Title: BIOCHAR/METAL COMPOSITES, METHODS OF MAKING BIOCHAR/METAL COMPOSITES, AND METHODS OF REMOVING CONTAMINANTS FROM WATER

Abstract: Embodiments of the present disclosure provide methods of removing a material (e.g., a nutrient or a contaminant) such as one or more types of anions such as phosphate, nitrate, arsenic anions, from a fluid (e.g., water) with biochar/metal composites, methods of making biochar/metal composites, structures including biochar/metal composites, and the like.
— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(III))
— of inventorship (Rule 4.17(iv))

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CLAIM OF PRIORITY TO RELATED APPLICATION

This application claims priority to co-pending U.S. provisional application entitled "BIOCHAR/METAL COMPOSITES, METHODS OF MAKING BIOCHAR/METAL COMPOSITES, AND METHODS OF REMOVING CONTAMINANTS FROM WATER" having Serial No.: 61/601,588, filed on February 22, 2012, which is entirely incorporated herein by reference.

FEDERAL SPONSORSHIP

This invention was made with Government support under Contract 00082762, awarded by the National Science Foundation. The Government has certain rights in this invention.

BACKGROUND

Biochar is a stable solid, rich in carbon and can sequester carbon in the soil for hundreds, even thousands of years. In addition, biochar can increase soil fertility, raise agricultural productivity, and increased soil nutrients and water holding capacity, and reduced emissions of other greenhouse gases from soils to mitigate global warming. More importantly, the amount of raw materials for potential biochar production is huge. Of more than 60 billion tons of carbon taken up annually by photosynthesis, around ten per cent eventually becomes available as agricultural residue such as corn and rice stalks, or forestry residue such as branch and leaf litter, as well as animal waste.

Recently, several efforts have been made to apply biochar as an alternative adsorbent to environmental pollutants for water and soil applications, in which the most common strategy is the direct trial of various biochar candidates without any modifications and selection of the best one to application as a result. Through this method, a certain types of biochar will finally be qualified for specific uses to remove organic and inorganic contaminants from aqueous solutions. However, it also will restrict their further improvements in chemical and physical properties and the applications of the rest of biomass species due to their natural drawbacks. For instance, most of the unmodified carbon
materials, including biochar, have limited ability to adsorb anionic contaminants, including phosphate, which is a one of the main contributors to eutrophication that not only affects the aquatic ecosystems but also indirectly hinders the economic progress.

SUMMARY

In accordance with the purpose(s) of the present disclosure, as embodied and broadly described herein, embodiments of the present disclosure provide methods of removing a material (e.g., a nutrient or a contaminant) such as one or more types of anions such as phosphate, nitrate, or arsenic anions, from a fluid (e.g., water) with biochar/metal composites, methods of making biochar/metal composites, structures including biochar/metal composites, and the like.

In an embodiment, the structure includes: a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, and wherein the composite has an affinity for an anion in a fluid.

In an embodiment, the method of removing contaminants from a fluid includes: exposing a biochar/metal composite and a fluid to one another, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, wherein the fluid includes an anion of interest, wherein the composite has an affinity for anions of interest in the fluid; and adsorbing one or more types of anions of interest onto the biochar/metal composite.

In an embodiment, the method of making a biochar metal composite includes: mixing a biomass with a precursor metal solution; drying the biomass; and pyrolysis of the biomass to form a a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination
of on and within the biochar, wherein the biochar is porous, and wherien the composite has an affinity for an anion in a fluid.

In an embodiment, the method of making a biochar metal composite includes: irrigating a biomass with one or more metal ion solutions; harvesting and drying the biomass; and pyrolysing the biomass to form a a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, and wherien the composite has an affinity for an anion in a fluid.

In an embodiment, the method of making a biochar metal composite includes: bacterial treatment of a biomass; drying the treated biomass; and pyrolysing of the biomass to form a a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, and wherien the composite has an affinity for an anion in a fluid.

Other systems, methods, features, and advantages will be, or become, apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional structures, systems, methods, features, and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Many aspects of this disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the principles of the present disclosure. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

Figure 1.1 illustrates wide angle XRD patterns of various MgO-biochar nanocomposites.
Figure 1.2 illustrates SEM images showing morphological structures (a, b, and c) and cross section (d) of MgO-biochar nanocomposite. The inset in c is a high resolution SEM image of nano-MgO flakes.

Figure 1.3 illustrates TEM images of MgO-biochar nanocomposites (a), HRTEM image of nanosized MgO particles in biochar matrix (b), TEM image of the bulk biochar matrix (c), and HRTEM image of the nano-MgO surface (d). The inset in (a) shows the selected area electron diffraction (SAED) pattern.

Figure 1.4 illustrates the removal of P and N from aqueous solutions by various MgO-biochar nanocomposites: a) Compare of all composites; b) Adsorption isotherms of P on SBT MgO-biochar; and c) Adsorption isotherms of N on PS MgO-biochar.

Figure 1.5 illustrates XRD and XPS analyses of biochar/y-Fe$_2$O$_3$ composite: (a) wide angle XRD patterns and (b) Shirley background-subtracted Fe$_2$pl/2 and Fe$_2$p3/2 XPS spectra.

Figure 1.6 illustrates SEM image of biochar/y-Fe$_2$O$_3$ composite: (a) and (b) morphological structures; (c) micro-sized y-Fe$_2$O$_3$ particles; (d) nano-sized y-Fe$_2$O$_3$ particles and (e) EDS analysis.

Figure 1.7 illustrates TEM image of biochar/y-Fe$_2$O$_3$ composite: (a-b) low-magnification and (c) high-magnification images of biochar/y-Fe$_2$O$_3$ composite. The inset in c shows the selected-area electron diffraction (SAED) pattern.

Figure 1.8 illustrates adsorption of As(V) on biochar/y-Fe$_2$O$_3$ composite: a) Kinetics and b) Isotherms.

Figure 1.9 illustrates magnetic hysteresis loop of biochar/y-Fe$_2$O$_3$ composite. The inset shows the adsorption of methyl blue on biochar/y-Fe$_2$O$_3$ and magnetic separation.

Figure 1.10 illustrates wide angle XRD pattern of biochar/AIOOH nanocomposite.

Figure 1.11 illustrates SEM images (a) morphological structure of biochar/ AIOOH sample; (b)-(d) nano-sized AIOOH flakes and (e) EDX analysis of Biochar/AIOOH.

Figure 1.12 illustrates (a) TEM images of Biochar/AIOOH; b) the selected area marked by blue for EDS analysis and (c) EDS analysis of Biochar/AIOOH shows the Al on carbon surface. The inset in (a) shows the selected-area electron diffraction (SAED) pattern.

Figure 1.13 illustrates adsorption of As(V) and P on Biochar/AIOOH nanocomposite: a) As kinetics, b) As isotherm, c) P kinetics, and d) P isotherm.

Figure 2.1 illustrates a SEM (a), EDS (b), XRD (c), and XPS analysis of NE-biochar (Mg-biochar nanocomposite) produced from tomato leaf enriched with Mg.
Figure 2.2 illustrates sorption characteristics of P on Mg-enriched biochar (MgEC). (A) Sorption kinetic and (B) isotherm, symbols are experimental data and lines are model results. (C) XRD spectrum of P-laden MgEC. (D) SEM image of P-laden MgEC morphological structures. (E) and (F) XPS spectra of the Mg 1s and P 2p3/2 region for P-laden MgEC, respectively.

Figure 2.3 is illustration of adsorption and desorption mechanisms of P on biochar surface (S).

Figure 2.4 illustrates P-laden MgEC as a slow-release fertilizer. (A) Desorption kinetics, symbols are experimental data and the line is model results. (B) Successive and repeatable release of phosphate by P-laden MgEC as each time fresh solution was introduced to the system to mimic conditions under plant growth. (C) Comparison of grass seedlings between biochar and control groups. (D) Comparison of grass shoot length between biochar and control groups.

Figure 3.1 illustrates SEM images (left) and corresponding EDS spectra (right) of the two biochar samples: A) STC, 500X; B) DSTC, 500X; and C) DSTC, 7000X. The EDS spectra were obtained at the same location as shown in the SEM images.

Figure 3.2 illustrates XRD spectra of the two biochars. Crystallites were detected with peaks labeled as Q for quartz (SiO2), C for calcite (CaCCb), and P for periclase (MgO).

XRD

Figure 3.3 illustrates a comparison of phosphate removal by different adsorbents

Figure 3.4 illustrates an adsorption of phosphate on DSTC: a) Kinetics and b) Isotherm.

DETAILED DESCRIPTION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller
ranges may independently be included in the smaller ranges and are also encompassed within
the disclosure, subject to any specifically excluded limit in the stated range. Where the stated
range includes one or both of the limits, ranges excluding either or both of those included
limits are also included in the disclosure.

Unless defined otherwise, all technical and scientific terms used herein have the same
meaning as commonly understood by one of ordinary skill in the art to which this disclosure
belongs. Although any methods and materials similar or equivalent to those described herein
can also be used in the practice or testing of the present disclosure, the preferred methods and
materials are now described.

All publications and patents cited in this specification are herein incorporated by
reference as if each individual publication or patent were specifically and individually
indicated to be incorporated by reference and are incorporated herein by reference to disclose
and describe the methods and/or materials in connection with which the publications are cited.
The citation of any publication is for its disclosure prior to the filing date and should not be
construed as an admission that the present disclosure is not entitled to antedate such
publication by virtue of prior disclosure. Further, the dates of publication provided could be
different from the actual publication dates that may need to be independently confirmed.

As will be apparent to those of skill in the art upon reading this disclosure, each of the
individual embodiments described and illustrated herein has discrete components and features
which may be readily separated from or combined with the features of any of the other
several embodiments without departing from the scope or spirit of the present disclosure.
Any recited method can be carried out in the order of events recited or in any other order that
is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated,
techniques of chemistry, organic chemistry, organometallic chemistry, microbiology, and the
like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art
with a complete disclosure and description of how to perform the methods and use the
compositions and compounds disclosed and claimed herein. Efforts have been made to
ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors
and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight,
temperature is in °C, and pressure is at or near atmospheric. Standard temperature and
pressure are defined as 20 °C and 1 atmosphere.
Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a support" includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

**Definitions:**

In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

"Biomass" can include as-products, by-products, and/or residues of the forestry and agriculture industries. Biomass includes, but is not limited to, algae, plants, trees, crops, crop residues, grasses, forest and mill residues, wood and wood wastes, fast-growing trees, and combinations thereof.

