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AND METHODS OF REMOVING CONTAMINANTS FROM WATER

(57) Abstract: Embodiments of the present disclosure provide methods of removing a material (e.g., a contaminant) such as one
or more types of metals (e.g., heavy metals such as lead), phosphate (and esters), nitrate (and esters), and/or nitrite (and esters),
from a fluid (e.g., water) with biologically activated biochar (e.g., digested residue derived biochar), methods of making biologi-
cally activated biochar, biologically activated biochar, structures including biologically activated biochar, and the like.



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**BIOLOGICALLY ACTIVATED BIOCHAR, METHODS OF MAKING
BIOLOGICALLY ACTIVATED BIOCHAR, AND METHODS OF REMOVING
CONTAMINANTS FROM WATER**

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to U.S. provisional application entitled, "METHODS OF REMOVING METAL FROM WATER," having serial number 61/300,956, filed on February 3, 2010, which is entirely incorporated herein by reference.

BACKGROUND

Biochar is a byproduct of low-temperature pyrolysis, one of many technologies to produce fuel from biomass. Pyrolysis uses direct thermal decomposition of biomass in an oxygen-starved environment to obtain bioenergy. Recent development of the biochar technology, however, has turned the production-interest of low-temperature pyrolysis from biofuel to the biochar. Because biochar has the potential to store massive amounts of carbon in soils for hundreds to even thousands of years, land application of biochar has been proposed as a novel approach to establish a significant, long-term sink for atmospheric carbon dioxide in terrestrial ecosystems. Land application of biochar may also reduce soil emissions of other greenhouse gases (*e.g.*, nitrous oxide and methane) to mitigate global warming. In addition, presence of biochar in soil may also have other potential advantages, such as improved soil quality and crop productivities.

SUMMARY

Embodiments of the present disclosure provide methods of removing a material (*e.g.*, a contaminant) such as one or more types of metals (*e.g.*, heavy metals such as lead), phosphate (and esters), nitrate (and esters), and/or nitrite (and esters), from a fluid (*e.g.*, water) with biologically activated biochar (*e.g.*, digested residue derived biochar), methods of making biologically activated biochar, biologically activated biochar, structures including biologically activated biochar, and the like.

An embodiment of a method of removing contaminants from a fluid, among others, includes exposing a biologically activated biochar and a fluid to one another, wherein the fluid includes one or more types of ions selected from a metal cation and its analogue, a phosphate ion and its analogue, a nitrate ion and its analogue, a nitrite ion and its analogue, and a combination thereof; and adsorbing at least one type of ion onto the biologically activated biochar.

An embodiment of a structure, among others, includes a biologically activated biochar, where the biologically activated biochar is a product of a pyrolysis of bioenergy residue.

An embodiment of a making a biochar, among others, includes: anaerobic or bacterial digestion of a material selected from a biomass, a carbon-rich waste, and a combination thereof, to produce a bioenergy residue; and pyrolyzing the bioenergy residue to form a biologically activated biochar.

Other structures, methods, features, and advantages of the present disclosure 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, 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 the disclosed devices and methods 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 relevant principles. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

FIG. 1.1 illustrates the production and uses of biologically activated biochar.

FIGS. 1.2A to 1.2C show the lead removal by DSTC, DSPC, and DMC, respectively, under a range of pH conditions (2-10).

FIGS. 1.3A and 1.3B illustrate the SEM-EDS analysis of the Pb-loaded DAWC and DSPC confirmed the exiting of lead crystals, respectively.

FIG. 1.4 illustrates a comparison of phosphate removal by different adsorbents, AC: activated carbon, STC: biochar derived from sugar beet tailings, and DSTC: biologically activated biochar derived from digested sugar beet tailings.

FIG. 2.1 illustrates a schematic of the experimental set-up for anaerobic digestion.

FIG. 2.2 illustrates a time course of methane yield during anaerobic digestion of sugarcane bagasse.

FIGS. 2.3A to 2.3D illustrate SEM images of raw bagasse (a), digested bagasse residue (b), raw bagasse biochar (c), and digested bagasse biochar (d). The scale is shown at the bottom of each picture.

FIG. 2.4 illustrates FTIR spectra of biochars from digested (DBC) and undigested (BC) bagasse.

FIG. 3.1A illustrates lead sorption kinetics onto DBC, BC, and AC.

FIG. 3.1B illustrates the relation between Pb adsorbed onto BC and square root of time before equilibrium.

FIG. 3.2 illustrates lead sorption isotherms onto DBC, BC, and AC

FIG. 3.3 illustrates XRD patterns of (1) fresh DBC, (2) post-adsorption DBC, (3) fresh AC, (4) post-adsorption AC, (5) fresh BC, (6) post-adsorption BC, and (7) background signal. The minerals were detected in the post-adsorption DBC with peak labeled as H for hydrocerrusite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and C for cerrusite (PbCO_3).

FIG. 3.4 illustrates an SEM image of the post-adsorption DBC.

FIGS. 3.5A and 3.5B illustrate FTIR spectra of fresh and post-adsorption DBC and fresh and post-adsorption BC, respectively.

FIGS. 4.1A to 4.1C illustrates SEM images of the two biochar samples: STC, 500X; DSTC, 500X; and DSTC, 7000X, respectively, and their corresponding EDS spectra of the two biochar samples: STC, 500X; DSTC, 500X; and DSTC, 7000X, respectively.

FIG. 4.2 illustrates XRD spectra of the two biochars. Crystallites were detected with peaks labeled as Q for quartz (SiO_2), C for calcite (CaCO_3), and P for periclase (MgO).

FIG. 4.3 illustrates FTIR spectra of the two biochar samples.

FIG. 4.4 illustrates the comparison of phosphate removal by different adsorbents.

FIGS. 5.1A and 5.1B illustrate SEM image and EDS spectra and of the post-adsorption DSTC at 7000X, respectively. The EDS spectra were obtained at the same spots as showing in the SEM image.

FIGS. 5.2A and 5.2B illustrate XRD and FTIR spectra of the original and post-adsorption DSTC, respectively. Crystallites were detected with peaks labeled in the XRD spectra as Q for quartz (SiO_2), C for calcite (CaCO_3), and P for periclase (MgO).

FIGS. 5.3A and 5.3B illustrate phosphate sorption kinetics: full kinetics; and pre-equilibrium plot against square root of time, respectively.

FIG. 5.4 illustrates the adsorption isotherm for phosphate on DSTC.

FIGS. 5.5A and 5.5B illustrate the effect of a) pH and b) coexisting anions on phosphate adsorption onto DSTC.

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, physics, 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. In particular, biomass can include sugarcane bagasse, manure, sugar beet tailing, and sugar beet pulp.

“Carbon-rich waste” can include a material containing a high content of carbon. It includes, but is not limited to, agricultural residues, wood wastes, yard trashes, food waste, animal waste, manure, other animal products (e.g., feathers, hairs, bones, blood, egg shells, and dead animals), algae, municipal sludge, waste plastic, waste tires, and combinations thereof. In particular, carbon-rich waste can include manure, sugarcane bagasse, sugar beet tailing, and sugar beet pulp.

“Residue materials from bioenergy production (bioenergy residues)” can include a solid residue material after bioenergy production. Bioenergy residues include the residues after anaerobic or other bacterial digestions of biomass, carbon-rich waste, and combinations thereof. In particular, bioenergy residues can include residue materials from anaerobically digested sugarcane bagasse, manure, sugar beet tailing, and sugar beet pulp.

The term “manure” refers to feces. Common forms of animal manure include farmyard manure, farm slurry, poultry manure, cattle manure, swine manure, poultry litter, and the like

“Pyrolysis” is the thermal conversion of a base material, a biomass or carbon-rich waste, such as plant material, in the absence of oxygen at elevated temperatures generally of about 200 to 800° C, or in some cases above about 800° C. When treated at these temperatures, the base material is carbonized to form biochar and bio-energy such as bio-oil and syngases.

“Biochar” is a carbonized form of a 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).

“Biologically Activated Biochar” is a carbonized form of a bioenergy residue. In an embodiment, the biologically activated biochar can be specifically produced for non-fuel applications. The process of production (*i.e.*, pyrolysis of bioenergy residues) can give the biologically activated biochar properties that make it suitable for applications such removing contaminants (*e.g.*, materials such as metals and analogues thereof, phosphates and their analogues, and combinations thereof) from water and other environmental remediation.

The phrase “anaerobically digested” refers to using microorganisms (*e.g.*, bacteria) to break down bioenergy residues (*e.g.*, biomass and/or carbon-rich waste) in the absence of oxygen.

The phrase “bacterially digested” refers to using microorganisms (*e.g.*, bacteria) to break down bioenergy residues (*e.g.*, biomass and/or carbon-rich waste). In particular, the microorganisms can break down the biomass and/or carbon-rich waste under anaerobic or aerobic conditions.

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 contaminant) such as one or more types of metals (*e.g.*, heavy metals such as lead), phosphate (and esters), nitrate (and esters), and/or nitrite (and esters), from a fluid (*e.g.*, water) with biologically activated biochar (*e.g.*, digested residue derived biochar), methods of making biologically activated biochar, biologically activated biochar, structures including biologically activated biochar, and the like. Embodiments of the present disclosure can be used in waste water treatment, water purification, soil remediation, solid waste reclamation, and the like.

Embodiments of the present disclosure are advantageous because the alternatives (*e.g.*, activated carbon and resin) for removing a contaminant such as lead cation, phosphate anion, nitrate anion, and/or nitrite anion, are more expensive. In addition, embodiments of the present disclosure are capable of removing a larger amount of a material (*e.g.*, lead, or phosphate) from a fluid (*e.g.*, a fluid such as water, discharged water, processing water, and the like) than some alternatives. Furthermore, some of the exhausted biologically activated biochars (*e.g.*, phosphate-loaded biologically activated biochar) can be reused as fertilizers to improve soil productivity.

Although most of the current biochar research is focused on its applications in carbon sequestration and soil amendment, a few studies found that biochar may contain many nano-structured pore networks to potentially adsorb and store chemical species including some of the common water contaminants. In addition, studies have also indicated that biochar can be further converted with certain cost benefits into activated carbon, a high-value adsorbent, through additional physical or

chemical activations. However, no study has been conducted to explore the feasibility to make activated biochar/charcoal/carbon through biological means.

The inventors recently discovered that residual materials from bioenergy productions, which are the solid wastes after anaerobic or bacterial digestion, can be used as feedstocks to produce high quality biochars (*i.e.*, biologically activated biochar). Laboratory studies showed that the biologically activated biochars possess many desirable properties for contaminant remediation, particularly with respect to remove common contaminants (*e.g.*, lead and phosphate) from fluids such as water. These findings introduce the possibility of using bioenergy production or bacterial digestion as a means to produce biologically activated biochar. Biological activation of biochar from pyrolysis of bioenergy residual materials is much lower in cost and may be more effective compared to the traditional physical or chemical activation methods. Thus, embodiments of the present disclosure may provide new opportunities to develop high-quality, low-cost, activated biochar (activated carbon) to solve environmental or other problems.

Embodiments of the present disclosure include using residual materials from bioenergy production (anaerobic digestion or other bacterial digestion) to produce biologically activated biochar. The biologically activated biochar can be used for water treatment to remove contaminants, such as lead and phosphate. This innovative approach of turning bioenergy residues into biologically activated biochar may present multiple economic and environmental benefits. When biochar is produced from bioenergy residues, not only may solid waste management costs be reduced, but bioenergy may be made as well as biologically activated carbon that may be used for water purification and other applications (See FIG. 1.1).

As described in greater detail in the Examples, four biologically activated biochars were produced from the bioenergy residue materials of anaerobically digested sugarcane bagasses, sugar beet tailings, sugar beet pulp, and manure. The resulted biochars are labeled as DBC, DSTC, DSPC, DMC, respectively. It was discovered that all the tested bioenergy residues are comparable with or even better than undigested raw materials, and thus can be used as feedstock to produce biologically activated biochar. Examples 1 and 3 provide additional details regarding the production and characterizations of biologically activated biochar from digested sugarcane bagass and sugar beet tailings.

