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Functionalized biochar derived from heavy metal rich feedstock: Phosphate recovery and reusing the exhausted biochar as an enriched soil amendment

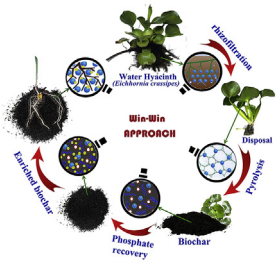
Ahmed Mosa*, Ayman El-Ghamry, Mona Tolba

Soils Department, Faculty of Agriculture, Mansoura University, 35516 Mansoura, Egypt

HIGHLIGHTS

- *In-situ* functionalization of biochar *via* rich heavy metals content was studied.
- Physicochemical analyses confirmed the functionalization of Fe-B, Zn-B and Cu-B.
- Functionalized biochars showed higher phosphate recovery.
- The exhausted biochar improved water and nutrient supply potentials of sandy soil.
- Restriction should be placed on soil application of the exhausted biochar.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper provides a circular win-win approach for recycling rhizofiltration biomass into multifunctional engineered biochar for various environmental applications (e.g. phosphate recovery) with a potential reuse of the exhausted biochar as an enriched soil amendment. Functionalized biochars were derived from the disposals of water hyacinth (*Eichhornia crassipes*) plants grown in synthetic contaminated water spiked with either Fe^{2+} (Fe-B), Mn^{2+} (Mn-B), Zn^{2+} (Zn-B) or Cu^{2+} (Cu-B) comparing with the original drainage water as a control treatment (O-B). The *in-situ* functionalization of biochar *via* the inherently heavy metal-rich feedstock produced homogenous organo-mineral complexes on biochar matrix without environmental hazards (e.g. volatilization or chemical sludge formation) associated with other post-synthetic functionalization methods. Physicochemical analyses (SEM-EDS, XRD, FTIR, BET and zeta potential (ζ)) confirmed the functionalization of Fe-B, Zn-B and Cu-B due to organo-mineral complexes formation, maximizing specific surface area, lowering the electronegativity, originating positively charged functional groups, and thus improving the anion exchange capacity (AEC) comparing with O-B. In contrary, physicochemical characteristics of Mn-B was in similarity with those of O-B. Phosphate recovery by the functionalized biochar was much greater than that of the unfunctionalized forms (O-B and Mn-B). Precipitation was the dominant chemisorption mechanisms for phosphate sorption onto biochar compared to other mechanisms (ion exchange, electrostatic attraction and complexation with active functional groups). The exhausted biochar showed an ameliorating effect on the low water and nutrient supply potentials of sandy soil, and thus improved fresh biomass yield and nutritional status of maize seedlings with some restrictions on its high micronutrient content.

* Corresponding author.
E-mail address: ahmedmosa@mans.edu.eg (A. Mosa).

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1. Introduction

Heavy metals recovery from urban and industrial water effluents is becoming an important issue with the fast growing urbanization and industrialization. Taking into account the enormous costs associated with classical physicochemical purification methods, phytoremediation could be considered as one of the most effective and affordable methods for heavy metals clean-up (Garbisu and Alkorta, 2001). Rhizofiltration is one of phytoremediation sub-processes, which involves hyper accumulating plants to extract heavy metals from contaminated effluents into their biomass (Ali et al., 2013). Several aquatic plants have been investigated for their potential to clean-up polluted water effluents including duckweed (*Lemna minor* L.) (Sasmaz et al., 2015), water lettuce (*Pistia stratiotes*) (Qin et al., 2016), water dropwort [*Oenathe javanica* (BL.) DC.] (Wang et al., 2002), and cattails (*Typha latifolia* L.) (Ben Salem et al., 2017). Among them, water hyacinth (*Eichhornia crassipes*) has received more attention for wastewater decontamination due to (i) its high reproductive capacity (biomass yield duplication within 8–10 days, and 3000 offspring regeneration within 50 days) (Idrees et al., 2014), (ii) its extensive rooting network, which creates a dense filtering layer (Feng et al., 2017), (iii) its optimal growth in wide range of aquatic ecosystems (Mayo and Hanai, 2017), and (iv) its high resistance to biotic and abiotic stresses due to its high content of melatonin (Zhang et al., 2015). Numerous studies have reported the effectiveness of heavy metals decontamination by water hyacinth (Gupta and Balomajumder, 2015; Qin et al., 2016; Zheng et al., 2016). However, disposing water hyacinth biomass following rhizofiltration is associated with various financial and environmental challenges given its high water and metals contents. With respect to traditional disposing methods (e.g. composting, landfilling, stockpiling or combustion), additional problems may arise surrounding the release of the immobilized heavy metals to the pedosphere, hydrosphere, atmosphere, and biosphere.