"Pyrolysis" is the thermal conversion of a biomass, such as plant material, in an oxygen starving environment at elevated temperatures generally of about 200 to 800° C, or in some cases above about 800° C. When treated at these temperatures, the biomass is carbonized to form biochar.

"Biochar" is a carbonized form of a biomass, such as plant material, that is specifically produced for non-fuel applications. The production processes can be batch or continuous, where the base material of particle sizes ranging from a few millimeters to several centimeters is placed in a retort, with or without carrier gas flowing through. Carrier gases may be non-reactive such as nitrogen, or reactive such as steam. The retort may be heated by external heat or directly heated by combusting a portion of the base material. Vapors emanating may be captured for other applications. After a period of several minutes to hours, the residual material remaining is biochar. Biochar is composed of mainly carbon
(generally more than about 30%) and is porous. It also includes other elements (such as nitrogen, oxygen, hydrogen, and nutrient elements).

"Biochar/metal composites" are multiphase biochar-based porous materials where the metal phase can have one, two, or there dimension of less than 100 nanometers (i.e., nanocomposites) and/or the metal phase can be microsized (i.e., ultrafine composites). The production of composites can be through either pre-treatment of feedstock biomass or post-treatment of biochar. The metal can be an oxide, a hydroxide, or an oxyhydroxide. In an embodiment, the biochar/metal composite can include one or more metals, where each metal can be present in one or more forms (e.g., an oxide, a hydroxide, or an oxyhydroxide).

The term "fluid" can refer to water (e.g., fresh water, salt water, tap water, sewer water, discharged water, processing water, agriculture drainage water, animal husbandry drainage water, other grey and black water, other natural water, combinations thereof, and the like), solvents, and combinations thereof. In an embodiment, the fluid is water and can be obtained or derived from discharged water, processing water, natural water bodies, combinations thereof, and the like.

General Discussion

Embodiments of the present disclosure provide methods of removing a material (e.g., a nutrient or a contaminant) such as one or more types of anions such as phosphate, nitrate, or arsenic anions, from a fluid (e.g., water) with biochar/metal composites, methods of making biochar/metal composites, structures including biochar/metal composites, and the like. Embodiments of the present disclosure can be used in water treatment, water purification, soil remediation, soil amendment, solid waste reclamation, and the like.

Embodiments of the present disclosure provide methods of synthesizing a material (i.e., biochar/metal composites) with nanosized and/or ultrafine metal oxides/hydroxides/oxyhydroxides particles on the carbon surfaces within the biochar matrix. Embodiments of the present disclosure provide methods of enriching biomass with metal elements (metal pretreatment) as a precursor for producing biochar/metal composites. The metal enrichment of the biomass can be realized through: 1) direct treatment of biomass with a metal solution (e.g., Mg$^{2+}$, Al$^{3+}$, and Fe$^{3+}$), see Example 1; 2) bioaccumulation of metals into biomass during plant growth, see Example 2; and 3) bacterial treatment of biomass (e.g., anearobical digestion) to encrese metal concentrations, see Example 3.
Embodiments of the present disclosure are advantageous because the alternatives (e.g., activated carbon and resin) for removing a contaminant, such as a phosphate anion, are ineffective and/or more expensive. In addition, embodiments of the present disclosure are capable of removing a larger amount of a material from a fluid (e.g., a fluid such as water, discharged water, processing water, storm water, and the like) than some alternatives. Furthermore, some of the exhausted biochar/metal composites (e.g., nutrient-loaded biochar/metal composites) can be reused as fertilizers to improve soil productivity.

Thus, embodiments of the present disclosure may provide new opportunities to develop high-quality, low-cost, biochar/metal composites to solve environmental or other problems.

Embodiments of the present disclosure include using biomass from one or various sources to produce biochar/metal composites. The biochar/metal composites can be used for water treatment to remove contaminants, such as anions (e.g., phosphate, nitrate, and arsenic anions). An exemplary embodiment of the present disclosure includes a biochar/metal composite that has an affinity for anions when exposed to a fluid including the anions of interest. In an embodiment, the biochar/metal composites have an absorption capacity of about 90,000 mg*kg^{-1} for nitrates, about 100,000-800,000 mg*kg^{-1} for phosphates, and about 3,000-42,000 mg*kg^{-1} for As(V).

In an embodiment, the structure can be nano-sized metal structures to micro-sized metal structures. In an embodiment, the nano-sized metal structures and/or micro-sized metal structures can be disposed on or within the biochar (e.g., the surface, within pores, and the like). In particular, the nano-sized metal structure micro-sized metal structures can be embedded on the surface of the biochar. The metal structure can become disposed on or within the biochar during pyrolysis of a biomass that was exposed to a precursor metal solution.

In an embodiment, the metal structure is in the form of a nanostructure or a microstructure or a portion of the plurality of metal structures can be nanostructures and another portion microstructures. In an embodiment, the metal structure can have one or more morphologies such as a flake, spherical structure, semi-sphereical structure, cubic structure, other crystal structures, and the like. In an embodiment, at least one dimension (e.g., length, width, thickness) of the nanostructure is about 500 nm or less, about 250 nm or less, or about 100 nm or less. In an embodiment, when the nanostructure is a flake, the nanostructure can have a thickness of about 10 to 25 nm or about 1 to 100 nm. In an embodiment, at least one
dimension (e.g., length, width, thickness) of the microstructure is about 500 nm to 100 µm, about 500 nm to 50 µm, or about 500 nm to 10 µm.

As noted above, the composite can include one or more types of metal structures. In an embodiment, the metal structure can be a metal oxide, a metal hydroxide, or a metal oxyhydroxide. In an embodiment, the metal can be Mg, Al, Fe, Zn, or others. In an embodiment, the metal oxide is selected from a Mg oxide, a Al oxide, a Fe oxide, Zn oxide, other metal oxide, or a combination thereof. In an exemplary embodiment, the metal structure can be a Mg(OH)₂ nanoparticle or a MgO nanoparticle. In an exemplary embodiment, the metal structure can be a γ-Fe₂O₃ nanostructure or a γ-Fe₂O₃ microstructure. In an exemplary embodiment, the iron structure can be magnetic and separate from the composite as needed. In an exemplary embodiment, the metal structure can be a AIOOH nanostructure or a AIOOH microstructure. The type and/or amount of metal structure can be selected based upon the desired anions to be adsorbed.

In an embodiment, the biochar is porous. In an embodiment, the biochar can include mesopores (e.g., greater than about 100 nm in diameter, generally in the micrometer range) and/or nanopores (e.g., less than about 100 nm in diameter).

In an exemplary embodiment, the biochar/metal composite can be produced by mixing a biomass with a precursor metal solution (Example 1). The biomass is described in detail above. In an embodiment, the precursor metal solution is a solution that can be processed to form the desired metal structure. In an embodiment, the precursor metal solution can include a precursor Mg²⁺ solution (e.g., MgCl₂, Mg(CH₃COO)₂, MgBr₂, or a combination thereof), a precursor Al³⁺ solution (e.g., AlCl₃, AlBr₃, Al(CH₃COO)₃, or a combination thereof), a precursor Fe³⁺/Fe²⁺ solution (e.g., FeCl₂, FeC₂O₄, FeBr₃, FeBr₂, Fe(CH₃COO)₃, Fe(CH₃COO)₂, or a combination thereof), Zn²⁺ solution (e.g., ZnCl₂, ZnBr₂, Zn(CH₃COO)₂, or a combination thereof), or other metal cation solution, or a combination thereof. The amount of the precursor metal solution mixed with an amount of biomass and/or the time frame of the mixing may depend upon the type of biomass, the biochar formed, the precursor metal solution, the desired amount of metal structure disposed on the biochar, the metal structure formed, and the like. A detailed example of making biochar Mg(OH)₂, MgO, and γ-Fe₂O₃, composites are provided in the Example 1.

In an exemplary embodiment, the biochar/metal composite can be produced from direct pyrolysis of metal-accumulated biomass (Example 2). In an embodiment, the precursor biomass is a biomass such as a plant, crop, and the like, that can bioaccumulate
metal elments when irrigated with metal solutions. In an embodiment, the metal solution can include \( \text{Mg}^{2+} \) (e.g., \( \text{MgCl}_2 \), \( \text{Mg(CH}_3\text{COO)}_2 \), \( \text{MgBr}_2 \), or a combination thereof). In an embodiment, the metal solution can include \( \text{Al}^{3+} \) (e.g., \( \text{AlCl}_3 \), \( \text{AlBr}_3 \), \( \text{Al(CH}_3\text{COO)}_3 \), or a combination thereof). In an embodiment, the metal solution can include \( \text{Fe}^{3+} \) (e.g., \( \text{FeCl}_2 \), \( \text{FeCl}_3 \), \( \text{FeBr}_3 \), \( \text{FeBr}_2 \), \( \text{Fe(CH}_3\text{COO)}_3 \), \( \text{Fe(CH}_3\text{COO)}_2 \), or a combination thereof). In an embodiment, the metal solution can include \( \text{Zn}^{2+} \) solution (e.g., \( \text{ZnCl}_2 \), \( \text{ZnBr}_2 \), \( \text{Zn(CH}_3\text{COO)}_2 \), or a combination thereof). In an embodiment, the metal-bioaccumulated in the biomass can be processed to form the desired metal structure (e.g. nanostructure and/or microstructure as described herein) in the biochar composites. A detailed example of making biochar \( \text{Mg(OH)}_2/\text{MgO} \) composites are provided in the Example 2.

In an exemplary embodiment, the biochar/metal composite can be produced from direct pyrolysis of bacterial digested biomass, which are rich in metal elements (Example 3). In an embodiment, the precursor biomass is residual of anaerobically digested biomass, in which, the bacterial digestion has concentrated metal elements (e.g., \( \text{Mg}, \text{Ca}, \text{Fe}, \text{Zn}, \) and \( \text{Al} \), such as those described herein) in the remaining biomass. The metals in the bacterial digested residues can be processed to form the desired metal structure (e.g. nanostructure and/or microstructure as described herein) in the biochar composites. A detailed example of making biochar \( \text{MgO} \) composites from residual of anaerobically digested sugarbeet tailings are provided in the Example 3.