It was determined that bioenergy production (*i.e.*, anaerobic or other bacterial digestion, which extracts large amounts of carbon, hydrogen, and/or oxygen elements out the feedstock), can concentrate other minerals and elements in the residual materials (*e.g.*, Table 1 in Example 3). When making the biologically activated biochar from them, pyrolysis may further concentrate the minerals in the resulted biochars, which in turn results in greater adsorption capacity for various contaminants. Elemental composition analysis of three biologically activated biochars showed elevated mineral concentrations such as calcium, magnesium, phosphorus, and potassium (Table 1 below). As a result, the mineral concentrated, biological activated biochar may have an enhanced ability to remove contaminants from a fluid such as water.

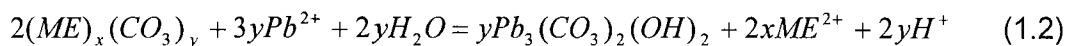
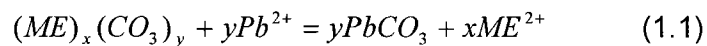
Table 1. Mineral concentrations in three biologically activated biochar.

	P	K	Ca	Mg	Zn	Mn	Cu	Fe	Al
DSTC	2.18%	1.97%	9.78%	9.79%	0.03%	-	-	0.59%	0.64%
DSPC	1.51%	0.64%	5.50%	1.08%	0.05%	0.04%	0.01%	1.54%	1.30%
DMC	0.87%	2.33%	1.89%	0.55%	0.019%	0.019%	0.004%	0.009%	0.016%

As shown in Example 3 (FIG. 4.3), calcium in the biologically activated biochar is mainly in the form of calcite (CaCO_3) and the magnesium are presented on the biochar surface as periclase (MgO), which can enhance the adsorption ability of the biologically activated biochar to both metals (*e.g.*, lead) and anion (*e.g.*, phosphate).

It was determined that all the four biologically activated biochars can effectively remove lead from water. FIGS. 1.2A to 1.2C shows the lead removal by DSTC, DSPC, and DMC, respectively under a range of pH conditions (2-10). In this test, 0.1g of each adsorbent was added into 50 mL lead solution of 200 ppm in a vial and shaken for 24h at room temperature. The lead removal rates were determined based the final and initial aqueous lead concentrations.

The lead removal by the biochars was mainly through the precipitation mechanism, such as:

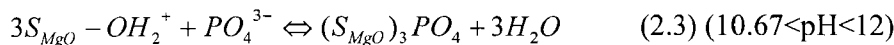
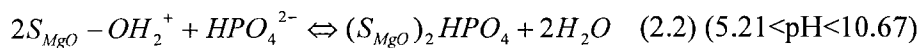
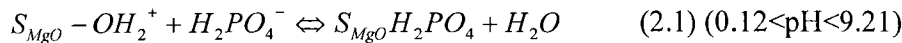


where $(ME)_x(CO_3)_y$ represents the concentrated carbonate minerals, such as calcite, $CaCO_3$, in the biologically activated biochar. The biologically activated biochar releases carbonate and/or phosphate species into the solution to precipitate metal ions, such as lead. SEM-EDS analysis of the Pb-laden DMC and DSPC confirmed the exiting of lead crystals in the post-adsorption biochars (FIGS. 1.3A to 1.3C).

Example 2 provides a detailed description of the mechanisms and characteristics of lead removal by DBC (digested sugarcane bagasse derived biochar).

It was also determined that at least one of the biologically activated biochar (*i.e.*, DSTC) can effectively remove phosphate from water. The inventors compared the phosphate removal ability of the DSTC to biochar derived from raw sugar beet tailings (STC), an activated carbon (AC), and their Fe-modified forms. The DSTC showed the highest phosphate removal ability with a removal rate around 73%, which is even better than Fe impregnated biochar/AC (FIG. 1.4).

This removal may be caused by that the biological activation (digestion and pyrolysis) creates many colloidal and nano-sized periclase (MgO) on the DSTC surface (FIG. 4.2 in Example 3). In most natural aqueous conditions, the MgO surface is positively charged and can electrostatically attract negatively charged phosphate species through reactions such as:



where S_{MgO} denotes the MgO surface. Additional details about the phosphate removal by biologically activated biochar are provided in Example 4.

As mentioned above, embodiments of the present disclosure include a method of removing a material (*e.g.*, a metal, phosphate, nitrate, and/or nitrite) 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, 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 biologically activated biochar by passing the fluid through an area including the biologically activated biochar and/or the biologically activated biochar can be disposed into the fluid (e.g., a pond or holding area) to remove the material. The fluid and/or the biologically activated biochar can be agitated to ensure that the fluid or a large portion thereof comes into contact with the biologically activated biochar or vice versa to ensure a maximum amount of material is removed from the fluid. After a period of time the biologically activated biochar is removed from the fluid and can be processed to remove the material and reused or recycled.

In an embodiment the biologically activated biochar starting material can be one or a combination of a residue material from bioenergy production (bioenergy residue), either anaerobically or bacterially digested material, such as digested biomass or a carbon-rich waste and specifically a sugarcane bagasse, sugar beet tailings, sugar beet pulp, and manure. In an embodiment, the biologically activated biochar starting material is anaerobically or bacterially digested and then pyrolyzed.

In an embodiment, the bacterially digestion can be performed under anaerobic conditions or aerobic conditions. In an embodiment, the biologically activated biochar starting material can initially be processed under either anaerobic conditions or aerobic conditions and then processed under conditions not used in the first processing step.

In an embodiment, the biologically activated biochar formed can be a digested sugarcane bagasse based biochar, a digested sugar beet tailings based biochar, a digested sugar beet pulp biochar, a digested manure based biochar, other digested bioenergy residues, and a combination thereof. The pyrolyzation process is described herein and in Examples 1 and 3.

The material to be removed from the fluid can be a metal cation, a phosphate anion and/or their analogues, a nitrate anion and/or their analogues, and/or nitrite anion and/or their analogues. In an embodiment, the metal cation can be a lead cation, a copper cation, a zinc cation, a cadmium cation, a nickel cation, a chromium cation, an iron cation, an aluminium cation, a cobalt cation, a magnesium cation, a mercury cation, or their analogue (e.g., a cation of any of these precipitated by anion

released by the activated biochar, such as carbonate and/or phosphate species), and a combination thereof.

In an embodiment, the anion can be negatively charged phosphate species, or their analogues (*e.g.*, arsenate and molybdate), negatively charged nitrate species or their analogues, negatively charged nitrite species or their analogues, or a combination thereof.

In an embodiment, the material (*e.g.*, metal cation or phosphate, nitrate, or nitrite anion) can be adsorbed onto the surface of the biologically activated biochar. The term “adsorbed” can refer to any exposed surface (*e.g.*, including micro- or nano-channels, and micro- or nano-particles) of the biologically activated biochar 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 biologically activated biochar. Once adsorbed onto the surface of the biologically activated biochar, the material may form a compound including the material such as a mineral compound (*e.g.*, a crystal complex), phosphate compound or complex, nitrate compound or complex, or nitrite compound or complex. In an embodiment, the biologically activated biochar includes colloidal and/or nano-sized minerals and/or metal oxides after exposure to a fluid.

In an embodiment, the metal compound formed on the biologically activated biochar can include a lead mineral (*e.g.*, hydrocerussite and/or cerussite), a copper mineral (*e.g.*, cupric carbonate), a zinc mineral (*e.g.*, smithsonite), a cadmium mineral (*e.g.*, otavite), a nickel mineral (*e.g.*, nickelous carbonate), a chromium mineral (*e.g.*, chromium carbonate and/or stichtite), an iron mineral (*e.g.*, siderite), an aluminium mineral (*e.g.*, aluminum carbonate and/or stontiodesserte), a cobalt mineral (*e.g.*, cobaltous carbonate), a magnesium mineral (*e.g.*, magnesite and/or stichtite), or other metal carbonate/phosphate, and a combination thereof.

In an embodiment, the ions formed on the biologically activated biochar can include negatively charged phosphates and their analogues such as arsenate and molybdate.

In an embodiment, the ions formed on the biologically activated biochar can include negatively charged nitrates and their analogues.

In an embodiment, the ions formed on the biologically activated biochar can include negatively charged nitrites and their analogues.

In an embodiment where the material that is removed from the fluid is a plant nutrient (e.g., zinc, iron, or phosphate or compounds/minerals/salts including these), the exhausted biologically activated biochar can be directly applied to soil as a fertilizer. For the case when the material belongs to toxicants (e.g., lead), the exhausted biologically activated biochar can be either sent to a landfill or be washed with acid/base to remove the toxicants and then the cleaned biologically activated biochar can be applied to soil as amendment to sequester carbon.

Examples

Now having described the embodiments of the present disclosure, in general, Examples 1 to 4 describes some additional embodiments of the present disclosure. While embodiments of present disclosure are described in connection with Examples 1 to 4 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. In addition, reference to "biochar" in the examples should be considered to be a reference to "biologically activated biochar" unless it is clear from the discussion that the biochar referred to is not biologically activated biochar.

Example 1:

Brief Introduction

This Example was designed to investigate the effect of anaerobic digestion on biochar produced from sugarcane bagasse. Sugarcane bagasse was anaerobically digested to produce methane. The digested residue and fresh bagasse was pyrolyzed separately into biochar at 600 °C in nitrogen environment. The digested bagasse biochar (DBC) and undigested bagasse biochar (BC) were characterized to determine their physicochemical properties. Although biochar was produced from the digested residue (18% by weight) and the raw bagasse (23%) at a similar rate, there were many physiochemical differences between them. Compared to BC, DBC had higher pH, surface area, cation exchange capacity (CEC), anion exchange capacity (AEC), hydrophobicity and more negative surface charge, all properties that are

generally desirable for soil amelioration, contaminant remediation or wastewater treatment. Thus, these results suggest that the pyrolysis of anaerobic digestion residues to produce biochar may be an economically and environmentally beneficial use of agricultural wastes.

Introduction:

The conversion of biomass into value-added products such as biofuel and biochar has attracted tremendous research interest. This can be attributed to the rising energy demands and concerns over greenhouse gas emissions, as well as worldwide soil degradation (Laird et al., 2009; Lehmann, 2007). As one of the most popular bioenergy conversion technologies, thermal pyrolysis of carbon-rich biomass is unique because it produces biochar (charcoal) in addition to biofuel. Recent studies have highlighted the benefits of biochar technologies, particularly with respect to carbon sequestration via land application of biochar (Laird et al., 2009; McHenry, 2010). As a result, the conversion of biomass into biochar and biofuel has been receiving greater attention from government regulation agencies and the general public. For example, the 2008 Farm Bill established the first federal-level policy in support of biochar production and utilization programs nationally, and biochar has been mentioned in the United Nations Framework Convention on Climate Change in Dec. 2009.

Sugarcane bagasse is the residual material derived from sugarcane after extracting cane juice. Like most agricultural residues, bagasse is a carbon-rich biomass, highly abundant and suitable for biofuel or biochar production. Several studies have been conducted to explore the potential of biofuel production from bagasse through pyrolysis (Mothe and de Miranda, 2009), but limited attention has been paid to biofuel production from anaerobic digestion of bagasse or possible uses of its residues. Over 850,000 tons of bagasse generated in Florida in the United States are either burnt directly as fuel in sugar mills or disposed of in landfills (Burnham, 2010). Anaerobic digestion of bagasse could be an additional source of biofuel (Osman et al., 2006).

Bagasse is a complex lignocellulosic material which consists primarily of 50% cellulose, 25% hemicellulose, and 25% lignin, in addition to other components such as pentosans, α -cellulose, and inorganic compounds referred to as ash (Pandey et

al., 2000). Anaerobic digestion of most lignocellulosic materials like bagasse proceeds at low loading rates, long solid retention times and low conversion efficiencies (Kivaisi and Eliapenda, 1995). A few studies showing the feasibility of biogasifying sugar cane bagasse for biofuel (mainly methane) production, have indicated the hydrolysis of cellulose as the rate limiting step and the crystallinity of cellulose as a major obstacle in the digestion process (Kivaisi and Eliapenda, 1995; Rodriguezvazquez and Diazcervantes, 1994). In overcoming these challenges, researchers have suggested the use of steam explosion, and acid and alkaline pre-treatment methods to enhance the digestion of bagasse to methane (Amjed et al., 1992).

