subjected to AAS.

2.9 Cadmium Leaching Test
The evaluation of long-term Cd immobilization in soil was conducted following the proposed method of the Geo-Environmental Protection Center of Japan (GEPC) [10]. In this method, the amended soil was mixed with the leaching solution containing simulated rain water, the pH which has been previously adjusted to the total acid content of 100 years of acid rain. The leaching solution contained cations typically found in rainwater and the pH was adjusted to 2.8 by titration with nitric acid.

About 2 g of artificially contaminated soil was mixed vigorously with 20 mL of leaching solution at 200 rpm for 6 hours in a mechanical shaker. Afterwards, the mixture was centrifuged and filtered. The filtrate was subjected to AAS to analyze the amount of cadmium (Cd²⁺) that was leached out. The same method was done to investigate the effects of biochar amendment where 2 g of contaminated soil was amended with 5% biochar and subjected to the leaching test.
3. Results and Discussion

3.1. Surface Morphology
The produced biochars were examined through the SEM. At x2000 magnification, it can be observed that the UMBC have layers with several openings which is shown in Fig. 1a. The openings on the surface of the UMBC, indicate potential adsorption sites. By phosphoric acid treatment, the PABC have developed an increased number of opening and a higher surface area compared to the UMBC as shown at x800 magnification in Fig. 1b. The surface morphology of the PABC improves its capability as an adsorbent due to the higher number of adsorption sites. The produced MBC via magnetization with the magnetite on its surface can be seen at x800 magnification in Fig. 1c. The occupation of precipitated magnetite on its surface resulted in a lower surface area than the UMBC, which suggest that the MBC would be less likely to adsorb and retain the adsorbate in terms of surface morphology.

![SEM Images](image_url)

**Figure 1.** SEM Images of (a) UMBC at x800, (b) PABC at x2000, (c) MBC at x2000, and (d) Soil at x800

3.2 Proximate Analysis
The UMBC had the most volatile matter content with a weight percentage of 14.52%. It was observed that the PABC had the greatest quantity of fixed carbon while the UMBC had the least. This was because the MBC decomposed faster compared to the PABC since the decomposition of organic matter and other carbon-additive combinations were still in the process as the MBC was decomposed completely. Due to the high fixed carbon content of the PABC compared to the two biochars, it is a more stable adsorbing material and has substantial carbon sequestering capabilities. Table 1 summarizes the proximate analysis.

|  |  |  |  |
|---|---|---|---|
|  |  |  |  |
|  |  |  |  |
| **Table 1.** Proximate Analysis in Weight Percent |  |  |  |
3.3 Surface Functional Groups
The recorded spectra were from 400 cm⁻¹ to 4000 cm⁻¹ with a total of 60 scans. The interpretation and characterization of the spectra was done using IR and Raman spectroscopy. As observed, the frequencies of both unmodified biochar and modified biochar are almost identical in shape but only differ in percent transmittance, intensity and the weak C-N bond present on the modified biochar. However, the common functional groups present in the biochar are C-O, C-NH, C=O, and P-H, and O-H. The presence of an O-H and C=O indicates that a carboxylic acid is present for the three biochar. This means that the UMBC, PABC, and MBC show a great affinity for heavy metals.

3.4 Organic Matter and pH
The organic matter (OM) content in soil can affect a wide range of soil functional properties. The soil and mixtures of soil with 5% biochar were tested using the Walkley-Black loss on ignition method. The soil without biochar contains 3.36% OM. On the other hand, the soil with the UMBC, PABC, and MBC have percent organic matter of 4.69%, 5.88%, and 5.21%, respectively. Among all the three biochar, the soil with 5% PABC had the highest increase in the organic matter content of the unamended soil of about 2.52% of its original OM content. This means that the higher content of organic matter found in soil will result to a higher holding capacity and nutrient supply for the soil. Thus, this affirms that all the biochar produced exhibit qualities for soil amendment.

The pHs of the soil, UMBC, PABC, MBC, and mixtures of soil with 5% biochar were determined using a Mettler Toledo pH meter in a 1:20 water to biochar ratio. The soil, UMBC, PABC, and MBC generated a pH of 7.10, 9.59, 5.07, and 4.17, respectively. This means that only the UMBC was alkaline while PABC and MBC were acidic. The acidity of MBC was generated by the occurrence of ferric ions on its surface, while the presence of residual phosphoric acid from treatment contributed to the acidity of PABC. The pH of the soil with 5% biochar in UMBC, PABC, and MBC generated a pH of 7.93, 6.37, and 5.73, respectively. Soil with 5% UMBC exhibited a higher pH than the other two. The neutralizing capability of the UMBC for acidic soils and of the PABC and MBC for alkaline soils were indicated by these results.