Once the biomass is enriched with metal through one of the above methods, it can be subjected to pyrolysis to form a biochar metal composite. During pyrolysis metal oxide nanoparticles are formed from the precursor metal material. The conditions (e.g., temperature, temperature ramp, time frame, and the like) of the pyrolysis can be adjusted to form the desired biochar metal oxide composite. Under certain conditions, particularly humid conditions, nano-sized metal oxides and/or micro-sized metal oxides on the biochar surfaces may become nano-sized metal and/or micro-sized metal hydroxides or metal oxyhydroxides. In an embodiment, the biochar metal composite can be a biochar metal-oxide composite, a biochar metal-hydroxide composite, a biochar metal-oxyhydroxides composite, or a biochar having a combination of metal-oxide, metal-hydroxide, and/or metal-oxyhydroxide. Each of the biochar metal-oxide, the biochar metal-hydroxide, and the biochar metal-oxyhydroxides composite have similar functions and can be used to remove contaminants from water.
As mentioned above, embodiments of the present disclosure include a method of removing a material (e.g., an anion) from a fluid (e.g., water). In an embodiment, the fluid can be water obtained or derived from discharged water, processing water, other grey and black water, storm water, other natural water, and the like. The fluid including the material can be mixed in a processing plant or pond with uncontaminated fluid (e.g., water) prior to removal of the material. The fluid can be exposed to the biochar-metal composites by passing the fluid through an area including the biochar-metal composite and/or the biochar-metal composite can be disposed into the fluid (e.g., a pond or holding area) to remove the material. The fluid and/or the biochar-metal composite can be agitated to ensure that the fluid or a large portion thereof comes into contact with the biochar-metal composite or vice versa to ensure a maximum amount of material is removed from the fluid. After a period of time the biochar-metal composite is removed from the fluid and can be processed to remove the material and reused or recycled.

As mentioned above, the material to be removed from the fluid can be a nutrient anion (e.g., phosphate, nitrate, and/or their analogues), and/or a metal anion (e.g., arsenic anion (arsenate, arsenite) or their analogue). In an embodiment, the material (e.g., metal anion or nutrient anion) can be adsorbed onto the surface of the biochar/metal composites. The term "adsorbed" can refer to any exposed surface (e.g., including micro- or nano-channels, and micro- or nano-particles) of the biochar-metal composite and can include precipitating, attaching, crystallization, bonding (e.g., ionic, covalent, hydrogen, Van der Waals interaction, and the like) onto the surfaces and/or embedding into pores of the biochar-metal composite.

In an embodiment, exhausted biochar/metal composites that include a plant nutrient (e.g., phosphate, nitrate) can be directly applied to soil as a fertilizer (See Example 2). For the case when the material belongs to toxicants (e.g., arsenic anion), the exhausted biochar/metal composites can be either sent to a landfill or be washed with salt/acid/base to remove the toxicants and then the cleaned biochar/metal-oxide composites can be reused or applied to soil as amendment to sequester carbon.

**Examples**

Now having described the embodiments of the present disclosure, in general, Example 1 describes the synthesis and application of biochar/metal composites prepared from biomass pretreated with metal solutions. In particularly, it discusses biochar composites produced from Mg$^{2+}$, Fe$^{3+}$, and Al$^{3+}$ treated biomass and their application in removing...
phosphate (P), nitrate (N), arsenic (As(v)), and other contaminants from water. Example 2 describes the synthesis and application of biochar/metal composites prepared by direct pyrolysis of metal-accumulated plant biomass (bioaccumulation). In particularly, it discusses the removal of P by a Mg-biochar composite produced from Mg-enriched tomato tissues, and the application of the spent, P-laden biochar composites as slow release fertilizer. Example 3 describes the synthesis and application of biochar/metal prepared from anaerobically digested biomass. In particularly, it discusses the removal of P by a Mg-biochar composite produced from anaerobically digested sugar beet tailings.

While embodiments of present disclosure are described in connection with the Examples and the corresponding text and figures, there is no intent to limit embodiments of the present disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

Example 1:
Brief Introduction:

New synthesis was developed to create highly porous metal-biochar nanocomposite material consisting of MgO nano-flakes, nanosized y-Fe2O3 particles, or, nanosized AIOOH particles within a biochar matrix that has high sorption ability for ionic contaminations (e.g., P, N, and As(y)). The synthesis method was used in laboratory to produce metal-biochar nanocomposites from a variety of carbon-rich biomass pretreated with Mg2+, Fe3+, Al3+ solutions. Physical and chemical properties of the synthesized nanocomposites were studied systematically with X-ray powder diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and energy-dispersive X-ray analysis. In addition, batch sorption experiment was conducted to determine the sorption ability of the metal-biochar nanocomposites to aqueous phosphate, nitrate, and As(v). The results showed that the nanocomposites have uniform morphologies with metal oxides/hydroxides/oxyhydroxides disperse uniformly on the surface of the biochar matrix. As a result, all the tested metal nanocomposites showed excellent removal efficiencies to ionic contaminants in water. The Langmuir adsorption capacities of these nanocomposites are much higher than the reported values of other adsorbents.

Materials and methods:
Feedstocks:

Five common biomass feedstocks were used to make the metal-biochar nanocomposites: sugar beet tailings (SBT), sugarcane bagasse (SB), cottonwoods (CW), pine woods (PW), and peanut shells (PS). The SBT and SB were provided by the American Crystal Sugar Company (East Grand Forks, MN) and Florida Crystals Corporation (Okeelanta, FL), respectively. The other three feedstocks were obtained locally in Gainesville FL. All feedstocks were air dried and milled into powders of ~2 mm prior to use.

Method to make metal-biochar nanocomposites:

Magnesium Chloride Hexahydrate (MgCl₂·6H₂O), Ferric Chloride Hexahydrate (FeCl₃·6H₂O) and Aluminum Chloride Hexahydrate (AlCl₃·6H₂O) were purchased from Fisher scientific to prepare a magnesium chloride solution to pretreat the biomass feedstocks. All the solutions used in this work were prepared with deionized (DI) water (Nanopure water, Barnstead), which was also used to rinse and clean the samples. The metal solution was prepared by dissolving 40 g of the each salt in 60 mL of deionized water. Each feedstock was immersed into one of the metal salt solutions for 2 hours. The mixture of biomass and metal chloride was then oven dried at 80 °C to remove the water. A dry mixture of biomass pretreated with one of metal salts was heated at 10 °C/min up to 600 °C under N₂ flow for 1 hour. Maintain the N₂ flow is important because it could bring out byproduct gases including HCl to facilitate the formation of metal oxide/hydroxide/oxyhydroxide particles in the biochar matrix. The biochar nanocomposites produced from pyrolysis was gently crushed and sieved into two size fractions: <0.5 and 0.5-1 mm. Only the latter was used in the experiments to minimize the presence of residual ash particles. In addition, the selected samples were washed with DI water for several times, oven dried (80 °C), and sealed in a container for further tests.

Characterizations:

Microscopic features of the biochar nanocomposites were characterized with both field emission gun scanning electron microscopy (FEG-SEM, JEOL 6335F) equipped with an energy-dispersive X-ray analyzer and high-resolution transmission electron microscopy (HR-TEM, JEOL 2010F). X-ray diffraction (XRD) analysis was carried out to identify any crystallographic structure for the samples using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal
monochromator. Surface area of the nanocomposites was determined using N₂ sorption isotherms at 77K run on NOVA 1200 and the Brunauer-Emmet-Teller (BET) method to determine mesopore-enclosed surfaces and using CO₂ sorption isotherms run on a Quantachrome Autosorb measured at 273 K and interpreted using grand canonical Monte Carlo simulations of the non-local density functional theory for micropore-enclosed (<1.5 nm) surfaces. Magnetic properties of the biochar/y-Fe₂O₃ composite were measured using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design.

Removal of P, N, and As(v) from aqueous solutions:

P, N, and As(v) solutions were prepared by dissolving potassium phosphate dibasic anhydrous (K2HPO4, certified A.C.S, Fisher Scientific), sodium nitrate (NaNCh, certified A.C.S, Fisher Scientific), and sodium arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O, certified A.C.S, Fisher Scientific) in DI water, respectively.

Adsorption kinetics of these ionic contaminants on biochar nanocomposite samples were examined by mixing 0.1 g of the adsorbent with 50 mL adsorbate solutions (50mg/L P or As(V) or 20mg/L N) in 68 mL digestion vessels (Environmental Express) at room temperature (22±0.5 °C). The vessels were then shaken at 200 rpm in a mechanical shaker. At appropriate time intervals, the vessels were withdrawn and the mixtures were immediately filtered through 0.22 μm pore size nylon membrane filters (GE cellulose nylon membrane).

Adsorption isotherms of P, N, or As(V) to biochar nanocomposite were determined by mixing 0.1 g the adsorbent with 50 mL adsorbate solutions of different concentrations ranging from 1 to 200 mg/L in the digestion vessels. The vessels were shaken in the mechanical shaker for 24 h at room temperature, this time period having been previously determined by kinetic experiments as sufficient for adsorption equilibrium to be established. The samples were then withdrawn and filtered to determine adsorbed adsorbate concentrations.

The As(V) concentrations in the liquid phase samples were determined by using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma 3200). The phosphate concentrations of the liquid phase samples were then determined by ICP-AES or the ascorbic acid method (ESS Method 310.1; USEPA, 1992) with aid of a spectrophotometer (Thermo Scientific EVO 60). The nitrate concentrations of the liquid phase samples were analyzed by using ion chromatography (IC) (DIONEX-120, USA). Adsorbate concentrations on the solid phase were calculated based on the initial and final
aqueous concentrations. All the experimental treatments were performed in duplicate and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference larger than 5%.

Results and discussion:
MgO-biochar nanocomposites remove P and N

The new synthesis successfully produced biochar from all the MgCl₂-pretreated biomass feedstocks. Elemental analysis of the magnesium showed that the biochar samples contained 8.3-26.1% of MgO (Table 1.1), suggesting the samples actually are in form of composites of MgO and biochar. The AOAC method of acid digestion was used to determine the Mg content and the entire Mg element in the samples was assumed to be in the MgO form.