Using a variety of these anaerobic digestion pre-treatment methods, a maximum bagasse digestibility of 75% by weight has been reached (Rodriguezvazquez and Diazcervantes, 1994). Consequently, at least 25% of the bagasse will remain as residue after the digestion process. Large-scale anaerobic digestions of sugarcane bagasses, therefore, would require recycling of the digested residues (sludge) in an economic and environmentally friendly way. Traditionally, residues obtained from anaerobic digestion are often applied as compost to soils directly. But increasing concerns on the potential contamination of the food chain by toxic trace elements have necessitated alternative methods of sludge recycling (Tyagi et al., 1988). Pyrolysis of anaerobically digested bagasse residue to produce biochar has been proposed as an beneficial product that could be obtained from digestion residuals (Sialve et al., 2009).

This Example examined the conversion of sugarcane bagasse into biochar and biofuel using anaerobic digestion and thermal pyrolysis. Anaerobic digestion of bagasse was carried out to generate methane and possibly improve the stock material properties for biochar production. Two feedstock materials were employed in the pyrolysis study: raw bagasse and the residue obtained from anaerobically digested bagasse. These materials were converted into biochar and biofuel at 600 °C. The conversion rates of biochar and biofuel were determined. In addition, physicochemical properties of the biochar produced were characterized. Some of the objectives were to: 1) determine the methane potential of sugarcane bagasse via anaerobic digestion, 2) examine the feasibility of using the digested sugarcane bagasse residue as a feed stock for biochar production, and 3) compare the

physicochemical properties of biochar obtained from digested bagasse residue to those of biochar obtained from pyrolysis of sugarcane bagasse directly.

Materials and Methods

Raw materials

The feed stock, sugarcane bagasse (sized 0.5 – 1 mm), was obtained from Florida Crystals, Okeelanta, Florida and stored in air-tight ziploc bags and refrigerated until ready for use. Prior to the digestion of the samples, 150 g aliquots of the refrigerated bagasse were dried in an oven at 105 °C for 24 hours. Volatile solid (VS) content of bagasse was determined by ashing 100g of the dried samples in a muffle furnace at 550 °C for 2 hours and determining the ash-free dry weight (Koppar and Pullammanappallil, 2008). The total solids (TS) and volatile solids (VS) content of the feedstock were determined gravimetrically before and after the digestion process.

Anaerobic digestion of bagasse

A thermophilic anaerobic digester was used to biogasify the raw bagasse (FIG. 2.1). The design and procedures of the anaerobic digestion experiment were similar to those of Koppar and Pullammanappallil (2008). In brief, 400 g of fresh bagasse (wet weight) was added to the digester and mixed with porous volcanic rocks (average grain size 25 mm, from a landscaping supplier) to prevent compaction of the solids. To initiate the anaerobic digestion process, 2 L of mixed liquor (inoculum), obtained from a currently operational, active and stable thermophilic digester was added to the vessel containing the feedstock. The digester was then sealed and incubated at a constant temperature of 55 °C until the end of the experiment. The pH of the mixture was monitored daily. Biogas produced from the anaerobic digester under batch conditions was monitored with a positive displacement gas meter consisting of a clear PVC U-tube filled with anti-freeze solution, solid state time delay relay, a float switch, a counter, and a solenoid valve. The U-tube gas meter was calibrated in-line to determine volume of biogas. A gas syringe was used to draw samples from the digester port daily and concentrations of methane and carbon dioxide produced were determined with a gas chromatograph (Fisher Gas Partitioner 1200). Anaerobic digestion was considered complete when

no further gas production was recorded by the gas meters. The sealed digester was opened and emptied and the solid residue was separated from the inoculum and dried at 105 °C in the oven. A fraction of the dried residue was analyzed for TS and VS content and the remaining mass was used for biochar production. The methane yield from the anaerobic digestion of bagasse was reported in terms of the values of VS obtained.

Biochar and biofuel production

Both raw bagasse and digested bagasse residue were converted into biochar using a bench-scale pyrolyzer. For each experiment, 15 g of dried samples were fed into a mini tubular reactor (6 cm diameter cylinder 28 cm long) designed to fit inside a bench-top furnace (Barnstead 1500M). The tubular 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. The controller of the bench-top furnace was programmed to drive the furnace temperature to 600 °C at a rate of 10 °C/minute and held at the peak temperature for 1.5 h before cooling to room temperature. Biochar produced from the pyrolysis was crushed and sieved into two size fractions: <0.5 mm and 0.5-1mm. Only the latter was used in the characterizations to minimize the influences of residual ash particles.

Physicochemical properties of biochar

A range of physicochemical properties (e.g., pH, surface properties, elemental compositions, etc.) of the digested bagasse biochar (DBC) and the undigested bagasse biochar (BC) were determined. The pH of the biochar was measured by adding biochar to deionized water in a mass ratio of 1:20. The solution was then hand shaken and allowed to stand for 5 minutes before measuring the pH with a pH meter (Fisher Scientific Accumet Basic AB15). The surface area of the biochar was determined through a surface area analyzer (NOVA 1200) using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method at 77K.

The surface charge of the samples was determined by measuring the zeta potential (ζ) of colloidal biochar according to the procedure of Johnson et al. (1996).

About 1g of each sample was added to 100 ml of de-ionized water and the solution was shaken at 250 rpm for 30 minutes using a mechanical shaker. The shaken solution was then placed in a sonic bath to break the particles into colloids and the solution filtered using a filter paper. The ζ of each supernatant solution obtained was determined using a Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, NY). Smoluchowski's formula was used to convert the electric mobility into zeta potential.

Elemental carbon, hydrogen, and nitrogen of the raw bagasse, DBC, and BC was determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of resulting CO₂, H₂ and NO₂ gases, respectively. The oxygen content was determined by weight difference assumed that the total weight of the samples was made up of C, H, N and O only.

Cation exchange capacity (CEC) and anion exchange capacity (AEC) of the samples were determined simultaneously using the point of zero net charge method (Zelazny et al., 1996). The samples were mixed with KCl solutions to saturate the biochar's exchangeable cation and anion sites. NaNO₃ solutions were used to displace the bound K⁺ and Cl⁻. Concentrations of the displaced K⁺ and Cl⁻ were determined using flame atomic absorption spectrometry (FAAS; Varian 220 FS with SIPS, Walnut Creek, CA) and an ion chromatograph (Dionex ICS90), respectively. CEC and AEC of the samples were calculated based on the measured cation and anion concentrations and the sample weight.

Scanning electron microscope (SEM) imaging of the raw materials and biochar samples were carried out using a Hitachi S-4000 FE-SEM with maximum resolution of 1.5 nm. Varying magnifications were used to compare the structure of the bagasse and biochar samples before and after the anaerobic digestion. The accelerating voltage of the instrument was maintained at 10kv.

Fourier Transform Infrared (FTIR) analysis of BC and DBC was carried out to characterize the surface functional groups present on these samples. To obtain the observable adsorption spectra, BC and DBC were ground and mixed with KBr to 0.1 wt% and then pressed into pellets. The spectra of the samples were measured using a Bruker Vector 22 FTIR spectrometer (OPUS 2.0 software).

Results and Discussion:

Methane yield from anaerobic digestion of sugarcane bagasse

The total methane yield from the anaerobic digestion of sugarcane bagasse was about 84.75 L/kgVS at the end of 40 days (FIG. 2.2). Similar low yields of methane from the digestion of untreated bagasse have been reported by Osman et al. (2006) with a total biogas (includes methane and carbon dioxide) production of 0.02 L/kgVS.

The methane yield was much lower from anaerobic digestion of bagasse than from other feedstock materials such as beet pulps (336 L/kgVS) and sugar beet tailings (295 L/kgVS) (Koppar and Pullammanappallil, 2008; Liu et al., 2008). This can be attributed to the crystalline cellulosic structure of sugarcane bagasse, which usually has a very low biodegradability. Nevertheless, the cellulose in bagasse was sufficiently degraded by the inoculum to alter the appearance of the digested residue and create a more porous structure in comparison to the raw bagasse (FIGS. 2.3A and 2.3B). The low yield of methane from bagasse in this study compared to other feedstock materials could also be attributed to pH inhibition of the digestion process. During anaerobic digestion of the bagasse, pH in the digester increased from 7.6 to 9.4, which was above the optimum value of 7.0 - 7.5. The average pH during the first 30 days of digestion was 8.5 which increased to 9.0 thereafter. Increase in pH has also been observed during batch digestion of biomass feedstocks like sugarbeet pulp, citrus pulp and sorghum stalks. This could be due to mobilization of cations like K and Ca from the biomass during digestion. High pH conditions have been found to suppress methanogens growth requiring methanogenic Archae to expend more energy for homeostasis than anabolism, resulting in slow degradation of the substrate (Gutierrez et al., 2009). Because there was no detectable nitrogen in the DBC (Table 1, Example 1), the growth of the degradation bacterial, particularly the methanogens, in the substrate could be limited by nitrogen deficiency, which may have also caused the low methane yield.

Table 1, Example 1. Elemental analysis of raw bagasse and biochar samples.

Sample	% C	% H	% N	% O
Raw Bagasse	46.08	6.88	0.74	46.30
DBC	73.55	2.41	-	24.04
BC	76.45	2.93	0.79	19.83

Advancement in research efforts for improving the digestion of bagasse including hemicellulose hydrolysis and conversion of crystalline cellulose to more fermentable sugars could make bagasse digestion a more economically attractive process for biofuel production.

Modeling Methane Yield from Sugarcane Bagasse:

Methane production in an anaerobic digester is a microbial associated growth product and often described using sigmoidal curve bacterial growth models such as the Gompertz equation (Koppar and Pullammanappallil, 2008). In this study, the modified Gompertz equation derived by Zwietering et al. (1990) was used to simulate methane evolution from sugarcane bagasse, such that:

$$y = A \exp \left\{ -\exp \left[\frac{\mu_m \cdot e}{A} (\lambda - t) + 1 \right] \right\} \quad (1)$$

where y is the cumulative methane production (L/kgVS), A is the maximum methane yield potential (L/kgVS), μ_m is the maximum methane production rate (L/kgVS/day), e is the Euler's number (2.72), the λ is the duration of the lag phase (day), and t is time (day). The model successfully reproduced the experimental data with a goodness of fit statistic, R^2 , exceeding 0.98. The model-estimated A , μ_m , and λ were 81.29 L/kgVS, 5.08 L/kgVS/day, and 1.96 days, respectively. These values suggest that the anaerobic digestion efficiency of sugarcane bagasse is relatively low in comparison to other feedstock materials (Koppar and Pullammanappallil, 2008; Liu et al., 2008). The digested sugarcane bagasse residue, therefore, has the potential to be used as a feedstock material for biochar and biofuel production through pyrolysis.

Biochar and biofuel production from digested and undigested bagasse:

The biochar produced from the pyrolysis of digested bagasse residue and undigested bagasse was similar with efficiencies of 18% and 23% of initial dry weight, respectively. The slightly lower rate of biochar production from pyrolyzed digested bagasse is probably because of the slight reduction in the carbon content of the bagasse after degradation as indicated by elemental analysis (Table 1, Example 1). Generally, decreased formation of char during volatilization of the biomass is usually accompanied by increased yield in bio-oil products (Demirbas et al., 2006). The biofuel (*i.e.*, bio-oil and non-condensable gas) production rates from the pyrolysis of digested bagasse residue and undigested bagasse were 82% and 77%, respectively; suggesting that substantial amount of biofuel can still be extracted from the digested bagasse residue through pyrolysis. These figures suggest that it is feasible to use digested bagasse residue as a feedstock for both biochar and further biofuel production.

Effect of anaerobic digestion on biochar properties:

Biochar can be used as a soil amendment to improve soil quality which, due to its refractory nature, will also sequester atmospheric carbon for long time periods, and as a low-cost adsorbent to remove contaminants from wastewater (Cao et al., 2009; Liu and Zhang, 2009; Novak et al., 2009). The effectiveness of biochars in these potential applications will be determined by its physicochemical properties, such as pH, surface charge, BET surface area, CEC, and AEC. Laboratory characterizations of the DBC and BC revealed that anaerobic digestion had a substantial effect on these physicochemical properties (Table 2, Example 1).