3.5 Adsorption Kinetics
Kinetic models, specifically Lagergren’s pseudo first order (PFO) and Ho’s pseudo second order (PSO) were used to describe the adsorption kinetics of cadmium (Cd²⁺) on the soil-biochar adsorbents. The linear forms of the kinetics models used are shown in Table 2. Based on the calculations, the PSO model showed a higher correlation coefficient (R²>0.99) than the PFO model for all the soil-biochar adsorbents. The plot of the PFO and PSO are shown in Figure 2 and Figure 3 respectively. Moreover, the calculated theoretical equilibrium capacity from the PSO model showed a relatively closer value to the experimental equilibrium capacity. Thus, the PSO model is considered sufficient in representing the adsorptive behavior of cadmium onto soil amended with biochar and provided a better fit to the kinetic data. Following the PSO model indicates that the adsorption process was controlled by chemisorption where inner sphere complexation and precipitation were the main mechanisms involved [11,12]. Furthermore, the values of the rate constants (k) showed that the Soil-UMBC had the fastest adsorption while the Soil-PABC had the slowest (Soil-UMBC>Soil-MBC>Soil-PABC). Table 3 and Table 4 present the summary of the kinetic data obtained from the pseudo-first order and the pseudo-second order plots respectively.
Table 2. Linearized Kinetic Models

| Pseudo-first Order | ln(\(Q_e - Q_t\)) = ln(\(Q_e\)) - \(k_1t\) |
|--------------------|---------------------------------|
| Pseudo-second Order | \(\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}\) |

Table 3. Pseudo-first Order Kinetic Parameters

| Q\(_{\text{experimental}}\) (mg/g) | \(k_1\) | Q\(_{\text{calculated}}\) (mg/g) | \(R^2\) |
|-------------------------------|--------|-------------------------------|--------|
| Soil                           | 46.9988 | 0.0345                        | 4.8409 | 0.5989 |
| Soil-UMBC                      | 48.1114 | 0.0270                        | 1.8132 | 0.3131 |
| Soil-PABC                      | 46.0427 | 0.0294                        | 5.0668 | 0.5475 |
| Soil-MBC                       | 45.5860 | 0.0288                        | 4.4772 | 0.5026 |

Table 4. Pseudo-second Order Kinetic Parameters

| Q\(_{\text{experimental}}\) (mg/g) | \(k_2\) | Q\(_{\text{calculated}}\) (mg/g) | \(R^2\) |
|-------------------------------|--------|-------------------------------|--------|
| Soil                           | 46.9988 | 0.1296                        | 46.9484 | 0.99 |
| Soil-UMBC                      | 48.1114 | 0.5408                        | 48.0769 | 0.99 |
| Soil-PABC                      | 46.0427 | 0.1070                        | 46.0829 | 0.99 |
| Soil-MBC                       | 45.5860 | 0.1180                        | 45.4545 | 0.99 |

Figure 2. Pseudo-first Order Fit for the Adsorption of Cd in Biochar Amended Soil
3.5 Adsorption Isotherms

The Langmuir isotherm model is based on a monolayer adsorption that occurs on homogeneous surfaces with no interactions among adsorbed ions [13,14]. The Langmuir equation can be expressed and linearized in four different types as summarized in Table 5. From the obtained Langmuir parameters presented in Table 6, Langmuir – 2 gave the best fit to all the adsorbents. The Soil-UMBC showed the highest maximum adsorption capacity ($Q_m$) among all the adsorbents. Furthermore, using the unamended soil as basis, it was revealed that the UMBC increased the maximum adsorption of the soil while the PABC and MBC showed a decrease. From these results, a sequence from highest to lowest, in terms of maximum adsorption capacity was generated (Soil-UMBC > Soil-PABC > Soil-MBC). The favorability of adsorption can be determined when fitted to the Langmuir isotherm using the separation factor ($R_L$). The adsorption process can be described as unfavorable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$), and favorable ($0 < R_L < 1$) [13,14]. The separation factors for all the adsorbents presented in Table 7, showed values ($0 < R_L < 1$) that indicated a favorable adsorption.