Table 1.1. Production and some physicochemical properties of MgO-biochar nanocomposites.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Production rate (%)</th>
<th>MgO content (%)</th>
<th>MgO size (nm)</th>
<th>N₂ surface area (m²/g)</th>
<th>CO₂ surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBT</td>
<td>31.0</td>
<td>26.1</td>
<td>19.6</td>
<td>70.0</td>
<td>253.4</td>
</tr>
<tr>
<td>CW</td>
<td>30.6</td>
<td>26.0</td>
<td>39.3</td>
<td>50.1</td>
<td>270.7</td>
</tr>
<tr>
<td>SB</td>
<td>40.2</td>
<td>13.4</td>
<td>66.9</td>
<td>122.5</td>
<td>338.0</td>
</tr>
<tr>
<td>PS</td>
<td>42.3</td>
<td>14.9</td>
<td>42.6</td>
<td>18.9</td>
<td>346.5</td>
</tr>
<tr>
<td>PW</td>
<td>48.9</td>
<td>8.3</td>
<td>37.2</td>
<td>2.8</td>
<td>432.6</td>
</tr>
</tbody>
</table>

Figure 1.1 shows the wide angle XRD patterns of various MgO-biochar samples. Apparently these samples had similar diffraction peaks, which could be indexed as the cubic symmetry of MgO (JCPDS card no. 75-0447). The XRD results confirmed that MgO particles in all the samples were highly crystalline. The broadness of the XRD peaks was used to calculate the average crystalline size of MgO particles using the Debye-Scherrer equation. The results showed that the MgO particles in all the tested samples were nanosized with size between 19.6 and 66.9 nm (Table 1.1), indicating the novel synthesis method can produce MgO-biochar nanocomposites from biomass feedstocks.

To investigate their morphological structures, the MgO-biochar nanocomposites were imaged using scanning electron microscopy (SEM) and the transmission electron microscopy (TEM). Figure 1.2 shows SEM images of MgO-biochar nanocomposites produced from SBT, which reveal that MgO particles are in form of nano-flakes within the biochar matrix. In
general, the surface morphologies of the nanocomposites were rough and porous due to the intrinsic nature of biochar (Figure 1.2a). Figure 1.2b shows that the MgO flakes are uniformly deposited across the entire substrates, having thicknesses of 10-25 nm (similar to calculated value from the Debye-Scherrer equation) and lengths of 0.2-1 μm (Figure 1.2c). As shown in the cross sectional SEM image (Figure 1.2d), the nanostructures are randomly oriented growing off the biochar surface and the largest structures orient in a near-vertical direction.

The TEM image in Figure 1.3a is in good agreement with the morphology as presented in the SEM images. The TEM results suggest that good dispersion of individual nano-MgO flakes throughout the biochar matrix without notable aggregations. Selected area electron diffraction (SAED) patterns of the MgO-biochar nanocomposite (inset in Figure 1.3a) show circled rings, indicating polycrystalline nature of the sample. Figure 1.3b (high-resolution TEM images) reveals the lattice fringe with a lattice distance of 0.21 nm, indicating the spacing between the (200) planes of MgO. Figure 1.3c shows the mesoporous structure of the biochar matrix of the nanocomposite, which has average pore size of about 50 nm. In addition, Figure 1.3d indicated that the nano-MgO flakes were composed of nanosized MgO grains and there were many pores on them with an aperture of about 2-4 nm. This confirms that the whole flake structures are polycrystalline due to the anisotropic assembly of the building blocks [1]. Such morphology would render the MgO-biochar nanocomposites high surface area (Table 1.1), and facile mass transfer with the biochar matrix.

As shown in Figure 1.4a, almost all of the tested MgO-biochar nanocomposites showed removal efficiencies to aqueous phosphate (20 ppm) and nitrate (20 ppm), except the PW MgO-biochar showed a relatively low removal of P of 0.5%. The SBT MgO-biochar sample had the highest phosphate removal rate of 66.7%. Because surfaces of most unmodified carbon-base adsorbents (including biochars) are negatively charged, they have little or no ability to remove anions, particularly with respect to phosphate and nitrate [2, 3]. The point of zero charge of MgO, however, is around 12 [4], indicating its surface is positively charged in most natural aqueous conditions [5]. As a result, it has been reported that MgO particles in the biochar matrix could strongly bind anions, such as phosphate ions, in aqueous solution through mono-, bi- and trinuclear complexions [5]. Under this mechanism, several factors could be considered as important in controlling phosphate removal by the nanocomposites, such as the amount of the MgO particles in the biochar
matrix, sizes and morphological structures of MgO, distribution of MgO in the matrix, and so on. Interestingly, the PS MgO-biochar nanocomposite was the best adsorbent to remove aqueous nitrate with a removal rate of 11.7%, which was much higher than that of the SBT biochar (3.6%), the best phosphate adsorbent. This suggests that different adsorption mechanisms could be responsible to the removal of phosphate and nitrate from aqueous solution by the MgO-biochar nanocomposites. Adsorption isotherms of phosphate on SBT MgO-biochar nanocomposite and nitrate on PS MgO-biochar nanocomposite (Figure 1.4b & 1.4c) showed strong adsorption ability of the two adsorbent. The Langmuir model was applied to determine the maximum sorption capacities of the two nanocomposites. The model assumes monolayer adsorption of adsorbents onto a homogeneous adsorbent surface with no interactions between the adsorbed molecules [5]. Simulations from the model matched both experimental isotherms very well with correlation coefficients ($R^2$) exceeding 0.90. The Langmuir maximum capacity of phosphate on the MgO-biochar (SBT) was around 835 mg/g, which is much higher than that of other adsorbents for the removal of phosphate from aqueous solutions [5-7]. For instance, the Langmuir maximum capacity of biologically activated biochar produced from anaerobically digested SBT, pure MgO, and surface modified MgO are only around 133, 3.17, and 75.1 mg/g, respectively [5, 8]. This makes the MgO-biochar nanocomposites very attractive and high efficiency adsorbents for the treatment of phosphate polluted water. The Langmuir maximum nitrate capacity of MgO-biochar (PS) sample was around 94 mg/g, also much higher than or at least comparable to many commonly used adsorbents, particularly carbon-based materials [9-11].

The remarkable high performance of MgO-biochar nanocomposites for removal of aqueous P and N could be attributed to the unique calcining process, which dramatically increased the surface area of individual MgO flakes through anisotropic assembly of the nano-MgO blocks and also improved porosity of biochar matrix through evaporation processes. The MgCl$_2$ hydrates, which originally used as precursors of MgO, could also play a role as activating agent during the calcining process when the hydrates were releasing the water and other chemical compounds.

y-Fe$_2$O$_3$-biochar nanocomposites remove As(v):

The new pyrolysis method successfully produced a biochar composite containing a large quantity of y-Fe$_2$O$_3$. Weight measurements showed that about 74.3% of the weight of
the biochar composite comes from Y-Fe$_2$O$_3$, indicating the ratio of y-Fe$_2$C>3 and biochar in the composite is approximately 3:1. Because the density of y-Fe$_2$O$_3$ (>5 g/cm$^3$) is more than 5 times that of biochar matrix (<1 g/cm$^3$), the biochar still dominate the composite volumetrically and serves as a host for the y-Fe$_2$C>3 particles.

The structure and phase purity of the biochar/y-Fe$_2$O$_3$ composite were investigated by X-ray diffractionmetry (XRD). Strong and sharp reflection XRD peaks suggest that the as-prepared iron oxides with the biochar matrix were well crystallized (Figure 1.5a). Maghemite was identified as the major crystalline phase in the biochar as characterized with diffraction peaks at 30.2°, 35.5°, 43.2°, 57.3°, and 62.9°. These peaks correspond to five indexed planes (220), (311), (400), (511), and (440) of Maghemite [12]. Although diffraction peaks of y-Fe$_2$O$_3$ and Fe$_3$C are very similar, X-ray photoelectron spectroscopy (XPS) results (Figure 1.5b) showed that the binding energies of Fe$^{2+}$ and Fe$^{3+}$ were 723.76 and 710.43 eV, respectively, close to the reported values of Fe(III) compounds [13]. This indicates that the iron oxides within the biochar matrix are y-Fe$_2$C>3 particles. Findings from the XRD and XPS analyses confirmed the success in synthesis of the biochar/y-Fe$_2$O$_3$ composite.

Details about the structure and morphology of the obtained composite were examined in the SEM and TEM studies. As shown in the SEM images (Figure 1.6), a good dispersion of nano- and micro-sized y-Fe$_2$O$_3$ particles have been achieved on the surface of biochar. Those particles are cubic and octahedral on the biochar surfaces and the surface morphologies of the composite are rough and porous due to the intrinsic nature of biochar (Figure 1.6a). Figure 1.6b shows that the y-Fe$_2$O$_3$ particles are partly embedded in the biochar matrix, thereby indicating good mechanical bonding between the biochar matrix and the iron oxide particles, which prevents the separation of the y-Fe$_2$C>3 particles from the biochar matrix when exposed to extraneous forces caused for example by water or gas flow. Figure 1.6c-d shows that the particles’ shape changes with their sizes from cubic to octahedral. Figure 1.6c indicates that the octahedral shape is dominant when the particle size is larger than 1 micron. On the other hand, the homogeneously-dispersed cubic y-Fe$_2$C>3 particles are dominant for particle size is smaller than 1 micron. Coupled with energy dispersive X-ray spectroscopy (EDS) facility, the composition of the nanostructures can be analyzed at the same time. EDS spectra in Figure 1.6e reveal that the biochar/y-Fe$_2$C>3 composite comprises only 3 elements, i.e., carbon, iron, and oxygen, which is consistent with the XRD results.

The TEM images in Figure 1.7 were in good agreement with the morphology as presented in the SEM images. Figure 1.7 shows the TEM micrographs of different-sized
cubic $\text{y-Fe}_2\text{O}_3$ particles within the pores of the biochar matrix. A good dispersion of $\text{y-Fe}_2\text{O}_3$ particles has also been achieved within the pores of the bulk biochar (Figure 1.7a). The particles are clearly separated from each other inside the biochar matrix, and their sizes range from 50 nm to 1 micron (Figure 1.7b), which is consistent with the SEM measurements. The selected-area electron diffraction pattern (SAED) at the inset of Figure 1.7c (the red circle marks the region of interest where the SAED pattern was recorded) reveals that the $\text{y-Fe}_2\text{C}_3$ particles in the composite exhibit a single-crystal structure. SEM and TEM image analyses results indicate that the biochar produced in this work is a nano-/colloidal composite.