Table 2, Example 2. Summary of the physicochemical properties of biochar samples

Sample	pH	Zeta potential (mv)	BET surface area (m ² /g)	CEC (cmol/kg)	AEC (cmol/kg)
DBC	10.9	-61.7	17.66	14.30	11.19
BC	7.7	-28.1	14.07	4.19	6.64

Measurements of biochar pH showed DBC had a higher pH (10.9) than BC (7.7) (Table 2, Example 2). The high pH of DBC can be attributed to the factor that anaerobic digestion may concentrate recalcitrant cationic species (Pb, Cd, Zn, Cr, Cu, Ni) as well as exchangeable cations (Ca, Mg, Na) into the residue (Gu and Wong, 2004; Hanay et al., 2008). The DBC also had a higher zeta potential of -61.7 mV in comparison to BC (-28.1 mV), indicating that the surface charge of the DBC was more negative than that of BC. Corresponding to the SEM images (FIGS. 2.3C and 2.3D), the BET surface area of DBC (18 m²/g) was higher than that of BC (14 m²/g) and may reflect microbial utilization of more labile pore in-filling organic matter, leaving the refractory pore framework intact (Zimmerman, 2010). Because pH, surface charge, and surface area are among the most important factors that govern a material's interaction with chemical compounds, particularly with respect to cationic metal species. The digested bagasse biochar, therefore, may have a better ability to sequester metal species than non-digested bagasse biochar.

The measured CEC and AEC of DBC were 14.30 cmol/kg and 11.19 cmol/kg, respectively, which were higher than those of BC (6.64 cmol/kg and AEC 4.194 cmol/kg, respectively). When used as a soil amendment, DBC would likely be better able than BC to improve the nutrient holding capacities of the soils. However both biochars would significantly improve the exchange properties of both soils and act similarly to enrichments in natural organic matter. It is further notable that the AEC found for both of these chars has not previously been measured in any biochar (Cheng et al., 2008; Liang et al., 2006).

The effect of anaerobic digestion on the properties of biochar produced can be further discriminated through its surface functional groups as determined by FTIR spectroscopy (FIG. 2.4). It has been reported that surface functional groups present in biochar are mainly a function of the pyrolysis temperature and pyrolysis conditions under which it was produced (Chun et al., 2004). Here, however, it was found that biomass pretreatment may also play a role in the resulting functional group distribution. The infrared spectra of DBC were characterized by four significant bands at wave number 3452 (O-H functional group), 2357 (C≡C bond group), 1626 (alkene, C=C bond group), and 646 (C-H aromatic group) cm⁻¹ (FIG. 2.4). The spectrum of BC was characterized by four significant bands at wave number 3130 (O-H functional group), 1600 (alkene, C=C bond group), 1090 (phenolic, C-O stretch

absorption band), and 826 (C-H aromatic group) cm^{-1} . So the major differences include the appearance of the dominant phenolic component in the undigested biochar only and the presence of alkynes ($\text{C}\equiv\text{C}$ bond group) in the digested biochar only.

All of the observed functional groups have been reported as chemical groups characterizing many carbon sorbents (Cao et al., 2009; Nguyen et al., 2009; Ozcimen and Karaosmanoglu, 2004; Purevsuren et al., 2003; Suhas et al., 2007) as well as in other biochars (Rutherford, 2008; Rutherford, 2004). The presence of an additional phenolic, C-O stretch band with high absorption intensity in BC at wave number 1090 cm^{-1} suggests that the alkalinity of BC was lower than that of DBC because the phenolic functional group promotes acidity in the biochar (Lopez-Ramon et al., 1999). This result is corresponding to the pH measurements. Furthermore, the presence of oxygen functional groups in BC would produce a relatively more hydrophilic characteristic than DBC which has a greater degree of aromaticity as indicated by FTIR. The digested bagasse biochar, therefore, may have a better ability to adsorb organic compounds than the raw bagasse biochar.

Based on the characterization of its physicochemical properties, it is evident that anaerobic digestion of bagasse enhances the adsorption and ion exchange abilities of biochar produced from digested relative to undigested bagasse residues. Therefore, the method of combining anaerobic digestion and pyrolysis can be used to produce additional biofuel or heat while generating high quality biochars to be used as low-cost adsorbents or as soil amendments.

Conclusion:

Anaerobic digestion of bagasse was carried out to investigate the effects of the digestion process on biochar production via pyrolysis of the digestion residues. Biochar produced from anaerobically digested bagasse residue had a higher pH, surface area, CEC and AEC, and hydrophobicity, as well as a more negative surface charge in comparison to the undigested bagasse biochar. These characteristics suggest that the digested bagasse biochar may be efficiently used as a soil amendment to improve soil quality, to serve as a contaminant remediation barrier, or a low-cost adsorbent to remove contaminants from wastewater.

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Example 2

Brief Introduction:

Alternative, low-cost sorbents are needed for many environmental applications including water purification. This study examined the ability of two sugarcane bagasse biochars to remove lead from water. The lead sorption ability of biochar made from raw (BC) and anaerobically digested sugarcane bagasse (DBC) was compared with a commercial activated carbon (AC) using batch sorption experiments. While both BC and DBC were effective sorbents of lead from water, DBC was even better than AC. The maximum lead sorption capacity of DBC ($653.9 \text{ mmol kg}^{-1}$) was about double that of AC ($395.3 \text{ mmol kg}^{-1}$) and about twenty times higher than that of BC ($31.3 \text{ mmol kg}^{-1}$). Post-sorption characterizations using X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that the enhanced sorption of lead by DBC was, at least partly, related to a precipitation mechanism, while surface adsorption governed the sorption of lead onto BC. Desorption studies showed that Pb-laden biochar samples could be regenerated by acid washing, with lead recovery rates of about 75%. These results suggest that biochars made from bagasse and other agricultural residues may be effective alternative, low-cost environmental sorbents of lead or other metals.

Introduction:

Heavy metal pollution in wastewater has become a pressing environmental concern due to its highly refractory nature which presents a great challenge to remediation efforts ^[1]. Lead is a highly toxic heavy metal which may be introduced to a water body from various sources ranging from battery to ammunition industries ^[2].

Lead poses a risk to public health when consumed in drinking water in even very low concentrations due to bioaccumulation ^[3-7].

Various methods have been employed to remove lead from wastewater including ion exchange, chemical precipitation, membrane filtration, electrodialysis, and granular filtration ^[8-12]. Most of these methods, however, have high operational costs ^[13-15]. It is therefore desirable to develop alternative and less costly lead removal technologies.

Biochar is a black carbon derived from the combustions of carbon-rich biomass (e.g., agricultural residues and organic waste) in an inert atmosphere (pyrolysis). The use of biochar to remove contaminants such as metals or organic contaminants from aqueous solutions is a relatively novel and promising wastewater treatment technology. Several studies have recently reported the effective removal of lead by biochar sorbents ^[16-19]. For example, Cao et al. ^[16] reported that biochar made from animal manure was six times more effective than activated carbon in adsorbing lead and had a sorption capacity of up to 680 mmol/kg. And Sekhar et al. ^[19] showed biochar made from coconut shell and commercial activated carbon to have a similar lead sorption capacity of about 145 mmol/kg. These authors have attributed the effective lead removal by biochar sorbents to either precipitation of lead onto the biochar surface or electrostatic interactions between lead species and negatively charged functional groups on biochar's surface ^[16, 18]. Like many other traditional sorbents, the high affinity for lead and other metal ion species bound by biochar may be controlled by other mechanisms as well, including complexation, chelation, and ion exchange ^[20, 21].

Studies have attempted to improve the metal sorption abilities of biochar from pyrolyzed agricultural residues such as bagasse ^[22], pine wood and rice husk ^[17]. The presence of cellulose, hemicellulose, proteins, sugars, and lipids in these materials provide a variety of functional groups that can be physically activated through pyrolysis and further steam or CO₂ treatment to enhance their uptake of compounds such as lead. There has also been notable work on the chemical activation of agricultural residue derived biochar for lead sorption ^[23]. To our knowledge, however, no research has explored the use of anaerobic digestion as a means of biological activation to enhance the sorption ability of agricultural residue-derived biochar.

This Example investigated the enhanced removal of lead by an anaerobically digested sugarcane bagasse biochar. Raw and digested sugarcane bagasses were pyrolyzed into biochar at 600 °C in the laboratory. Bench-scale batch sorption and desorption experiments were conducted to compare the lead sorption ability of the digested bagasse biochar to that of the undigested bagasse biochar and a commercial activated carbon. Mathematical models and material characterization techniques were used to aid the experimental data interpretation. A goal was to understand the effect of anaerobic digestion on the ability of bagasse biochar to remove lead from water, and thus, to develop a biological activation technology. Some objectives were to: a) compare the sorption kinetics of lead onto digested and undigested bagasse biochar and activated carbon, b) compare the equilibrium sorption of lead onto these sorbents, and c) identify the mechanisms governing lead sorption onto the biochar samples.

Materials and methods:

Materials

Biochar samples were obtained by pyrolyzing the feedstock materials (digested bagasse residue and undigested bagasse) for 1.5 hours at 600 °C in a N₂ environment. The digested bagasse biochar (DBC) and raw bagasse biochar (BC) were crushed and sieved to a size fraction of 0.5-1 mm. Physicochemical properties of the biochar samples were reported previously ^[24].

Lead solution was prepared from lead nitrate (certified A.C.S) from Fisher Scientific. Granulated activated carbon (AC, from steam activated coconut shell) was also obtained from Fisher Scientific and was crushed and sieved to the same size as the biochar samples. A range of physicochemical properties, including pH, surface potential, surface area, cation exchange capacity (CEC), and anion exchange capacity (AEC), of the AC were determined using methods detailed elsewhere ^[24].

Sorption

Sorption kinetics of lead onto the sorbents (i.e., DBC, BC, and AC) were determined by mixing 50 mL Pb(NO₃)₂ (20 ppm) solutions with 0.1 g of each sorbent in 60 mL plastic vials at room temperature (22±0.5 °C). The vials were then shaken at 200 rpm in a mechanical shaker. Over the course of 24 h, the vials were

withdrawn at time intervals and the mixtures were immediately filtered through 0.1 μm pore size nylon membranes (GE cellulose nylon membrane). Equilibrium sorption isotherm experiments were conducted similarly using $\text{Pb}(\text{NO}_3)_2$ solutions with initial Pb concentrations ranging from 5 to 200 ppm and apparent sorption equilibrium times of 24 h. Following the experiments, the solids were collected, washed with deionized water, and dried at 100 °C in an oven before post-sorption characterizations as described below. The Pb concentrations of the liquid phase samples were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma 3200). The solid phase Pb (i.e., sorbed Pb) concentration was calculated based on the difference between Pb in the initial and final aqueous solutions. Blank controls containing sorbents and solutions with no Pb were tested in parallel with each kinetic and isotherm experiment and Pb release was found to be negligible. 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 10%.

Kinetic and equilibrium sorption models were used to understand the interaction mechanisms between lead and the sorbents. The model parameters were calibrated to fit the experimental data using inverse analysis techniques ^[25].

Post-sorption characterizations

X-ray diffraction (XRD) analysis was carried out on DBC, BC, and AC before and after Pb sorption to investigate the possible formation of Pb mineral phases using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. Scanning electron microscope (SEM) imaging of DBC and BC after Pb sorption was carried out using a field emission scanning electron microscopy (FE-SEM, Hitachi S-4000) with maximum resolution of 1.5 nm. The accelerating voltage of the instrument was maintained at 10 kv.

Fourier transform infrared (FTIR) spectrographic analysis of BC and DBC before and after sorption was carried out to characterize the samples' surface functional groups and to investigate any possible interaction with the Pb ion. Samples were ground and mixed with KBr to approximately 0.1 wt.% and pressed

into a pellet manually using a mechanical vice. Spectra were collected on a Bruker Vector 22 FTIR with OPUS 2.0 software.

Desorption

Desorption of lead from the lead-laden sorbents was investigated by conducting Pb stripping experiments using an acid solution. Duplicates of 0.1 g sorbents were reacted for 24 h with 50 mL of 80 ppm Pb solution. After filtration (as above), aqueous Pb concentrations in the filtrates were used to determine sorbed Pb concentrations using the method described above. The solids on the filters were rinsed three times with 50 mL of distilled water to remove any residual Pb. The rinsed samples were then transferred into plastic vials and mixed with 30 mL of 0.1 M HCl. These mixtures were agitated for 0.5 h using a mechanical shaker, filtered, and aqueous Pb concentration was measured in the filtrate. The desorption rate of each sorbent was calculated based on the ratio of the amount of Pb released to the initial amount of Pb adsorbed. Samples without sorbed Pb were also treated with the acid solution followed the same procedures to test for pre-existing Pb in the sorbents.