Thermochemical conversion of water hyacinth biomass under oxygen-limited conditions (pyrolysis) to produce energy (bio-oil and syngas) and a residual charcoal-like substance (biochar) can create a win-win situation beyond rhizofiltration. Biochar has been credited with multiple agro-environmental beneficiations including maximizing water and nutrient supply potentials of soil (Głąb et al., 2016; Khadem and Raiesi, 2017), wastewater decontamination (Mosa et al., 2016; Sewu et al., 2017), and carbon sequestration (Hansen et al., 2016; Sheng et al., 2016). Although biochar has proved its effectiveness in sorption of positively-charged ions (e.g. heavy metals), its high alkalinity (pH 7–12), negatively charged surfaces at circumneutral pH, low pH_{PZC} (<4), and thus the limited AEC values (<5 cmol kg^{1}) has greatly hindered its widespread application in the removal of negatively-charged ions (e.g. phosphate) (Wan et al., 2017). More research, therefore, is needed to functionalize biochar with high sorption capacity for phosphate removal from aqueous solutions.

Recently, attention has been directed toward functionalizing biochar with higher positively charged sorption sites *via* impregnation of minerals with biochar (Rajapaksha et al., 2016). Slow pyrolyzed biomass pre-treated with iron trichloride ($FeCl_3$) greatly improved AEC through developing surface coating with Fe-oxyhydroxids that exhibit high points of zero net charge (Lawrinenko et al., 2017). MgO-impregnated biochar also showed nano-sized MgO flakes and nanotube-like porous carbon, and exhibited higher sorption capacity of phosphate and humate (Li et al., 2017a). Likewise, $MnO_{(\times)}$-modified biochars (manganosite-biochar and birnessite-biochar) showed a high tendency toward precipitating arsenate anions (Wang et al., 2015). On the other hand, there remain several drawbacks associated with the excessive use of mineral compounds during biochar functionalization taking into consideration the environmental and financial problematic issues of disposing the huge amounts of hazardous chemical sludge generated during impregnation, neutralization and drying.

The *in-situ*-self-functionalization of biochar *via* the inherent rich heavy metals content during thermochemical conversion can provide a value-added solution for disposing metal-accumulating plants. The novelty aspect of this research lies on studying the effect of abundant heavy metals (Fe, Mn, Zn and Cu) in feedstock (rhizofiltration biomass) on generating activated/functionalized biochar with high sorptive capacities. This research, therefore, helps to fill in the gap of knowledge regarding the self-functionalization of biochar during the thermochemical conversion of feedstock. This hypothesis can provide an eco-friendly and cost-effective technique for biochar functionalization rather than chemical impregnation with mineral compounds.

The functionalized biochar application in phosphate recovery from aqueous solutions is providing a sustainable remediation approach since the exhausted biochar can be recycled back as an enriched organic amendment. Recycling back exhausted biochar into the soil can enrich its fertility by a carbon-based-slow-released-fertilizer (phosphate and micro-nutrients). Therefore, the specific objectives of this study are: (1) studying the effect of rich heavy metals content of water hyacinth disposals on biochar production and functionalization, (2) evaluating and modeling phosphate recovery by the engineered biochars under kinetic and isothermal batch sorption experiments, (3) studying mechanisms responsible for phosphate sorption by the engineered biochars, (4) studying the effect of the exhausted biochar on water and nutrient supply potentials of sandy soil, and (5) studying the beneficial effect of the exhausted biochar additives on maize seedlings grown in sandy soil.

2. Materials and methods

2.1. Reagents

Ammonium iron(II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$), manganese(II) chloride tetrahydrate ($MnCl_2\cdot 4H_2O$), zinc chloride ($ZnCl_2$), copper(II) sulfate pentahydrate ($CuSO_4\cdot 5H_2O$) and monopotassium phosphate (KH_2PO_4) of analytical grade were purchased from Fisher Scientific. Chemical solutions preparation, rinsing and cleaning of samples were carried out using deionized water (18.2 MΩ) (Nanopure water, Barnstead).

2.2. Rhizofiltration experiment

Uniform water hyacinth plants at two true-leaf formation stage were sampled from an agricultural drain located at Belkas District, Dakahlia Governorate, Egypt (31°15′41″N 31°25′41″E). Plants were washed gently with tap water followed by deionized water before starting the rhizofiltration experiment. Plants were transplanted individually in plastic pots (350 mL volume) containing either drainage water from its original environment (control) or synthetic contaminated water treatments (Fig. S1, supporting information). Chemical analysis of agricultural drainage water samples was carried out according to (Chapman and Pratt, 1962), and illustrated in Table S_1 (supporting information). Artificially contaminated water was spiked with either Fe^{2+} ($(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$), Mn^{2+} ($MnCl_2\cdot 4H_2O$), Zn^{2+} ($ZnCl_2$) or Cu^{2+} ($CuSO_4\cdot 5H_2O$)) at concentration of 100 mg l^{-1}. All plants were grown under the original drainage water for a week until adaptation with the new environment. Thereafter, the rhizofiltration experiment was optimized until the end of the experiment (45 days from transplanting). Water