The adsorption of As(V) on the biochar/y-Fe$_2$O$_3$ composite was fast and reached equilibrium within 4 hours (Figure 1.8a). The relatively fast kinetics suggests that biochar might play an important role in the dispersion of $\text{y-Fe}_2\text{O}_3$ particles which efficiently increased the surface area of the particles and active sites of metal oxides by separation [14, 15]. The adsorption isotherm of As(V) to the biochar/y-Fe$_2$O$_3$ composite demonstrated a 'L' shape with a maximum capacity around 3,000 mg/Kg (Figure 1.8b). The Langmuir maximum adsorption capacity of the biochar/y-Fe$_2$O$_3$ composite to As(V) is 3,147 mg/Kg, which is comparable to or that of many commercial adsorbents, including iron modified activated carbon. If only contribution from the iron oxides is taken into consideration, the maximum arsenic adsorption capacity of the $\text{y-Fe}_2\text{O}_3$ particles in the composite is about 4,237 mg/kg, similar to that of the pure $\text{y-Fe}_2\text{O}_3$ particles (4,643 mg/kg) [16]. These results also indicate that the biochar/y-Fe$_2$O$_3$ composite can be used as a high efficiency adsorption in water treatment to remove arsenic from aqueous solutions.

To investigate the magnetic properties, a magnetic hysteresis curve for magnetic biochar/y-Fe$_2$O$_3$ was recorded at room temperature (Figure 1.9). The sample showed ferromagnetic properties, revealed by the coercive field of 34.1 Oe and the saturation magnetization of 69.2 emu/g for biochar/y-Fe$_2$O$_3$, a value that is very close to that of pure $\text{y-Fe}_2\text{O}_3$ materials (76.0 emu/g) [17]. Based on this measurement, the saturation magnetization of the $\text{y-Fe}_2\text{O}_3$ particles in the composite should be 93.2 emu/g, higher than that of pure $\text{y-Fe}_2\text{O}_3$. This suggests that the composite might containing other magnetic materials, such as elemental iron (Fe), which could be produced as the iron oxides tend to be reduced by carbon or reduction syngas [18, 19]. The biochar/y-Fe$_2$O$_3$ composite clearly showed a good magnate property to be attracted by a permanent magnet (Figure 1.9). This property is essentially important for the convenient recycling of contaminant-laden biochar/y-Fe$_2$O$_3$ adsorbents after use. For instance, the visual demonstration experiment showed that the biochar/y-Fe$_2$O$_3$
composite could completely remove the blue color of the solution, indicating strong adsorption ability to methylene blue, and the post-adsorption biochar/y-Fe203 composite could be easily separated from the solution with a permanent magnet (see the two pictures inserted in Figure 1.9).

AIOOH-biochar nanocomposites remove P and As(v):

Similarly, the new pyrolysis method successfully produced a biochar nanocomposite containing a large quantity of AIOOH particles. The structure and phase purity of Biochar/AIOOH were investigated by X-ray diffractometry (XRD). As shown in Figure 1.10, the strong and sharp reflection peaks suggest that the as-prepared fractal nanocrystals are well crystallized. Beohemite is believed to be the major crystalline phase for the synthesized nanosheets as identified by the diffraction peaks at 13.8°, 28.3°, 38.3°, 49.0°, and 64.7°. These peaks correspond to five indexed planes (020), (120), (031), (200), and (151), respectively, of AIOOH[20].

The morphological structures of the obtained Biochar/AIOOH were provided by SEM studies. In general, the surface morphologies of the Biochar/AIOOH are rough and porous due to the intrinsic nature of biochar (Figure 1.11a). Figure 1.11b shows that the AIOOH flakes are homogeneously and densely grown across the entire substrates and separated from each other, having about 30 nm thicknesses and hundreds nm lengths and widths (Figure 1.11c). Cross-sectional SEM measurement (Figure 1.11d) shows the nanostructures are randomly oriented growing off the surface with the largest structures oriented in a near-vertical direction. The result of the energy-disperse X-ray (EDX) analysis (Figure 1.11e) confirms that the AIOOH nano-flakes consisted of aluminum and oxygen, a chemical composition that agreed well with the aluminum oxide.

Figure 1.12 shows the TEM micrograph of a piece of AIOOH nano-flake that dropped off the Biochar/AIOOH. As shown in Figure 1.12a, it can be seen that the size of the flake was in good agreement with that as presented in the SEM images. The AIOOH nano-flake exhibits the wrinkles on the surface, which may favor the adsorption of the contaminations due to the greater surface area of wrinkled nano-flakes. The selected-area electron diffraction pattern (SAED) at the inset of Figure 1.12b reveals that our products exhibit a polycrystalline structure. Coupled with energy dispersive X-ray spectroscopy (EDX) facility, the composition of the nanostructures can be analyzed at the same time. EDX characterization in Figure 1.12c (the rectangle marks the region of interest where the EDX spectrum was
recorded in Figure 1.b.) revealed that the biochar/AIOOH composites consist only 3 elements, i.e., carbon aluminum and oxygen which is consistent with the XRD result.

The adsorption of As(V) onto the Biochar/AIOOH nanocomposites reached equilibrium after 12 h and had a Langmuir sorption capacity of 17.4 mg/Kg (Figure 1.13a &b), which is better than the reported adsorption capacities of AI2O3 and activated AI2O3 (170-8990 and 9200- 15900 mg/Kg, respectively) [21, 22]. The adsorption of P on the Biochar/AIOOH nanocomposites reached equilibrium much faster (after 6 h) with a Langmuir sorption capacity around 135 mg/g, which is much higher than that of other adsorbents for the removal of phosphate from aqueous solution [5-7]. These results indicate that the Biochar/AIOOH nanocomposites are very attractive and high efficiency adsorbents for the treatment of As(V) and P polluted water. We believe that the remarkable high performance of Biochar/AIOOH nanocomposites for removal of various contaminations could be attributed to the unique calcining process, which dramatically increased the surface area of individual AIOOH flakes through anisotropic assembly of the nano-AIOOH blocks and also improved porosity of biochar matrix through evaporation processes. The AlCl₃ hydrates, which originally used as precursors of AIOOH, could also play a role as activating agent during the calcining process when the hydrates were releasing the water and other chemical compounds.

Conclusions:

In summary, an innovative and simple method has been developed to synthesize porous Metal-biochar nanocomposites by crystallizing nano- or micro-sized metal oxides/hydroxides/oxyhydroxides on carbon surfaces within the biochar matrix through slow pyrolysis of biomass pretreated with metal solution (e.g., MgCl₂, FeCl₃, and AlCl₃). The biochar nanocomposites impressively showed highly nano-porous structures in both the metal particles and the biochar matrix. The synthesis method is widely applicable to various biochar precursors and endows the metal-biochar nanocomposites with excellent adsorption ability to P, N, and As(V) in aqueous solutions. On the whole, this approach of synthesizing metal oxides/hydroxides/oxyhydroxides nanocrystals impregnated in a biochar matrix provides new opportunities in developing low-cost and high-efficient adsorbent to benefit the environment and introduces nanofabrication techniques to engineer multi-functional biochars (i.e., engineered biochars).
Example 2:

Brief Introduction:

An innovative synthesis was developed to produce biochar nanocomposites from magnesium (Mg) enriched tomato tissues through slow pyrolysis in a N₂ environment. The resulting Mg-biochar composites showed excellent sorption ability to phosphate (P) in aqueous solutions. It contained nanoscale Mg(OH)₂ and MgO particles on carbon matrix surfaces within the pore structures. The maximum sorption capacity of P to the biochar could reach >100 mg/g and the sorption is mainly controlled by two mechanisms: precipitation of P through chemical reaction with Mg particles and surface deposition of P onto Mg crystals on biochar surface. Most of the P retained in the biochar through surface deposition was bioavailable and could be released equally at multiple successive extractions. In addition, the P-laden biochar significantly stimulated grass seed germination and growth. These results suggested the spent P-laden biochar can be applied directly to soils as a slow-release fertilizer.

Materials and methods

For Mg enrichment, tomato plants grown in a peat-based medium were irrigated with Hoagland solution at 25 mM Mg²⁺ twice a week dried and grounded into 1-2 mm pieces as feedstocks for biochar production. A tube furnace (MTI, Richmond, CA) was used to convert them into biochar samples in a N₂ environment at temperatures of 600 °C for one hour. The resulting biochar samples were washed several times with DI water and oven dried for further tests. The resulting biochar samples were henceforth referred to as MgEC.

Major elements of biochar and the feedstock were determined by the acid digestion method with inductively-coupled plasma atomic emission spectroscopy (ICP-AES) analysis. Scanning electron microscope (SEM) imaging analysis of the original and P-sorbed Mg-biochar was conducted using a JEOL JSM-6400 Scanning Microscope. Surface elemental analysis was also conducted simultaneously with the SEM at the same surface locations using energy dispersive X-ray spectroscopy (EDX, Oxford Instruments Link ISIS). X-ray diffraction (XRD) analysis was carried out using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a PHI 5100 series ESCA spectrometer (Perkin-Elmer) to determine the elemental composition on the sample surface.
P solutions were prepared by dissolving Potassium Phosphate Dibasic Anhydrous (K2HPO4, certified A.C.S, Fisher Scientific) in DI water. The P sorption ability of the biochar was examined using 68 mL digestion vessels (Environmental Express) at room temperature (22±0.5 °C) with a 1:500 (0.1g biochar in 50ml solution) biochar/solution (30 mg/L P) ratio for 24 h. Adsorption kinetics of P to the MgEC were examined using 30 mg/L P solutions at time intervals of 20min, 50min, 1.5h, 4h, 11.5h, 24h, and 48 h. Adsorption isotherm was determined by measuring the P sorption to the MgEC at solution concentrations ranging from 3.1 to 588.1 mg/L after 24 h of mixing. The post-sorption samples were filtered immediately through 0.22 μm pore size nylon membrane filters (GE cellulose nylon membrane) to determine residual P concentrations.

Bioavailable phosphorus test was carried out by the Mehlich 3 extraction method[23]. The Mehlich 3 extractant consists of 0.2 M CH3COOH, 0.25 M NH4NO3, 0.015 M NH4F, 0.013 M HNO3, 0.001 M EDTA. The final pH of the extracting solution was about 2.5 ±0.1. The samples were shaken at 200 rpm for 5 min at room temperature (22±0.5 °C), and then filtered through Whatman No. 42 filter paper to determine the extractable P concentrations.

Kinetics of phosphorus release from spent MgEC into DI water was tested by mixing 0.3 g of the P-laden biochar with 120 ml DI water at room temperature (22±0.5 °C). The contents of P in the aqueous solution were then determined after 1, 2, 3, 6, 10, 24, 48, 120, and 144 h. For the next 11 days, the P-laden biochar was filtered out from the solution and added to 120 ml fresh DI water every day to release P.