Results and Discussion:

Physiochemical properties

The physicochemical properties of the two biochar samples that may influence their sorption abilities have been reported previously^[24] and are compared with those of AC in Table 1, Example 2. The N₂-BET surface areas of both DBC and BC were below 20 m² g⁻¹, much less than that of activated carbon (1100 m²/g). These data suggest that, if surface adsorption dominates Pb sorption onto these materials, DBC and BC should have much lower sorption capacity than AC. Low specific surface areas are commonly reported for biochars derived from agricultural residues^[21, 26-29].

Table 1, Example 2. Summary of physicochemical properties of the adsorbents studied.

Sample	pH	Zeta potential (mV)	BET surface area (m ² /g)	CEC (cmol/kg)	AEC (cmol/kg)
DBC	10.9	-61.7	17.7	14.3	11.2
BC	7.7	-28.1	14.1	4.2	6.6
AC	9.5	-33.9	1100.0	19.3	6.4

The CEC and AEC of all the sorbents were comparable to those of natural soils (Table 1, Example 2). DBC and AC had a much higher CEC than BC, while DBC had the highest AEC compared to BC and AC. These data suggest the possibility of using at least some biochars as ion exchangers that may sequester both positively and negatively charged ions from water. The zeta potential of all the samples were negative (Table 1, Example 2), with that of DBC the lowest value (-61.7 mV), indicating strongly negatively charged surfaces that might facilitate the deposition of cations such as Pb onto these sorbents.

Sorption kinetics

The sorbents showed different lead sorption kinetic behaviors (FIG. 3.1A and B). Both DBC and AC reached sorption equilibrium within several minutes. Lead sorption onto BC, however, was much slower and reached equilibrium after about 5 hours. A rate-limited, first-order (pseudo-first-order) kinetic model was used to simulate the experimental data:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

where q_t and q_e are the amount of lead sorbed at time t and at equilibrium (mmol kg⁻¹), respectively, and k_1 is the first-order apparent sorption rate constant (h⁻¹). This model reproduced the kinetic data closely (FIG. 3.1A), with correlation coefficients (R^2) exceeding 0.98 for the three sorbents tested. Because there was no obvious difference in results for DBC and AC, the same model simulations are shown for both in FIG. 3.1. The model-estimated sorption first-order rate constants (k_1) for DBC, BC, and AC were 320.25, 0.55, and 320.25 hr⁻¹, respectively, suggesting the

anaerobic digestion can transform (or 'activate') bagasse such that its biochar has sorption characteristics similar to commercial activated carbons.

Previous studies on the kinetic behaviors of metal sorption onto microporous sorbents showed that intraparticle surface diffusion may be important to the sorption process^[30, 31]. In this study, the sorption of lead onto DBC and AC reached equilibrium very fast with no sign of diffusion limitation. This might indicate that the pores in the two sorbents were relatively large compared to some other microporous sorbents. The lead sorption kinetics of BC, however, was slower and the pre-equilibrium (i.e., before 5 h) lead sorption showed a strong linear dependency ($R^2=0.98$) on the square root of time (FIG. 3.1B). This result suggests that intraparticle surface diffusion may play an important role in controlling the sorption of lead onto the undigested bagasse biochar samples.

Sorption isotherms:

The maximum observed Pb sorption onto DBC was much greater than that of AC or BC (FIG. 3.2) despite its lower surface area suggesting mechanisms other than surface adsorption may be involved in the sorption process. Because all the isotherms are "L" type, the classic Langmuir model was used to simulate the sorption isotherms:

$$q_s = \frac{KQC_e}{1 + KC_e} \quad (2)$$

where K represents the Langmuir bonding term related to interaction energies ($L \text{ mmol}^{-1}$), Q denotes the Langmuir maximum capacity (mmol kg^{-1}), and C_e is the equilibrium solution concentration (mmol L^{-1}) of the sorbate. Simulations using the Langmuir model fit all the isotherm data well (FIG. 3.2), with R^2 exceeding 0.84. The best-fit values of the bonding term (K) for DBC, BC, and AC were 189.45, 13.54, and 13.52 $L \text{ mmol}^{-1}$, respectively. These results suggest that the digested bagasse biochar has much stronger bonding ability for lead than the undigested bagasse biochar and AC. The DBC also had the highest sorption capacity ($653.9 \text{ mmol kg}^{-1}$), about double that of AC ($395.3 \text{ mmol kg}^{-1}$) and about twenty times higher than that of BC ($31.3 \text{ mmol kg}^{-1}$). Thus, anaerobic digestion of sugarcane bagasse prior to pyrolysis activated biochar in such a way as to increase both its sorption strength

and sorption capacity for lead. Although BC had a much lower lead sorption capacity than AC, the K values of the two sorbents were almost identical suggesting their sorption of lead could be controlled by similar mechanisms.

Sorption mechanisms:

The enhanced sorption of lead by the digested sugarcane bagasse biochar (i.e., DBC) may be related to a precipitation mechanism such as that proposed by Cao et al. ^[16] for Pb sorption to biochar made from animal manure. The XRD analysis identified lead minerals on the DBC surface as hydrocerrusite – $[\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$ and cerrusite – $[\text{PbCO}_3]$ (FIG. 3.3). This was further confirmed by SEM images which clearly showed mineral crystals on DBC surface at a magnification of 10000 X after the sorption experiments (FIG. 3.4). The mineral crystals were neither found on the original biochars nor of the other biochars following Pb sorption. The precipitation of hydrocerrusite and cerrusite on the surface of DBC might be attributed to a collective contribution from its high pH (Table 1, Example 2) and specific surface functional groups ^[16]. Comparisons of the FTIR spectra between fresh DBC and Pb-laden DBC reveals an almost complete disappearance of the O=C=O band at wave number 2343 cm^{-1} after Pb sorption (FIG. 3.5a.). This suggests that the O=C=O functional groups on the digested bagasse biochar surface played an important role in the Pb precipitations onto this biochar. This corresponds to the results obtained from the XRD analyses of the cerrusite on the surface of post-sorption DBC. Additional investigation is needed to further explore the role of the O=C=O functional groups in controlling the precipitation of lead onto biochars.

Previous studies have concluded that the sorption of lead onto activated carbon is mainly through a surface adsorption mechanism ^[16, 32]. In this Example, both BC and AC showed no change in XRD patterns before and after Pb sorption, providing no evidence of mineral precipitation. In addition, Langmuir model simulations indicated that the bonding energy (i.e., K) of lead onto BC and AC were almost the same. These results suggest that the sorption of lead onto BC was probably also governed by a surface adsorption mechanism instead of precipitation. The FTIR analysis of BC indicated a disappearance of the OH band at wave number 1080 cm^{-1} after Pb sorption (FIG. 3.5B), suggesting that the deposition of lead onto the bagasse biochar surfaces was probably through coordination of a Pb d-election

to a hydroxyl group, producing a -O-Pb bond ^[16]. The FTIR spectrum of the fresh BC also showed the strongest signal at wave number 1080, indicating that OH functional groups were abundant (FIG. 3.5B). Despite this abundance, the total number of the OH functional groups on the biochar surface, however, may have been limited by its lower surface area (Table 1, Example 2). As a result, the undigested bagasse biochar showed lower lead removal ability, on a mass basis, compared to the AC.

Desorption rate:

Most of the sorbed Pb could be retrieved from the DBC (77.4%), BC (73.0%), and AC (77.0%) samples using the 0.1M HCl. This result suggests that acid solution can be used to regenerate the two biochar sorbents as well as the activated carbon after they are saturated with Pb ions. Acid washing has also been commonly used in regenerating other sorbents to recover metal ions ^[33]. The release of lead from BC and AC samples by acid washing might be controlled by similar surface desorption mechanisms. However, for DBC, Pb release likely involves the dissolution of the precipitated Pb minerals (i.e., hydrocerrusite and cerrusite) on the biochar surface.

Conclusions:

Both digested and undigested sugarcane bagasse biochars effectively removed lead from water, but the digested bagasse biochar showed a much better sorption ability than even a commercially activated carbon. Because bagasse is an abundant agricultural waste material, the cost to make bagasse-based biochar is low. In addition, Pb-laden biochars can also be regenerated with acid solution with Pb recovery rates higher than 70%. Biochars should therefore be considered a promising alternative water treatment or environmental remediation technology for lead removal.

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Example 3

Brief Introduction

Biochar converted from agricultural residues or other carbon-rich wastes may provide new methods and materials for environmental management, particularly with respect to carbon sequestration and contaminant remediation. Combination of biofuel generation with biochar production would provide further environmental and economic benefits. In this Example, two biochars were produced from anaerobically digested and undigested sugar beet tailings through slow-pyrolysis at 600 °C in a N₂ environment. 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%. Our results suggest that anaerobically digested sugar beet tailings can be used as feedstock materials to produce high quality biochars, which could be used as adsorbents to reclaim phosphate from water.

Introduction:

Biochar is a pyrogenic black carbon that has attracted increased attention in both political and academic arenas (1). A number of studies have suggested that terrestrial land application of biochar could effectively sequester carbon in soils and thus mitigate global warming (1, 2). When biochar is applied to soils, it may also present other potential advantages including enhanced soil fertility and crop productivity (3), increased soil nutrients and water holding capacity (4), and reduced emissions of NO_x and CH₄, two other greenhouse gases from soils (5).

In addition to its carbon sequestration and soil amelioration applications, studies have also indicated biochar's potential to be used as a low-cost adsorbent, storing chemical compounds including some of the most common environmental

pollutants. It has been demonstrated that biochars made from a variety of sources had strong sorption ability to different types of pesticides and other organic contaminants (6-9). The sorption ability of biochar has been shown to exceed that of the natural soil organic matter by a factor of 10-100 in some cases (10). In addition to strong organic compounds sorption ability, biochars have also been shown to remove metal contaminants from water and showed strong affinity for a number of heavy metal ions (11-13). Only few studies, however, have investigated the ability of biochar to remove nutrients from water, particularly with respect to phosphate (14). Ideally, if biochar can be used as a sorbent to reclaim nutrients such as phosphate from water, there would be no need to regenerate the exhausted biochar because it can be directly applied to agricultural fields as a slow release fertilizer to improve soil fertility and build (sequester) soil carbon. Although almost all biomass can be converted into biochar through thermal pyrolysis, a life cycle assessment of pyrolysis-biochar systems suggested that it is more environmentally and financially viable to make biochar from waste biomass (15). In this sense, agricultural residues (e.g., sugarcane bagasse, poultry litter, and manure) and other green waste have been proposed as good feedstock materials to make biochar (9, 16, 17). However, the applications and functions of those biochars are highly depending on their physicochemical properties (e.g., elemental composition, surface charge, and surface area) (16). Because biochar can be made of various waste biomass sources under different processing conditions, it is therefore very important to characterize their physicochemical properties before use.

In a recent study, Inyang et al. (18) explored the production of biochar from the residue materials of anaerobic digestion of sugarcane bagasse. Comparison of the physicochemical properties of the biochar from anaerobically digested bagasse to that from raw bagasse suggested that the former has more desirable characteristics for soil amelioration, contaminant remediation, or water treatment. Using anaerobically digested residue materials (or the remains of biofuel production) as feedstock to produce biochar could not only reduce the waste management cost, but also make bioenergy production more sustainable and eco-friendly. It is therefore very important to test the generality of this innovative approach by examining the feasibility of using another anaerobically digested material for biochar production.

Sugar beet tailings are the waste byproducts from the production of beet sugar, which have been mainly managed by landfill disposal or direct land applications. Because beet sugar accounts for almost 40% of all refined sugar consumed in the U.S., significant amount of sugar beet tailings are generated by the sugar industry as solid waste every day. It has been demonstrated that sugar beet tailings can be anaerobically digested to generate bioenergy (biogas) (19). Although this practice may also reduce the volume of the sugar beet tailing waste, disposal of residue materials from the anaerobic digestion still poses significant economic and environmental problems.

In this Example, biochars were made from both undigested and anaerobically digested sugar beet tailings at 600 °C through slow pyrolysis. Physicochemical properties of the biochar produced were characterized and a simple adsorption experiment was conducted as a preliminary assessment of the phosphate removal ability of the biochars. Some objectives were to: 1) determine whether the anaerobically digested sugar beet tailings can be efficiently used as feedstock for biochar and bioenergy production, 2) compare the physicochemical properties of biochar obtained from digested feedstock to those of biochar obtained from pyrolysis of sugar beet tailings directly, and 3) assess the phosphate removal ability of the biochars produced.