Table 5. Langmuir Isotherm Model

| Langmuir Equation | Linear Forms |
|-------------------|-------------|
| $Q_e = \frac{Q_m b C_e}{1 + b C_e}$ | $Q_e = \frac{Q_m b C_e}{1 + b C_e}$ |

| Linear Forms | |
|-------------|-------------|
| $\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b C_e}$ | $Q_e = \frac{Q_m}{b} \left( \frac{1}{C_e} - \frac{1}{Q_m} \right)$ |
| $\frac{1}{Q_e} = \frac{1}{Q_m} + \left( \frac{1}{Q_m b C_e} \right)$ | $Q_e = h Q_m - h Q_a$ |
Table 6. Langmuir Isotherm Parameters

| Langmuir - 1 | Soil | Soil-UMBC | Soil-PABC | Soil-MBC |
|--------------|------|-----------|-----------|----------|
| $Q_m$ (mg/g) | 285.7143 | 156.2500 | 200.0000 | 185.1852 |
| b (L/mg)    | 0.0343  | 0.1228    | 0.0553    | 0.0526   |
| $R^2$       | 0.2904  | 0.8137    | 0.5944    | 0.4659   |

| Langmuir - 2 | Soil | Soil-UMBC | Soil-PABC | Soil-MBC |
|--------------|------|-----------|-----------|----------|
| $Q_m$ (mg/g) | 158.7302 | 163.9344 | 129.8701 | 113.6364 |
| b (L/mg)    | 0.0758  | 0.1147    | 0.1075    | 0.1162   |
| $R^2$       | 0.9604  | 0.9886    | 0.9601    | 0.9431   |

| Langmuir - 3 | Soil | Soil-UMBC | Soil-PABC | Soil-MBC |
|--------------|------|-----------|-----------|----------|
| $Q_m$ (mg/g) | 113.6900 | 145.4100 | 129.6700 | 112.1100 |
| b (L/mg)    | -0.1454 | -0.1410   | -0.1131   | -0.1296  |
| $R^2$       | 0.1625  | 0.6992    | 0.5106    | 0.4033   |

| Langmuir - 4 | Soil | Soil-UMBC | Soil-PABC | Soil-MBC |
|--------------|------|-----------|-----------|----------|
| $Q_m$ (mg/g) | 397.9195 | -182.2515 | 198.0936 | 192.2562 |
| b (L/mg)    | 0.0236  | 0.0986    | 0.0577    | 0.0523   |
| $R^2$       | 0.1625  | 0.6992    | 0.5106    | 0.4033   |

Table 7. Separation Factor

|        | $R_L (C_0 = 50ppm)$ | $R_L (C_0 = 200ppm)$ |
|--------|---------------------|-----------------------|
| Soil   | 0.2087              | 0.0619                |
| Soil-UMBC | 0.1485              | 0.0418                |
| Soil-PABC | 0.1568              | 0.0444                |
| Soil-MBC | 0.1468              | 0.0412                |

4. Conclusion and Recommendation

Biochar derived from *Calophyllum inophyllum* (Bitaog) seed husks showed various physiochemical characteristics that signified its potential for soil amendment and as immobilizing agent for heavy metals such as cadmium. Two treatments, magnetization and phosphoric acid modification, were utilized to produce modified biochar that were expected to enhance adsorptive characteristics of the biochar. From the proximate analysis, PABC exhibited the highest fixed carbon content which signifies its long-term stability and strong carbon sequestering capacity. The Walkley-Black test revealed that the UMBC, PABC, and MBC increased the organic matter of soil when amended, with PABC providing the highest increase. Furthermore, the pH test showed that the UMBC was alkaline while both the PABC and MBC were acidic.

Results revealed that soil amended with the UMBC had an increased adsorption capacity for cadmium than in unamended soil. Conversely, the PABC and MBC amendments lowered the adsorption capacity of the soil. SEM images revealed that magnetization led to a decreased surface area on the MBC while the PABC developed a higher surface area compared to the UMBC. Adsorption data were fitted to kinetic models where it was revealed that the adsorption followed PSO kinetic model which gave the best fit. The PSO model showed that the adsorption was governed by a chemisorption process. Furthermore, the values of the rate constant ($k_2$) indicated that the Soil-UMBC had the fastest adsorption. The Langmuir parameters revealed the sequence (Soil-UMBC>Soil-PABC>Soil-MBC) based on the obtained maximum adsorption capacity. The soil amended with the UMBC significantly reduced the leached cadmium concentration by 40.02%. Whereas the PABC and MBC amendments increased the amount of leached cadmium by 67.69% and 88.86% respectively.
Studies on biochar modification mechanisms may be investigated to explain further the resulting changes in the physiochemical properties of the biochar and determine optimum parameters and methods that will maximize the improvements on the modified biochar as both soil amendment and immobilizing agent. Other types of biochar treatment may also be tackled and test its suitability for in-soil applications. Moreover, the application of biochar in soil contaminated with other types of heavy metal, including multi-metal competition in actual contaminated soil may be studied. Further studies on the mechanism of immobilization may be considered to elucidate the interactions of biochar with the soil and the heavy metal.

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