Seeds germination assay was carried out by spreading same number of grass seeds (Brown Top Millot) on a layer of filter paper moistened with DI water in containers with or without 0.1g P-laden MgEC with ≥ 4 replicates. All replicates were incubated at room temperature to determine the germination rates. The early stage (first 13 days) seedling growth was also determined and 10 seedlings from each group were randomly collected for statistical analysis.
Results and discussion

Table 2.1. Elemental analysis of feedstocks and biochars produced in this study (mass %).

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>K</th>
<th>Na</th>
<th>Mg</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Pb</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td>MgET</td>
<td>0.22±0.03</td>
<td>3.82±0.17</td>
<td>0.18±0.01</td>
<td>3.11±0.32</td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td>0.02±0.00</td>
<td>1.00±0.00</td>
<td>0.00±0.00</td>
</tr>
<tr>
<td>LCT</td>
<td>0.21±0.03</td>
<td>3.70±0.15</td>
<td>0.28±0.04</td>
<td>1.51±0.16</td>
<td>0.00±0.00</td>
<td>0.01±0.00</td>
<td>0.01±0.00</td>
<td>- 0.00±0.00</td>
<td></td>
</tr>
<tr>
<td>MgEC</td>
<td>0.74±0.06</td>
<td>1.25±0.10</td>
<td>0.1.14±0.01</td>
<td>8.79±0.82</td>
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<td>0.09±0.01</td>
<td>- 0.03±0.00</td>
<td></td>
</tr>
<tr>
<td>LCC</td>
<td>0.60±0.10</td>
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<td>0.11±0.01</td>
<td>3.53±0.33</td>
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<td>0.01±0.00</td>
<td>0.07±0.02</td>
<td>- 0.01±0.00</td>
<td></td>
</tr>
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</table>

We found tomato plants treated with 25 mM Mg accumulated much higher level of Mg in tissue compared to plants from the laboratory control (Table 2.1), indicating Mg can be substantially enriched in tomato plants. In the literature, a number of naturally occurring or genetically engineered plants have been reported to hyperaccumulate metals, such as arsenic, lead, cadmium, and mercury [24-26]. As shown in Table 2.1, pyrolysis process further concentrated Mg in the engineered biochar sample. These results demonstrated that the new synthesis can successfully produce engineered biochar composites (carbon-metal composites) from plant biomass enriched with cationic nutrient elements, such as Mg, through growth enrichment.

In our previous work, strong P sorption ability of the engineered biochars converted from digested and Mg-pretreated biomass was attributed to the presence of colloidal or nanosized MgO particles on the carbon surface within the pores [5]. XRD analysis of the Mg-enriched biochar obtained in this example, however, showed both MgO and Mg(OH)$_2$ (Figure 2.1c). Diffraction peaks at (001), (100), (101), (110), (211), (103) and (201) are readily recognized from the XRD pattern of the Mg(OH)$_2$ powder, and the peaks at (200) and (220) match the peak in the diffractions of MgO. The particle sizes of MgO and Mg(OH)$_2$ within the biochar matrix calculated using the Scherrer formula were about 46.0 nm and 6.3 nm, respectively [27]. SEM-EDX analysis showed the wide spread of nanoscale Mg flakes on the carbon surface (Figure 2.1a and 2.1b), which concur to the XRD results that the engineered biochar produced from Mg-enriched plant tissue is a biochar composites with Mg oxyhydroxides particles on carbon surfaces within the biochar matrix. Further characterization of the engineered biochar with the XPS showed strong signals of Mg on the surface (Figure 2.1 d), further confirming previous results. The XPS results also suggested that there might be more Mg(OH)$_2$ than MgO on the surface of the engineered biochar.
suggesting Mg(OH)$_2$ particles may play a bigger role than the MgO particles in controlling the surface interactions between P and the Mg-biochar composites.

Kinetics study indicated that the sorption of P on the Mg-biochar composites increased smoothly over time and reached equilibrium around 24 hrs (Figure 2.2A). This result is similar to the sorption kinetics of P on the MgO-biochar composites produced from digested sugar beet tailings, although the new engineered biochar contained both MgO and Mg(OH)$_2$ particles[3]. The maximum P sorption capacity of the engineered biochar obtained from the isotherm study was greater than 100 mg/g (Figure 2.2B), which is comparable to that of the MgO-biochar composites reported in our previous studies [3]. Furthermore, the P sorption ability of the new engineered biochar is superior to most of the reported values of other carbonaceous adsorbents.

In our previous studies, the strong sorption of P to the Mg-biochar composites was mainly controlled by the surface attraction between P ions and the colloidal or nanosized MgO particles within the biochar [3]. The surface deposition mechanism was further verified by characterization of post-sorption biochar samples. Because surfaces of the biochar produced in this work were dominated by the Mg(OH)$_2$ particles, the P sorption mechanism could be different from the previous studies. The XRD spectra of the post-sorption biochar (i.e., P-laden biochar) in this work showed strong signals of not only the pre-exist Mg oxyhydroxides but also new Mg-P crystals in the forms of MgHPO$_4$ and Mg(H$_2$P0$_4$)$_2$ with calculated particle sizes of 30.3 nm and 32.4 nm respectively (Figure 2.2C). This suggested that, in addition to surface deposition mechanism as reported previously, precipitation of P by Mg released from the engineered biochar could also play an important role in the P removal from aqueous solutions. The SEM-EDX analysis confirmed the formation of the new Mg-P crystals within the biochar matrix (Figure 2.2D). As shown in the SEM image, the post-sorption biochar showed clusters of nanoscale Mg-P rods on the carbon surface, which are not observed in the original biochar samples.

The precipitation of P on the Mg-biochar was further confirmed by XPS analysis (Figures 2.2E, 2.2F). The Mg Is spectrum (Figure 2.2E) clearly demonstrates the presences of four compounds on the P-laden biochar surface [28]. The molar percentage of Mg oxyhydroxides, MgHPO$_4$, and Mg(H$_2$P0$_4$)$_2$ on the biochar surface were around 21.9%, 25.8% and 52.3%, respectively. The Mg oxyhydroxides on the carbon surface decreased dramatically after the sorption, because they reacted with the P ions to form the Mg-P precipitates. Although both MgO and Mg(OH)$_2$ have low solubility, the presence of P anions
in the solution may facilitate their dissolution to form more insolubility of P salt, such as Mg(H₂P₀₄)₂ and MgHP₀₄.

It is interesting to draw attention to the XPS spectrum of P 2p3/2 on the surface of the P-laden biochar. The binding energies of P 2p3/2 peak represent three compounds. The binding energy at 132.3 eV corresponds to MgHP₀₄ (11.2%), while that at 135.2 eV to Mg(H₂P₀₄)₂ (24.8%) [29, 30]. The molar ratio between MgHP₀₄ and Mg(H₂P₀₄)₂ is 0.45, which is similar to that of the XPS analysis of Mg Is (0.49). The most intense component at a high binding energy of 138.16 eV associated with the presence of P analog (64.0%) in which there is no reaction between P anions and metallic cations. Therefore, the extremely high content of P₀₄ analog can be attributed to the surface deposition mechanisms. In addition to the interaction between P and MgO particles as reported in our previous studies, the other three Mg salts including the two precipitates can also adsorb additional P analog by hydrogen bonding [31-33]. The number of the additional P overlayers should be around 2 layers presumed from the fitting XPS spectrum of P 2p3/2. Findings from the XPS analysis of P 2p3/2 on post-sorption biochar indicated that, in addition to precipitation, surface deposition indicated that the removal of P by the new engineered biochar is mainly controlled by both the precipitation (strong chemical bond) and surface deposition (weak chemical bond) mechanisms (Figure 2.3).

Because the majority of the P (64%) in exhausted biochar is deposited on the Mg surface with the carbon matrix through weak chemical bonds, such as hydrogen bonding and electrostatic attraction, it may be bioavailable through desorption processes (Figure 2.3) when the exhausted biochar is applied to soils as amendment. Hence, the exhausted biochar may have the potential to serve as a slow release fertilizer and improve soil fertility. To assess the bioavailability of P, the extractable P content of the exhausted biochar was determined with the Mehlich 3 method, which is a widely accepted laboratory index of plant-available P in the soil. Results showed that the extractable P of the exhausted biochar was around 7555.5±10.5 mg P/kg, much higher than that of optimum P in soil for plant growth and crop yields, i.e. 45-50 mg P/kg[34]. About 19% of total P in post-sorption MgEC was Mehlich3 extractable which is consistent with findings of published studies[35]. This result suggest a high feasibility of using the engineered biochar to treat and reclaim P from wastewater and then applied the P-laden biochar directly to soil as a fertilizer for eco-friendly and sustainable production of crops.
Desorption kinetics study of the P-laden biochar showed the slow release of the P and the equilibrium was reached after 30 hrs (Figure 2.4A). Because of the strong sorption of P on the Mg surface, only small amount of P was released into the solution at equilibrium. As shown in Figure 2.4B, however, this release was repeatable when fresh solution was introduced to the system (to mimic conditions under plant growth - which depletes released P). During the 11 successive slow releasing experiments, about same amount of P (3.2% of total P in biochar) was released at each run, indicating the exhaust biochar could be used as a slow-P-release fertilizer when applied to soils.

Bioassay of seeds germination and early stage seedling growth is a simple and commonly used ecotoxicological test for evaluating the impact of biochar amendment on crop growth [36]. The assay results showed that the P-laden MgEC could promote seed germination. The addition of the biochar increased seed germination rate from 56.71% to 88.75% and the results are statistically significant (p < 0.001). After 13-day growth, the average shoot length of the grasses with biochar addition was 61.3±5.3 mm, which was much longer than that in the control groups (average shoot length 36.7±12.9 mm) (Figures 2.4C, 2.4D) with P value of 3.4×10^{-4}. Furthermore, leaves of the grasses from the biochar groups were greener and stronger (Figure 2.4C). These results further confirmed that the P-laden spent engineered biochar can be used as a slow-release fertilizer to be applied to soils to improve soil quality and productivity.