Materials and Methods

Biochar Production

Raw sugar beet tailings and anaerobically digested sugar beet tailing residues were obtained from American Crystal Sugar Company (East Grand Forks, MN). 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 0.5-1mm. 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).

A range of physicochemical properties of the digested sugar beet tailing biochar (DSTC) and the undigested sugar beet tailing biochar (STC) were determined. The pH of the biochar was measured by adding biochar to deionized water in a mass ratio of 1:20. The solution was then hand shaken and allowed to stand for 5 minutes before measuring the pH with a pH meter (Fisher Scientific Accumet Basic AB15). The surface area of the biochar was determined using N₂ sorption isotherms run on NOVA 1200 and the Brunauer-Emmett-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.

The surface charge of the samples was determined by measuring the zeta potential (ζ) of colloidal biochar according to the procedure of Johnson et al. (20). About 1g of each sample was added to 100ml of DI water and the solution was shaken at 250 rpm for 30 minutes using a mechanical shaker. The shaken solution was then placed in a sonic bath to break the particles into colloids and the solution filtered using a 0.45 μ m filter paper. The electric mobility of each supernatant

solution was determined using a Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, NY) and Smoluchowski's formula was used to convert the electric mobility into zeta potential.

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 (21).

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.

Fourier Transform Infrared (FTIR) analysis of the biochars was carried out to characterize the surface organic functional groups present on these samples. To obtain the observable FTIR spectra, STC and DSTC were ground and mixed with KBr to 0.1 wt% and then pressed into pellets. The spectra of the samples were measured using a Bruker Vector 22 FTIR spectrometer (OPUS 2.0 software).

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. (22) and Chen et al. (23). Briefly, 6 grams of AC, STC, and DSTC were added to 30 mL of 2M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 (K_2HPO_4 , 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 experiments, 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 (24, 25). 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 μ m 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 310.1; (26)) with aid of a spectrophotometer (Thermo Scientific EVO 60). The phosphate removal rates 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

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 (27), 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 1, Example 3. Elemental analysis of raw and digested sugar beet tailings, and their associated biochars, STC and DSTC, respectively (mass %)^a.

Sample	C	H	O ^b	N	P	S	Ca	Mg	K	Fe	Al	Zn	Na	Cu
Digested Tailing	33.94	4.53	46.89	2.35	0.34	0.28	9.68	1.20	0.79	- ^c	-	-	-	-
Raw Tailing	36.06	3.43	55.82	1.23	0.16	0.09	1.80	0.53	0.88	-	-	-	-	-
DSTC	30.81	1.38	39.87	2.74	2.18	0.46	9.78	9.79	1.97	0.75	0.24	0.03	-	-
STC	50.78	2.08	36.70	1.83	0.35	0.05	4.41	1.53	1.04	0.59	0.64	-	-	-

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 1, Example 3). This carbon content was only slightly lower than that of the undigested feedstock (Table 1, Example 3), 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 percents. 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 (28, 29).

After being converted into biochar through slow pyrolysis, the carbon content of DSTC (31.81%) was slightly lower than that of the feedstock, but the carbon content of STC increased dramatically to more than 50% (Table 1, Example 3). 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 1, Example 3). But some of the nutrient elements including phosphorous, calcium, and magnesium were much higher in the DSTC than in the STC (Table 1, Example 3). High levels of calcium and phosphorous were also found in studies of some other biochars (16). 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.

Zeta potential and pH

The surface of charcoals (biochar, activated carbon) is often negatively charged, which makes them unlikely to sorb negatively charged ions such as phosphate (30, 31). The measured zeta potentials of the STC (-54.23 mV) and DSTC (-18.11 mV) were both negative, confirming that the two biochars are negatively charged at circum-neutral conditions. The STC had a much lower zeta potential than the DSTC, however, suggesting that it might be more difficult for STC than for DSTC to adsorb phosphate. Measurements of the pH of the two biochars were alkaline (9.45 and 9.95 for STC and DSTC, respectively), which are similar to the reported values of other biochars produced at high temperatures (16, 18). The high pH of the two biochar samples suggests their potential to be used as amendments to reduce soil acidity (1).

Surface area

Two methods were used to determine the surface area of the biochars. The liquid N₂ adsorption BET method (77 K) is more commonly used. However, this method may be inaccurate for materials that include micropores (< 1.5 nm pore diameter) as N₂ may be kinetically limited in their diffusion into smaller pores at the low temperatures at which the measurement must be carried out (32-34). The CO₂ adsorption method (273 K) has, therefore, been promoted to be a better way to determine the true surface area of biochar samples (8, 35).

The CO₂ surface area measurements showed that the surface area of DSTC (449 m²/g) was much higher than that of STC (351 m²/g). While the DSTC had significant N₂ surface area (336 m²/g, indicating the presence of mesopores), the N₂ surface area of the STC was very small (2.6 m²/g), indicating that its surface was dominated by the micropores only. The surface area of DSTC is comparable to that of many commercial activated carbon (AC) adsorbents (36). Because surface area is one of most important factors that control a material's ability to adsorb chemical compounds, the digested sugar beet tailing biochar (i.e., DSTC) may be useful for water treatment or environmental remediation.

SEM-EDS

The SEM imaging of the STC (500 X) showed that the undigested sugar beet tailing biochar had smooth surfaces (FIG. 4.1A). 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 (FIG. 4.1A) identified the same elements detected in the elemental analysis (Table 1, Example 3). The SEM imaging of the DSTC (500 X), however, showed knaggy surfaces (FIG. 4.1B), perhaps reflecting the presence of mesopores indicated by the N₂ surface area measurement as reported in Table 1, Example 3. The EDS spectrum of the STC surface (FIG. 4.1B) also showed many elements detected in the elemental analysis (Table 1, Example 3). 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 (FIG. 4.1C). These crystals were mainly magnesium minerals as evidenced in the EDS spectrum at the same location (FIG. 4.1C), 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.

XRD

The XRD spectra of the DSTC and STC showed several peaks (FIG. 4.2), indicating the presence of mineral crystals. In the DSTC spectrum, the two strong

peaks at 43.2° ($d = 2.09 \text{ \AA}$) and 62.2° ($d = 1.49 \text{ \AA}$) 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 (SiO_2) and calcite (CaCO_3) were found in both the DSTC and STC, which is also consistent with the elemental analyses and EDS spectra of the two biochars.

Surface functional groups

The infrared spectra of the DSTC and STC were very similar (FIG. 4.3) with both biochars showing three significant bands at: 1) wave number near 1427, which could be attributed to O-H bending or C-O stretching vibration of phenol (30), 2) wave number near 1049, which could be attributed to C-O stretching vibrations of polysaccharides (37), and 3) wave near 874, which is characteristic of C-H bending vibration in a β -glucosidic linkage (30). All of the observed functional groups have been reported as chemical groups characterizing many other carbon based adsorbents including biochars and activated carbons (38-41).

Phosphate removal

Both AC and STC showed very low phosphate removal and AC even released a small amount of phosphate back into the solution (FIG. 4.4). This is consistent with the literature (30, 31) 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 enhanced removal of phosphate by the DSTC was probably 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 (42, 43). Precipitation of

ferric hydroxide onto the SDTC might cover the colloidal and nano-sized periclase, thus reducing the phosphate sorption ability of the biochar. Detailed discussion about the adsorption mechanisms and characteristics of phosphate onto the SDTC can be found in Example 4.

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) some of the physicochemical properties (e.g., pH and surface functional groups) of the two biochars are similar, but only the anaerobically digested sugar beet tailing biochar has colloidal and nano-sized periclase (MgO) on its surface, and 3) anaerobic digestion enhances the phosphate adsorption ability of biochar produced from digested sugar beet tailings relative to undigested ones. Our results indicate that the method of combining anaerobic digestion and slow-pyrolysis can be used to generate high quality biochars from sugar beet tailings to remove phosphate from water. Further investigations are needed to determine the detailed mechanisms and characteristics of phosphate adsorption onto the anaerobically digested sugar beet tailing biochar.

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Example 4

Brief Introduction:

In Example 3, we found that biochar derived from the residues of anaerobically digested sugar beet tailings (DSTC) showed promise as a low-cost but high-efficiency adsorbent to remove phosphate from water. To explore this further, laboratory experiments were conducted to determine its phosphate adsorption mechanisms and characteristics. 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. Batch adsorption experiments also showed that both initial solution pH and coexisting anions could affect the adsorption of phosphate onto the DSTC biochar. Of the mathematical models used to describe the adsorption kinetics of phosphate removal by the biochar, the N -th-order ($N=1.14$) model showed the best fit. Two heterogeneous isotherm models (Freundlich and Langmuir-Freundlich) fitted the experimental isotherm of phosphate adsorption onto the biochar better than the Langmuir adsorption model. 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.

Introduction

The release of phosphate from both point and non-point sources into runoff may impose a great threat on environmental health (1, 2). As a growth limiting nutrient, high level phosphate can promote excessive production of photosynthetic aquatic microorganisms in natural water bodies and ultimately becomes a major factor in the eutrophication of many freshwater and marine ecosystems (3). It is therefore very important to develop effective technologies to remove phosphate from aqueous solutions prior to their discharge into runoff and natural water bodies (4).

Many phosphate removal technologies including biological, chemical, and physical treatment methods have been developed for various applications, particularly for the removal of phosphate from municipal and industrial effluents (3). Both biological and chemical treatments have been well documented and proven to be effective to remove phosphate from wastewater. Addition of chemicals, such as calcium, aluminum, and iron salts into wastewater is considered a simple phosphate removal technique, which separates the phosphate from aqueous system through precipitation (5-8). However, the chemical precipitation methods require strict control

of operating conditions and may potentially introduce new contaminants into the water such as chloride and sulfate ions (2, 5, 9). Biological treatment of phosphate in waste effluents may have certain advantages over the chemical precipitation method because it does not require chemical additions and enhanced biological treatment has been reported to remove up to 97% of the total phosphorus in waste water (10). This technology, however, is very sensitive to the operation conditions and its phosphate removal efficiency may be, at times, much less (11). Both the chemical and biological treatment methods are also subjected to the costs and risks associated with phosphate-rich sludge handling and disposal (12).

Various physical methods have also been developed to remove phosphate from aqueous solution such as electrodialysis, reverse osmosis, and ion exchange (5, 13, 14). However, most of these physical methods have proven to be either too expensive or inefficient. Simple physical adsorption might be comparatively more useful and cost-effective for phosphate removal. Several studies investigated activated carbons as phosphate adsorbents, but showed that the adsorption capacity was very low (1, 15, 16). For example, Namasivayam et al. (16) reported that activated carbon made from coir pith with ZnCl_2 -activation had a phosphate adsorption capacity of only 5,100 mg/kg. Lower-cost materials, such as slag, fly ash, dolomite, red mud, and oxide tailings have also been explored by several studies as alternative adsorbents of phosphate from waste water (17-21).

Biochar is a low-cost adsorbent that is receiving increased attention recently because it has many potential environmental applications and benefits. While most of the current biochar studies are focused on biochar land application as an easy and cost-effective way to sequester carbon and increase fertility, a number of recent investigations suggest that biochar converted from agricultural residues have a strong ability to bind chemical contaminants in water including heavy metals and organic contaminants (22-24). The use of biochar to remove phosphate from aqueous solutions, however, is still a relatively unexplored, though promising concept. Not only may biochar represent a low-cost waste water treatment technology for phosphate removal, but the phosphate-laden biochar may be used as a slow-release fertilizer to enhance soil fertility that will also sequester carbon. But little research has been conducted to explore the phosphate removal potential of biochar.

In the Example 3, we characterize the physicochemical properties of two biochars and compared their phosphate removal abilities with activated carbon and their Fe-impregnated forms. These results showed that biochar derived from the residues of anaerobically digested sugar beet tailings had much better phosphate removal ability than all the other tested adsorbents. As a follow-up, laboratory adsorption experiments and mathematical models were used in this study to determine the mechanisms and characteristics of phosphate adsorption onto the digested sugar beet tailing biochar (DSTC). The specific objectives were to: a) identify the mechanisms governing the adsorption of phosphate onto the DSTC; b) measure the kinetics and equilibrium isotherms of phosphate adsorption onto DSTC; and c) determine the effect of initial solution pH and coexisting anions on the adsorption of phosphate onto the DSTC.

