ADSORPTION, LEACHING AND BIOAVAILABILITY OF CADIMUM AND LEAD IN AQUEOUS SOLUTION AND CONTAMINATED SOILS AMENDED WITH MODIFIED BIOCHAR

By

ALAA HASAN FAHMI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

November 2018

DEDICATION

I dedicate this work to those who taught, motivated, and helped me throughout my study; to my parents;

Hasan Fhmi and Nahyia Salman, brothers& sisters.

It is also dedicated to my dearest wife; Hiba Abbas and my kids; Ban, Bashar, Mayar, & Baneen for their encouragements and patience toward achieving this goal.

Also, finally to my country Iraq

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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Chairman : Samsuri Abd Wahid, PhD
Faculty : Agriculture

Cadmium (Cd) and lead (Pb) are among the global priority pollutants and contaminations of these heavy metals cover a wide range of soils. Biochar has been proven to be a very good adsorbent of heavy metals. Reduction of its particle size may increase the sorption and removal of heavy metals from soils or aqueous solution. The present study investigated the effects of crushing oil palm empty fruit bunch biochar (EFBB) to different particle sizes on the adsorptive removal of Cd and Pb from aqueous solution, extractable, leaching and phytoavailability of Cd and Pb in contaminated soil. Three different particle sizes of EFBB were used in this study; coarse (C-EFBB) (>2 mm), medium (M-EFBB) – (0.25 – 0.5 mm) and fine (F-EFBB) (< 0.05 mm). The F-EFBB was also coated with Fe to produce an iron coated F-EFBB (ICF-EFBB). A commercially available activated carbon (AC) was also included in the study as a benchmark for the sorption properties of the modified biochars. All the adsorbents were characterized for their physico-chemical and morphological properties using standard methods. A batch equilibrium study was performed using 0.1 g of each adsorbent with 40 mL of solution containing 0 – 500 mg L^{-1} Cd and/or Pb. The isotherm data was fitted to Freundlich and Langmuir's sorption isotherm models. The C-EFBB and F-EFBB at three different rates (0%, 0.5% and 1%) were added to soils contaminated with Cd and/or Pb and the extractable, leaching and phytoavailability of these two metals were studied.

The results indicated that F-EFBB had the highest CEC, pH, and acidic functional groups among the adsorbents but the AC had the highest BET surface area. The scanning electron micrographs suggested that crushing the biochar exposed the micropores which were otherwise hidden in the inner structure of the larger particle size biochar. There was no evidence of macropores presence in the AC. Sorption

isotherm data of the all adsorbents for Cd in the single system were better fitted to the Langmuir than the Freundlich model, except for AC. However, the bisorbate system were better fitted to the Freundlich than the Langmuir model, except for ICF-EFBB. The sorption isotherms of all the adsorbents for Pb in the single and bisorbate system were better fitted to the Langmuir than the Freundlich model, except for AC in the bisorbate system. The Q_{max} values for Cd and Pb adsorption follow the order of ICF-EFBB > F-EFBB > M-EFBB > C-EFBB> AC in the single systems (55.87, 40.32, 19.34, 17.79 and 14.31 mg g^{-1} for Cd and 142.86, 103.09, 58.14, 54.95 and 50.51 mg g^{-1} for Pb, respectively). The same order was observed for Pb adsorption in bisorbate systems (126.58, 98.04, 51.02, 45.25 and 43.86 mg g^{-1}, respectively). The order of Q_{max} values for Cd adsorption in bisorbate systems exhibited the following order: F-EFBB > ICF-EFBB > M-EFBB > AC > C-EFBB (20.79, 17.86, 12.87, 6.25 and 5.59 mg g^{-1}, respectively). The adsorption of Pb was more preferable than Cd by all the adsorbents.

Application of EFBB to the soils contaminated with Cd and/or Pb significantly reduced the synthetic rainwater (SRW) extractable Cd and Pb. The lowest SRW extractable Cd and Pb was recorded by the contaminated soils applied with 1% F-EFBB. The lowest extractable values of Cd from Cd-soil and Cd+Pb-soil were 0 and 10.786 µg kg^{-1} in week 8, respectively. The lowest extractable values of Pb from Pb-soil and Cd+Pb-soil were 4.180 and 9.770 µg kg^{-1} in week 8, respectively. Similar results were obtained from the leaching study, which showed the effectiveness of the F-EFBB in reducing the leaching of Cd and Pb from the soils compared to the other adsorbents. The growth parameters of mustard plants grown in Cd- and Cd+Pb-soil treated with EFBBs were significantly better compared to the untreated soil (control). However, there was no significant difference in the growth parameters of mustard plants grown in Pb-soil treated with EFBBs compared to the control soil. There was also no significant effect of EFBB particle size on the growth parameters of the mustard plants grown on the contaminated soils. However, the application of 1% F-EFBB to the contaminated soils showed significantly lower Cd and Pb concentrations in the roots and shoots of the mustard plants as compared to the mustard plants grown on the untreated contaminated soil. The lower values of Cd in roots were 448.6 and 346 mg kg^{-1}, while, the lower values in shoots were 115.200 and 99 $mgkg^{-1}$ in contaminated soils Cd-soil and Cd+Pb-soil, respectively. For the lower Pb values in roots were 4196 and 1529.5 mg kg^{-1}, while, in shoots were 78.467 and 35.733 mg kg^{-1}, in contaminated soils Pb-soil and Cd+Pb-soil, respectively. This may be attributed to the reduction in bioavailable Cd and Pb in soils treated with F-EFBB. It can be concluded from this study that all the EFBBs, regardless of their particle size adsorbed Cd and Pb better than the commercial AC. Reducing the EFBB particle size improved its adsorption capacity as well as reduce the extractable and leaching of Cd and Pb from contaminated soils. Therefore, the EFBB can be an alternative to the much costlier AC as an adsorbent for Cd and Pb.