Conclusions

As a first study of its kind, an innovative synthesis technique has been developed to produce metal-biochar nanocomposites directly from plant tissues enriched with Mg. The resulted Mg-biochar composites showed strong P removal ability from aqueous P solution. In addition, the spent biochar, which is P laden, behaved as a slow-release fertilizer and could release P into aqueous solution in multiple times (mimics slow release P source for plant uptake) to stimulate grass seeds’ emergence and growth. The concept and findings form this study can be used to develop new sustainable and eco-friendly strategies to synthesize and apply the engineered biochar to reclaim P, reduce eutrophication, improve soil quality, and sequester carbon.
Example 3:

Brief Introduction:

Two biochars were produced from anaerobically digested and undigested sugar beet tailings through slow-pyrolysis at 600 °C. The digested sugar beet tailing biochar (DSTC) and raw sugar beet tailing biochar (STC) yields were around 45.5% and 36.3% of initial dry weight, respectively. Compared to STC, DSTC had similar pH and surface functional groups, but higher surface area, and its surface was less negatively charged. SEM-EDS and XRD analyses showed that colloidal and nano-sized periclase (MgO) was presented on the surface of DSTC. Laboratory adsorption experiments were conducted to assess the phosphate removal ability of the two biochars, an activated carbon (AC), and three Fe-modified biochar/AC adsorbents. The DSTC showed the highest phosphate removal ability with a removal rate around 73%. Batch adsorption kinetic and equilibrium isotherm experiments and post-adsorption characterizations using SEM-EDS, XRD, and FTIR suggested that colloidal and nano-sized MgO (periclase) particles on the biochar surface were the main adsorption sites for aqueous phosphate. Our results suggest that biochar converted from anaerobically digested sugar beet tailings is a promising alternative adsorbent, which can be used to reclaim phosphate from water or reduce phosphate leaching from fertilized soils. In addition, there is no need to regenerate the exhausted biochar because the phosphate-laden biochar contains abundance of valuable nutrients, which may be used as a slow-release fertilizer to enhance soil fertility and to sequester carbon.

Materials and methods:

Biochar Production

Raw sugar beet tailings and anaerobically digested sugar beet tailings were obtained from American Crystal Sugar Company (East Grand Forks, MN). A two stage hybrid digester system was used to digest the tailings anaerobically at thermophilic temperature of 55 °C. The first stage was an unmixed solids digester and the readily leached out soluble components were digested in the second stage anaerobic filter (attached growth reactor). The digested tailings used for this study were collected from the bottom of the first stage vessel. These samples were rinsed with water and oven dried (80 °C). A bench-scale slow pyrolyzer was used to convert the samples into biochars. For each experiment, about 500 g of the dried samples were fed into a stainless cylinder reactor (50 cm diameter, 30 cm height) designed to fit inside of a furnace (Olympic 1823HE). The cylinder reactor was first purged with nitrogen gas (10 psi) and an oxygen sensor attached to the reactor ensured that the oxygen content in
the reactor was less than 0.5% before it was inserted into the furnace. The reactor was purged again with N₂ along with the furnace and sealed for pyrolysis. Stainless steel tubing and fittings were installed on the furnace and the reactor to collect the oil and the non-condensable gases evolved during the slow pyrolysis. The controller of the furnace was programmed to drive the internal biomass chamber temperature to 600 °C at a rate of 10 °C/min and held at the peak temperature for 2 h before cooling to room temperature. Biochar produced from the pyrolysis was gently crushed and sieved into two size fractions: <0.5 mm and 0.5-1 mm. Only the latter was used in the experiments to minimize the presence of residual ash particles. In addition, the biochar samples were then washed with deionized (DI) water for several times, oven dried (80 °C), and sealed in a container before use.

Biochar Properties

Elemental C, N, and H abundances were determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of the resulting CO₂, H₂ and NO₂ gases, respectively. Major inorganic elements were determined using the AOAC method of acid digesting the samples for multi-elemental analysis by inductively-coupled plasma emission spectroscopy (ICP-AES).

Scanning electron microscope (SEM) imaging analysis was conducted using a JEOL JSM-6400 Scanning Microscope. Varying magnifications were used to compare the structure and surface characteristics of the two biochar samples. Surface element analysis was also conducted simultaneously with the SEM at the same surface locations using energy dispersive X-ray spectroscopy (EDS, Oxford Instruments Link ISIS). The EDS can provide rapid qualitative, or with adequate standards, semi-quantitative analysis of elemental composition with a sampling depth of 1-2 microns [37].

X-ray diffraction (XRD) analysis was carried out to identify any crystallographic structure in the two biochar samples using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. Crystalline compounds in the samples were identified by comparing diffraction data against a database compiled by the Joint Committee on Powder Diffraction and Standards.
Other Adsorbents

Granulated activated carbon (AC, from coconut shell) was obtained from Fisher Scientific and was gently crushed, sieved, and washed using the same procedures as the biochar samples. In addition, each of the three biochars were modified by impregnating ferric hydroxide onto the AC (i.e., FeAC), STC (i.e., FeSTC), and DSTC (i.e., FeDSTC) samples according to the procedure employed by Thirunavukkarasu et al. [38] and Chen et al. [39]. Briefly, 6 grams of AC, STC, and DSTC were added to 30 mL of 2M Fe(NO₃)₃·9H₂O solution separately, and pH was then adjusted to 4-5 with NaOH to create an iron precipitate. The mixture was then heated at 105 °C overnight and the grains were separated, sieved, and washed thoroughly with DI water. The FeAC, FeSTC, and FeDSTC samples were then oven dried for further use.

Phosphate Adsorption

Phosphate solutions were prepared by dissolving Potassium Phosphate Dibasic Anhydrous (K₂HPO₄, certified A.C.S, Fisher Scientific) in DI water. The experiments were carried out in 68 mL digestion vessels (Environmental Express) at room temperature (22±0.5 °C). To initiate the adsorption experiment, 50 mL phosphate solutions of 61.5 mg/L (i.e., 20 mg/L P) and 0.1 g of each adsorbent (DSTC, FeDSTC, STC, FeSTC, AC, or FeAC) were added into the vessels. The pH of the solution was then adjusted to 7, which is not only the typical pH of secondary wastewater, but also among the optimal pH values for phosphate adsorption as reported by previous studies [40]. After being shaken at 200 rpm in a mechanical shaker for 24 h, the vials were withdrawn and the mixtures were filtered through 0.22 µm pore size nylon membrane filters (GE cellulose nylon membrane). The phosphate concentrations of the liquid phase samples were then determined by the ascorbic acid method (ESS Method 3 10.1; [41]) with aid of a spectrophotometer (Thermo Scientific EVO 60). The phosphate removal rates were calculated based on the initial and final aqueous concentrations. Adsorption kinetics and isotherms of phosphate to the DSTC were also measured using the procedures discussed previously. All the experimental treatments were performed in duplicate and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference larger than 5%.
Results and Discussion

Biochar and bioenergy production rates

On a weight basis, about nine percent more biochar was produced from digested sugar beet tailing residue feedstock than from the undigested sugar beet tailings. The biochar production rates of the digested and undigested materials were 45.5% and 36.3% of initial dry weight, respectively. Although studies have shown that increased biochar production through slow pyrolysis is often accompanied by decreased yield in bio-oil, the bio-oil production rates were similar for the digested and undigested sugar beet tailings with values of 12.5% and 10.9%, respectively. By summing to 100%, it follows that the amount of the non-condensable gases extracted from the digested sugar beet tailings (43.6%) must have been lower than that from the undigested sugar beet tailings (51.2%). These results suggest that residue materials from anaerobic digestion of sugar beet tailings are comparable with undigested sugar beet tailings, and thus can be used as feedstock for both biochar and further bioenergy production.

Table 3.1. Elemental analysis of raw and digested sugar beet tailings, and their associated biochars, STC and DSTC, respectively (mass %)³.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O³</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Fe</th>
<th>Al</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digested Tailing</td>
<td>33.94</td>
<td>4.53</td>
<td>46.89</td>
<td>2.35</td>
<td>0.34</td>
<td>0.28</td>
<td>9.68</td>
<td>1.20</td>
<td>0.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Raw Tailing</td>
<td>36.06</td>
<td>3.43</td>
<td>55.82</td>
<td>1.23</td>
<td>0.16</td>
<td>0.09</td>
<td>1.80</td>
<td>0.53</td>
<td>0.88</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DSTC</td>
<td>30.81</td>
<td>1.38</td>
<td>39.87</td>
<td>2.74</td>
<td>0.46</td>
<td>0.21</td>
<td>9.78</td>
<td>9.79</td>
<td>1.97</td>
<td>0.75</td>
<td>0.24</td>
<td>0.03</td>
</tr>
<tr>
<td>STC</td>
<td>50.78</td>
<td>2.08</td>
<td>36.70</td>
<td>1.83</td>
<td>0.35</td>
<td>0.05</td>
<td>4.41</td>
<td>1.53</td>
<td>1.04</td>
<td>0.59</td>
<td>0.64</td>
<td>-</td>
</tr>
</tbody>
</table>

a: Expressed on a total dry weight basis, b: Determined by weight difference assumed that the total weight of the samples was made up of the tested elements only, c: Below 0.01%.

Elemental composition

Elemental analysis of the feedstock materials showed that the residue of the anaerobically digested sugar beet tailings were carbon rich and had carbon content around 34% (Table 3.1). This carbon content was only slightly lower than that of the undigested feedstock (Table 3.1), confirming that the residue of anaerobically digested sugar beet tailings can be used as feedstock for biochar production. Compared to the undigested sugar beet tailings, the digested feedstock contained more hydrogen and nitrogen, but less oxygen.
element. It is notable that, after the anaerobic digestion, most of the inorganic elements in the residue materials increased except potassium. For instance, the magnesium content of the digested sugar beet tailings increased from about one-half percent to above one percent. The calcium content also increased dramatically from above one percent to about ten percent. These results are consistent with findings of published studies that anaerobic digestion may concentrate exchangeable cations, such as calcium and magnesium, into the residue materials [42, 43].

After being converted into biochar through slow pyrolysis, the carbon content of DSTC (30.81%) was slightly lower than that of the feedstock, but the carbon content of STC increased dramatically to more than 50% (Table 3.1). This indicates that the two biochars could be very different because of the effects of anaerobic digestion on the feedstock materials. The hydrogen, oxygen, and nitrogen contents of the two biochars were similar to each other (Table 3.1). But some of the nutrient elements including phosphorous, calcium, and magnesium were much higher in the DSTC than in the STC (Table 3.1). High levels of calcium and phosphorous were also found in studies of some other biochars [44]. However, the DSTC had a surprisingly high level of magnesium of about 10%, which is more than 6 times of the STC. These results suggest that the digested sugar beet tailing biochar may, when applied to soils, provide a more concentrated source of nutrients to crops.