Materials and Methods

Materials

The biochar sample (DSTC) used in this study was obtained by pyrolyzing residues of anaerobically digested sugar beet tailings at 600 °C inside a furnace (Olympic 1823HE) in a N₂ environment. The DSTC was then crushed and sieved to give a 0.5-1 mm size fraction. After washing with deionized (DI) water to remove impurities, the biochar samples were oven dried (80°C) and sealed in container before use. Detailed information about biochar production its physiochemical properties can be found in Example 3.

Phosphate solutions were prepared by dissolving Potassium Phosphate Dibasic Anhydrous (K₂HPO₄) in DI water. All the chemicals used in the study are A.C.S certified and from Fisher Scientific.

Adsorption kinetics

Adsorption kinetics of phosphate onto DSTC were examined by mixing 0.1 g of the biochar with 50 ml phosphate solutions of 61.5 mg/L (20 mg/L P) in 68 mL digestion vessels (Environmental Express) at room temperature (22±0.5 °C). The pH was then adjusted to close to 7 prior to the measurements of the adsorption kinetics. 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). The phosphate concentrations in the liquid phase samples were determined by the ascorbic acid method (ESS Method 310.1; (26)) and a spectrophotometer (Thermo Scientific EVO 60). Phosphate 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%.

Adsorption isotherm

Adsorption isotherm of phosphate onto DSTC was determined similarly by mixing 0.1 g DSTC with 50 ml phosphate solutions of different concentrations ranging from 15 to 640 mg/L in the digestion vessels. After pH adjustment to about 7, the vessels were shaken in the mechanical shaker for 24 h at room temperature, this time periods 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 phosphate concentrations by the same method. Following the experiments, the post-adsorption DSTC were collected, rinsed with deionized water, and dried at 80 °C in an oven for further characterizations.

Effect of pH and coexisting anions

The effect of initial solution pH on phosphate removal was studied over a range of 2 to 11 (i.e., 2.0, 4.0, 6.2, 7.1, 8.1, and 10.4). In addition, the effect of the common coexisting anions, chloride, nitrate, and bicarbonate, was also investigated by adding 0.01M of NaCl, NaNO₃, or NaHCO₃ to the 61.5 mg/L phosphate solutions into separate digestion vessels. The adsorbent to initial solution phosphate concentration were the same as the kinetics experiment. The vessels were shaken in the mechanical shaker for 24 h at room temperature. The same procedures were then used to determine aqueous and adsorbed phosphate concentrations.

Post-adsorption biochar characterization

To investigate the crystallographic structures on the post-adsorption DSTC, X-ray diffraction (XRD) patterns were acquired with a computer-controlled X-ray

diffractometer (Philips APD 3720) equipped with a stepping motor and graphite crystal monochromator. Fourier Transform Infrared (FTIR) spectra were collected using a Bruker Vector 22 FTIR spectrometer (OPUS 2.0 software) to identify the surface functional groups of post-adsorption DSTC samples. The P-loaded DSTC was ground and mixed with KBr to approximately 0.1 wt% and pressed into a pellet using a mechanical device. Scanning electron microscopy (SEM, JEOL JSM-6400) coupled with dispersive X-ray spectroscopy (EDS, Oxford Instruments Link ISIS) was used to the surface of the post-adsorption DSTC and to determine its surficial elemental composition. These characteristics of the phosphate-loaded DSTC were compared with those of the original biochar (Example 3) to determine the adsorption mechanisms.

Results and Discussion

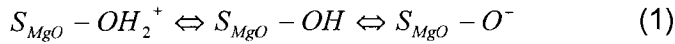
Main adsorption mechanism

Example 3 showed that DSTC had a relatively high surface area measured with N₂ (336 m²/g) and CO₂ (449 m²/g), which is generally desirable for phosphate adsorption. In addition, characterization results from elemental, SEM-EDS, and XRD analyses revealed that the DSTC surface was covered with colloidal or nano-sized MgO (periclase) particles, which could serve as the main adsorption sites for phosphate removal.

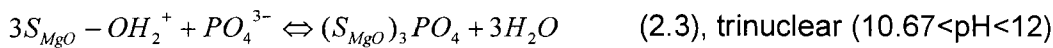
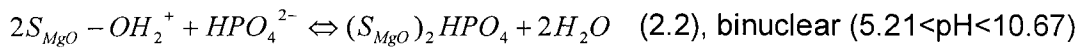
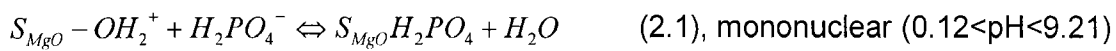
SEM-EDS analysis of the post-adsorption DSTC samples confirmed the hypothesis that the MgO particles on the DSTC surface may dominate the phosphate adsorption. At a high resolution of 7000X, when the SEM was focused on the MgO crystals on the P-loaded DSTC surface, the corresponding EDS spectrum showed an elevated peak of phosphorus (FIG. 5.1). Although phosphorus was also detected in the original DSTC (Example 3), its EDS signal of phosphorus was much lower. For the P-loaded DSTC, the phosphorus signal was even higher than those of the magnesium and oxygen, which showed the second and third highest EDS peaks (FIG. 5.1).

Metal oxides have showed strong ability to adsorb negative charged compounds, such as phosphate and arsenate (27). When in contact with water, the metal oxide surface becomes hydroxylated and thus introduces either a positive or

negative surface charge, depending on the solution pH. The charge development of MgO on the biochar surface can be described in a simplified manner as (28):



where S_{MgO} denotes the MgO surface. The point of zero charge (PZC) of MgO is very high ($PZC_{MgO}=12$, (29)), thus its surface is expected to be positively charged in most natural aqueous conditions. In aqueous solution, phosphate exists in four species with pKa values of 2.12 (pK_{a1}), 7.21 (pK_{a2}), and 12.67 (pK_{a3}). When solution pH is lower than PZC_{MgO} , the hydroxylated MgO surface can electrostatically attract negatively charged phosphate species to form mono-, bi-, and trinuclear complexes (28, 30):



Although most of the initial solution pH values in this study were around 7, the reductions of aqueous phosphate during the experiments would affect the dynamics of solution pH (15, 30). This would increase the heterogeneity of the adsorption processes of phosphate onto the biochar to trigger both mono- and multi-nuclear interactions (i.e., equation 2.1-2.3).

Other potential adsorption mechanisms

Element analysis indicated that there were large amount of calcium in both DSTC and STC (Example 3). If the calcium was released from the biochars into the solution as free ions, they may remove phosphate through precipitation. However, the preliminary assessment of STC showed almost no ability to remove aqueous phosphate (Example 3). In addition, the XRD spectra of the original and P-loaded DSTC were almost identical and showed no evidence of calcium-phosphate precipitates in the P-loaded biochar (FIG. 5.2A), suggesting that the precipitation might not be an important mechanism for phosphate removal. This could be explained by two reasons: 1) some of the calcium in the biochar was in form of calcite (FIG. 5.2A), which has a very low solubility; and 2) a portion of the calcium might be incorporated inside of the biochar and could not be released into the solution (31).

Because there was abundance of surface functional groups on the DSTC surface (Example 3), phosphate could also be removed by the biochar through interacting with the functional groups. However, again, the similarity between the FTIR spectra of the original and P-loaded DSTC provides no evidence of adsorption of phosphate onto the surface functional groups in the P-loaded biochar (FIG. 5.2B).

Adsorption kinetics

The adsorption of phosphate onto the DSTC increased smoothly over time and reached equilibrium after 24 h (FIG. 5.3a). The slow kinetics further suggests that precipitation might not play an import role in the removal of phosphate by the biochar. Mathematical models were used to simulate the experimental kinetics. In addition to the commonly used pseudo-first-order and pseudo-second order models, the Ritchie N_{th}-order model and Elevich model were also tested (32) and are represented by the following equations:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3.1), \text{ first-order}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3.2), \text{ second-order}$$

$$\frac{dq_t}{dt} = k_n(q_e - q_t)^N \quad (3.3), \text{ N}_{th}\text{-order}$$

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (3.4), \text{ Elevich}$$

where q_t and q_e are the amount of phosphate adsorbed at time t and at equilibrium, respectively (mg kg^{-1}), and k_1 , k_2 and k_n are the first-order, second-order, and N_{th}-order apparent adsorption rate constants (h^{-1}), respectively. Also, α is the initial adsorption rate (mg kg^{-1}) and β is the desorption constant (kg mg^{-1}). The first-order, second-order, and N_{th}-order models describe the kinetics of the solid-solution system based on mononuclear, binuclear, and N-nuclear adsorption, respectively, with respect to the sorbent capacity (32), while the Elevich model is an empirical equation considering the contribution of desorption.

All the models closely reproduced the kinetic data (FIG. 5.3a), with all correlation coefficients (R^2) exceeding 0.98 (Table 1, Example 4). However, the first-order, second-order, and N_{th}-order ($N=1.14$) models fitted the data slightly better than the Elevich model and N_{th}-order model had the highest R^2 (0.9970). This

result is consistent with the proposed predominant mechanism that phosphate removal by the biochar was mainly through adsorption onto the colloidal and nano-sized MgO crystals on DSTC surface. Both mononuclear and multinuclear adsorption of phosphate would be favored in the kinetics experiment, perhaps explaining why fittings from the N_{th}-order model were slightly better than that of either the first- or second-order model.

Table 1, Example 4. Best-fit parameter values for models of kinetic and isotherm data.

Model	Parameter 1	Parameter 2	Parameter 3	R ²
First-order	$k_1 = 0.1554 \text{ (h}^{-1}\text{)}$	$q_e = 23474.94 \text{ (mg kg}^{-1}\text{)}$	--	0.9968
Second- order	$k_2 = 5.211 \times 10^{-6} \text{ (kg mg}^{-1} \text{ h}^{-1}\text{)}$	$q_e = 28771.04 \text{ (mg kg}^{-1}\text{)}$	--	0.9949
N _{th} -order	$k_N = 0.000701 \text{ (kg}^N \text{ mg}^{-N} \text{ h}^{-1}\text{)}$	$q_e = 23927.64 \text{ (mg kg}^{-1}\text{)}$	N = 1.1359	0.9970
Elevich	$\beta = 0.000139 \text{ (mg kg}^{-1}\text{)}$	$\alpha = 5967.70 \text{ (mg kg}^{-1}\text{)}$	--	0.9855
Langmuir	$K = 0.02551 \text{ (L mg}^{-1}\text{)}$	$Q = 133084.7 \text{ (mg kg}^{-1}\text{)}$	--	0.9526
Freundlich	$K_f = 11642.39 \text{ (mg}^{(1-n)} \text{ L}^n \text{ kg}^{-1}\text{)}$	$n = 0.4527$	--	0.9781
Langmuir-Freundlich	$K = 0.01562 \text{ (L}^n \text{ mg}^{-n}\text{)}$	$Q = 705873.6 \text{ (mg kg}^{-1}\text{)}$	$n = 0.4954$	0.9785

Previous studies on the kinetic behaviors of microporous sorbents showed that intraparticle surface diffusion may be important to the adsorption process (33, 34). In this study, the adsorption of phosphate onto DSTC also showed diffusion limitation. The pre-equilibrium (i.e. before 24 h) phosphate adsorption showed a strong linear dependency ($R^2=0.9959$) on the square root of time (FIG. 5.3B). This result suggests that intraparticle surface diffusion may play an important role in controlling the adsorption of phosphate onto the biochar, likely due to its abundance of mesopores.

Adsorption isotherms

With the maximum observed phosphate adsorption of greater than 100,000 mg/kg (FIG. 5.4), the DSTC showed phosphate sorption ability to be superior to most of the reported values of other carbonaceous adsorbents (2, 15, 16). Three isotherm equations were tested to simulate the phosphate adsorption onto the biochar (32):

$$q_e = \frac{KQC_e}{1 + KC_e} \quad (4.1), \text{ Langmuir}$$

$$q_e = K_f C_e^n \quad (4.2), \text{ Freundlich}$$

$$q_e = \frac{KQ C_e^n}{1 + K C_e^n} \quad (4.3), \text{ Langmuir-Freundlich}$$

where K and K_f represents the Langmuir bonding term related to interaction energies (L mg^{-1}) and the Freundlich affinity coefficient ($\text{mg}^{(1-n)} \text{L}^n \text{kg}^{-1}$), respectively, Q denotes the Langmuir maximum capacity (mg kg^{-1}), C_e is the equilibrium solution concentration (mg L^{-1}) of the sorbate, and n is the Freundlich linearity constant. The Langmuir model assumes monolayer adsorption onto a homogeneous surface with no interactions between the adsorbed molecules. The Freundlich and Langmuir-Freundlich models, however, are empirical equations, which are often used to describe chemisorptions onto heterogeneous surface.