The SEM imaging of the STC (500 X) showed that the undigested sugar beet tailing biochar had smooth surfaces (Figure 3.1A). This is consistent with the findings from the N₂ surface area measurement, which suggested that micropores dominated the STC surface. The EDS spectrum of the STC surface (Figure 3.1A) identified the same elements detected in the elemental analysis (Table 3.1). The SEM imaging of the DSTC (500 X), however, showed knaggy surfaces (Figure 3.2B). The EDS spectrum of the DSTC surface (Figure 3.2B) also showed many elements detected in the elemental analysis (Table 3.1). Although the element analysis suggested that the DSTC had similar amount calcium and magnesium (i.e., about 10%), the EDS spectrum of the DSTC indicated a magnesium content greater than that of calcium, suggesting more magnesium may present on the biochar surfaces. This was further confirmed by the SEM-EDS analysis at a high resolution (7000 X). The SEM image of the DSTC taken at the high resolution showed evidence of mineral crystals on the biochar surface (Figure 3.1C). These crystals were mainly magnesium minerals as evidenced in the EDS spectrum at the same location (Figure 3.1C), which showed an extremely high peak of
magnesium. The magnesium crystals are colloidal or nano-sized and could contribute to the high surface area of the digested sugar beet tailing biochar.

The XRD spectra of the DSTC and STC showed several peaks (Figure 3.2), indicating the presence of mineral crystals. In the DSTC spectrum, the two strong peaks at 43.2° (d = 2.09 Å) and 62.2° (d = 1.49 Å) were identified as periclase (MgO), suggesting that the colloidal and nano-sized magnesium crystals on the DSTC surface (as shown in the SEM-EDS analysis) were MgO. Quartz (SiO₂) and calcite (CaCO₃) were found in both the DSTC and STC, which is also consistent with the elemental analyses and EDS spectra of the two biochars.

Phosphate removal

Both AC and STC showed very low phosphate removal and AC even released a small amount of phosphate back into the solution (Figure 3.3). This is consistent with the literature [45, 46] and the fact that STC has very high negative zeta potential. Although the zeta potential measurements showed that the surface of DSTC was also negatively charged, the DSTC demonstrated the highest phosphate removal with a rate about 73%, which was much higher than the phosphate removal rates of all the other adsorbents tested. The ferric hydroxide impregnation did increase the phosphate removal for the AC and STC, with FeAC and FeSTC removal of about 10% and 8% of phosphate, respectively. The Fe surface modification, however, reduced the phosphate removal rate of DSTC dramatically from around 73% to 22%. This preliminary assessment suggests that anaerobically digested sugar beet tailing biochar could be used as low-cost adsorbent to effectively remove phosphate from aqueous solution without any modification.

The adsorption of phosphate onto the DSTC increased smoothly over time and reached equilibrium after 24 h (Figure 3.4a). The slow kinetics further suggests that precipitation might not play an important role in the removal of phosphate by the biochar. With the Langmuir maximum capacity around 133,085 mg/kg (Figure 3.4b), the DSTC showed phosphate sorption ability to superior to most of the reported values of other carbonaceous adsorbents [40, 47, 48]. The enhanced removal of phosphate by the DSTC was because of the large amount of colloidal and nano-sized periclase (MgO) on its surface, which has a strong ability to bind phosphate in aqueous solution [49, 50].
Conclusions

Based on the characterization of biochar physicochemical properties and the preliminary phosphate sorption assessment, it is evident that 1) residue from the anaerobic digestion of sugar beet tailings can be used as a feed stock for biochar production, 2) The anaerobically digested sugar beet tailing biochar has colloidal and nano-sized periclase (MgO) on its surface (i.e., MgO-biochar composite) and 3) anaerobic digestion enhances the phosphate adsorption ability of biochar produced from digested sugar beet tailings relative to undigested ones. Thus, DSTC should be considered a promising alternative water treatment or environmental remediation technology for phosphate removal. In addition, when used as an adsorbent to reclaim phosphate from water, the exhausted biochar can be directly applied to agricultural fields as a fertilizer to improve soil fertility because the P-loaded MgO-biochar composites contains abundance of valuable nutrients. Potential additional environmental benefits from this approach include fuel or energy produced during both the anaerobic digestion and pyrolysis and carbon sequestration due to biochar's refractory nature. Because arsenate and molybdate are phosphate analogues [51], it is expected that the digested sugar beet tailing biochar would also be an effective adsorbent for them.

References, each of which is incorporated herein by reference


34. Pierzynski, G.M., Methods of phosphorus analysis for soils, sediments, residuals, and waters, 2000, North Carolina State University Raleigh.


In regard to the discussion herein including the Examples above and the claims, it should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term "about" can include traditional
rounding according based on how the value is determined, the measurement techniques, and the like. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

Many variations and modifications may be made to the above-described embodiments. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.
Claims

We claim:

1. A structure comprising:
   a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, and wherein the composite has an affinity for an anion in a fluid.

2. The structure of claim 1, wherein the metal structure is a nanostructure.

3. The structure of claim 2, wherein the metal structure is a \( \text{Mg(OH)}_2 \) nanoparticle or a \( \text{MgO} \) nanoparticle.

4. The structure of claim 3, wherein the nanostructure has a morphology of a flake or a crystal.

5. The structure of claim 3, wherein the nanostructure has at least one dimension that is about 100 nm or less.

6. The structure of claim 3, wherein the nanostructure has a length, width, and a thickness that are each about 500 nm or less

7. The structure of claim 1, wherein the metal structure is a \( \gamma\)-\( \text{Fe}_2\text{O}_3 \) structure.

8. The structure of claim 7, wherein the \( \gamma\)-\( \text{Fe}_2\text{O}_3 \) structure is a nanostructure or a microstructure.

9. The structure of claim 1, wherein the metal structure is a \( \text{AlOOH} \) structure.
10. The structure of claim 1, wherein the anions are selected from a phosphate anion, a nitrate anion, an arsenic anion, or a combination thereof.

11. The structure of claim 1, wherein the metal structure are nanostructure, wherein the biochar has nanostructures embeded on the surface of the biochar.

12. A method of removing contaminants from a fluid comprising:
   exposing a biochar/metal composite and a fluid to one another, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, wherein the fluid includes an anion of interest, whereien the composite has an affinity for anions of interest in the fluid; and adsorbing one or more types of anions of interest onto the biochar/metal composite.

13. The method of claim 12, wherein the fluid is water.

14. The method of claim 12, wherein the anions are selected from a phosphate anion, a nitrate, an arsenic anion, or a combination thereof.

15. The method of claim 12, wheien the metal structure is a Mg(OH)$_2$ nanoparticle or a MgO nanoparticle.

16. The method of claim 12, wheien the metal structure is a γ-Fe$_2$O$_3$ nanostructure or a γ-Fe$_2$O$_3$ microstructure.

17. The method of claim 12, wherien the metal structure is a AIOOH nanoparticle or a AIOOH microstructure.

18. A method of making a biochar metal composite, comprising:
   mixing a biomass with a precursor metal solution;
drying the biomass; and
pyrolysis of the biomass to form a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, where the biochar is porous, and wherein the composite has an affinity for an anion in a fluid.

19. The method of claim 18, wherein the precursor metal solution is selected from a precursor Mg solution, a precursor Al solution, a precursor Fe solution, or a combination thereof.

20. The method of claim 18, wherein the biomass is selected from: algae, a plant, a tree, a crop, a crop residue, a grass, a forest and mill residue, wood and wood waste, a fast-growing tree, other carbon-rich materials, or a combination thereof.

21. The method of claim 18, wherein the metal structure is a Mg(OH)$_2$ nanoparticle or a MgO nanoparticle.

22. The method of claim 18, wherein the metal structure is a $\gamma$-Fe$_2$O$_3$ nanostructure or a $\gamma$-Fe$_2$O$_3$ microstructure.

23. The method of claim 18, wherein the metal structure is an AIOOH nanostructure or an AIOOH microstructure.

24. A method of making a biochar metal composite, comprising:
   - irrigating a biomass with one or more metal ion solutions;
   - harvesting and drying the biomass; and
   - pyrolysing the biomass to form a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is
disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, and wherein the composite has an affinity for an anion in a fluid.

25. The method of claim 24, wherein the irrigation metal solution is selected from a Mg solution, a Al solution, a Fe solution, or a combination thereof.

26. The method of claim 24, wherein the biomass is selected from: algae, a plant, a tree, a crop, a vegetable, a grass, a fast-growing tree, or a combination thereof.

27. The method of claim 24, wherein the metal structure is a Mg(OH)$_2$ nanoparticle or a MgO nanoparticle.

28. The method of claim 24, wherein the metal structure is a γ-Fe$_2$O$_3$ nanostructure or a γ-Fe$_2$O$_3$ microstructure.

29. The method of claim 21, wherein the metal structure is a AlOOH nanostructure or a AlOOH microstructure.

30. A method of making a biochar metal composite, comprising:
   bacterial treatment of a biomass;
   drying the treated biomass; and
   pyrolysing of the biomass to form a a biochar/metal composite, wherein the metal in the composite is a metal structure, wherein the metal is selected from Mg, Al, Fe, Zn, or a combination thereof, wherein each metal structure is one or more of the following: an oxide, a hydroxide, or an oxyhydroxide, wherein each metal structure is disposed: on the biochar, within the biochar, or a combination of on and within the biochar, wherein the biochar is porous, and wherein the composite has an affinity for an anion in a fluid.

31. The method of claim 30, wherein the metal structure is a Mg(OH)$_2$ nanoparticle or a MgO nanoparticle.
32. The method of claim 30, wherein the metal structure is a Y-Fe₂O₃ nanostructure or a γ-Fe₂O₃ microstructure.

33. The method of claim 30, wherein the metal structure is an AIOOH nanostructure or an AIOOH microstructure.

34. The method of claim 30, wherein the bacterial treatment includes bacterial digestion.
FIG. 1.1
FIG. 1.2
FIG. 1.4
FIG. 1.8
FIG. 1.10
FIG. 1.13C

FIG. 1.13D
FIG. 2.1A and 2.1B

FIG. 2.1C
**FIG. 2.2**

SUBSTITUTE SHEET (RULE 26)
FIG. 3.3
FIG. 3.4
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

C02F 3/10(2006.01)i, C02F 1/28(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F1/42, B01J21/18, B01D50/00, B01D39/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: biochar, metal oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search
17 June 2013 (17.06.2013)

Date of mailing of the international search report
17 June 2013 (17.06.2013)

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Facsimile No. 82-42-472-7140

Authorized officer
LEE, Dong Wook
Telephone No. 82-42-481-8163

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