All the models reproduced the isotherm data fairly well (FIG. 5.4), with correlation coefficients (R^2) exceeding 0.95 (Table 1, Example 4). However, fittings of the Freundlich and Langmuir-Freundlich matched the experimental data better than those of the Langmuir model, suggesting the adsorption of phosphate onto the DSTC was controlled by heterogeneous processes. This result is consistent with the proposed predominant adsorption mechanism of phosphate removal by the biochar through both mononuclear and multinuclear adsorption onto the colloidal and nano-sized MgO particles on DSTC surface.

Effect of pH and coexisting anions

The adsorption of phosphate onto the DSTC depended on initial solution pH (FIG. 5.5A). The phosphate adsorption was lowest when pH equaled 2.0. When pH was increased from 2.0 to 4.1, the adsorption of phosphate by the biochar increased. Further increases in pH from 4.1 to 6.2, 7.1, 8.1, and 10.4, however, decreased the adsorption of phosphate onto the DSTC (FIG. 5.5A), suggesting the existence of an optimum pH for the maximum phosphate adsorption. Similar results were found in studies of the pH effect on phosphate removal from aqueous solution by other carbon-based adsorbents (15).

Although molecular concentrations of the coexisting anions were about 15.5 times of the phosphate, chloride and nitrate had little effect on the adsorption of phosphate (4.3 and 11.7 percent decrease, respectively) onto the biochar (FIG. 5B), suggesting low competitions between phosphate and these two ions for the MgO

sites on the DSTC surface. The existence of high concentrations of bicarbonate in the solution, however, reduced the phosphate adsorption for about 41.4% (FIG. 5.5b). Two factors could be responsible for the reduction: 1) the competition for the adsorption site between bicarbonate and phosphate; and 2) the increase of solution pH due to the addition of bicarbonate.

Conclusions

Biochar converted from anaerobically digested sugar beet tailings (DSTC) demonstrated superior ability to remove phosphate from water under a range of pH and competitive ion conditions. Batch sorption experiments and post-sorption characterizations suggested that phosphate removal was mainly controlled by adsorption onto colloidal and nano-sized MgO particles on the DSTC surface. Because both the original and anaerobically digested sugar beet tailings are waste materials, the cost to make DSTC should be very low. However, the use of pre-digested sugar beet tailings has the benefit of additional energy generation and more efficient production (with less CO₂ release during production). 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 biochar 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 of the similarities among phosphate, arsenate, and molybdate (27), it is expected that the digested sugar beet tailing biochar would also be an effective adsorbent for arsenate and molybdate.

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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 to significant figures of the numerical value. 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 method of removing contaminants from a fluid comprising:
 exposing a biologically activated biochar and a fluid to one another,
 wherein the fluid includes one or more types of ions selected from a metal cation and its analogue, a phosphate ion and its analogue, a nitrate ion and its analogue, a nitrite ion and its analogue, and a combination thereof; and
 adsorbing at least one type of ion onto the biologically activated biochar.
2. The method of claim 1, wherein the fluid is water.
3. The method of claim 1, wherein the type of cation is selected from the group consisting of: lead, copper, zinc, cadmium, nickel, chromium, iron, aluminium, cobalt, magnesium, mercury, and a combination thereof.
4. The method of claim 1, wherein the type of anion is selected from the group consisting of: a phosphate, a nitrate, a nitrite, an analogue of each of these, and a combination thereof.
5. The method of claim 1, wherein the biologically activated biochar is a product of a pyrolysis of a bioenergy residue.
6. The method of claim 5, wherein the bioenergy residue is selected from one of a digested biomass or a digested carbon-rich waste.
7. The method of claim 1, wherein the type of cation is lead.
8. A structure comprising:
 a biologically activated biochar, wherein the biologically activated biochar is a product of a pyrolysis of a bioenergy residue.

9. The structure of claim 9, wherein the bioenergy residue is selected from one of a digested biomass or a digested carbon-rich waste.
10. The structure of claim 9, wherein the bioenergy residue is selected from the group consisting of: an anaerobically digested sugarcane bagasse, an anaerobically digested manure, an anaerobically digested sugar beet tailing, an anaerobically digested sugar beet pulp, and a combination thereof.
11. The structure of claim 9, wherein the biologically activated biochar has the characteristic of adsorbing one or more types of ions selected from: a metal cation and its analogue, a phosphate ion and its analogue, a nitrate ion and its analogue, a nitrite ion and its analogue, and a combination thereof.
12. The structure of claim 9, wherein the biologically activated biochar has colloidal, nano-sized minerals, metal oxides, or a combination thereof, embedded on the surface of the biologically activated biochar.
13. A method of making a biochar, comprising:
 - anaerobic or bacterial digestion of a material selected from a biomass, a carbon-rich waste, and a combination thereof, to produce a bioenergy residue; and
 - pyrolyzing the bioenergy residue to form a biologically activated biochar.
14. The method of claim 13, wherein the bioenergy residue is selected from the group consisting of: an anaerobically digested sugarcane bagasse, an anaerobically digested manure, an anaerobically digested sugar beet tailing, an anaerobically digested sugar beet pulp, and a combination thereof.
15. The method of claim 13, wherein the digestion is a bacterial digestion.

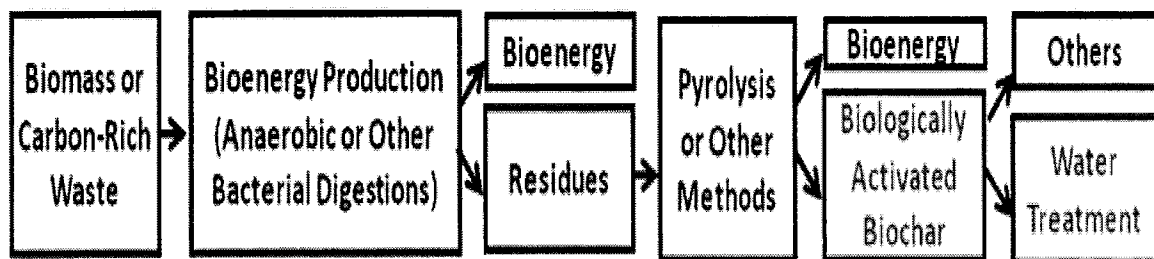


FIG. 1.1

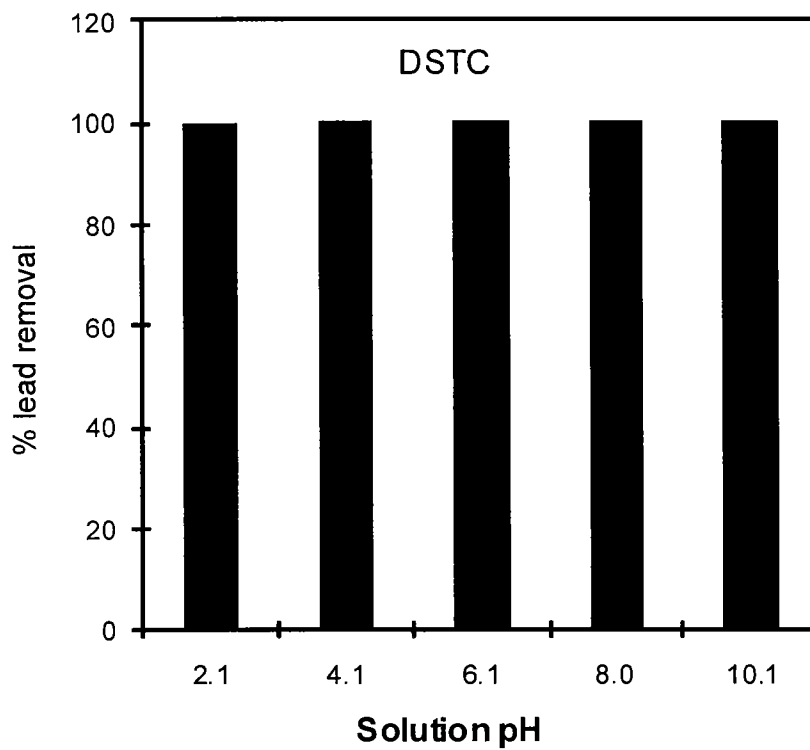


FIG. 1.2A

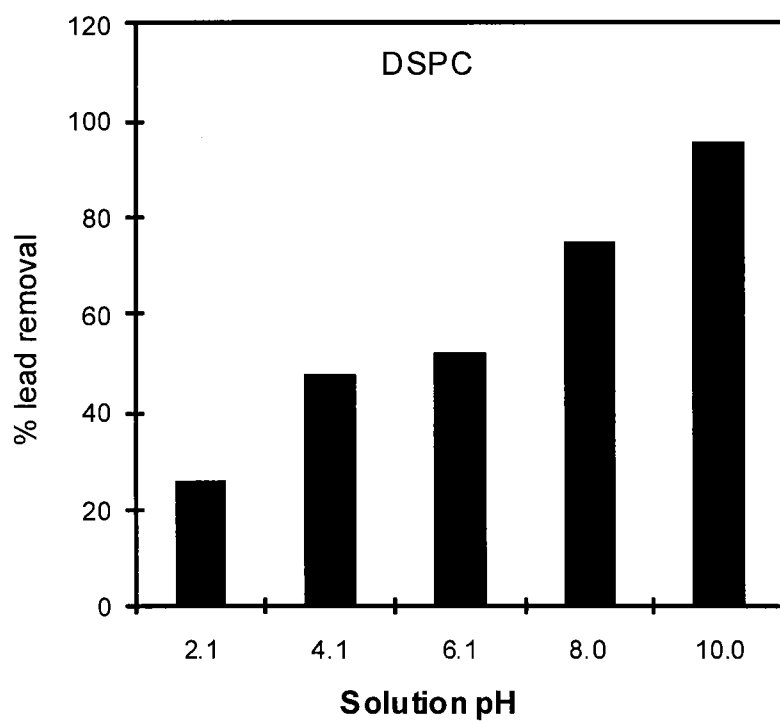


FIG. 1.2B

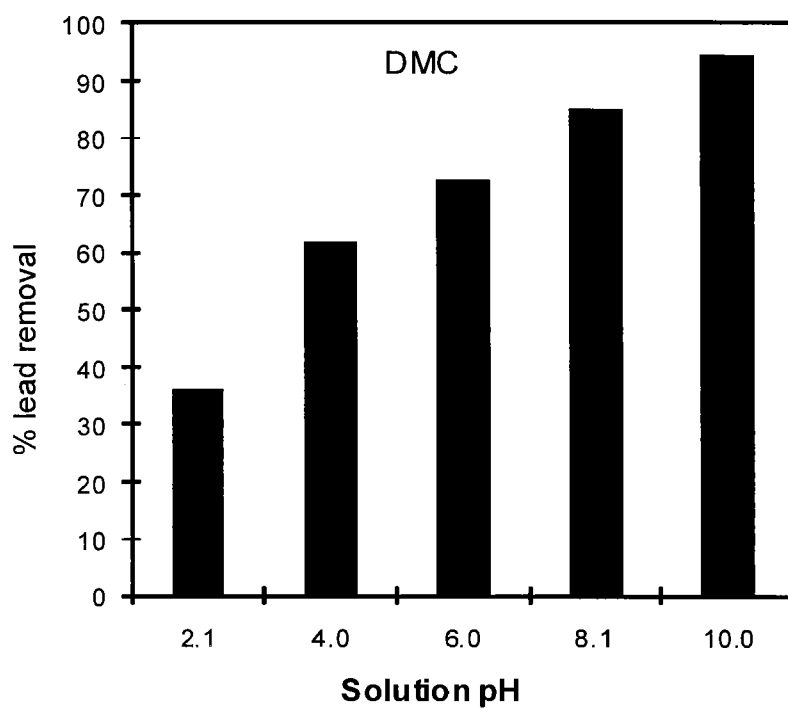


FIG. 1.2C

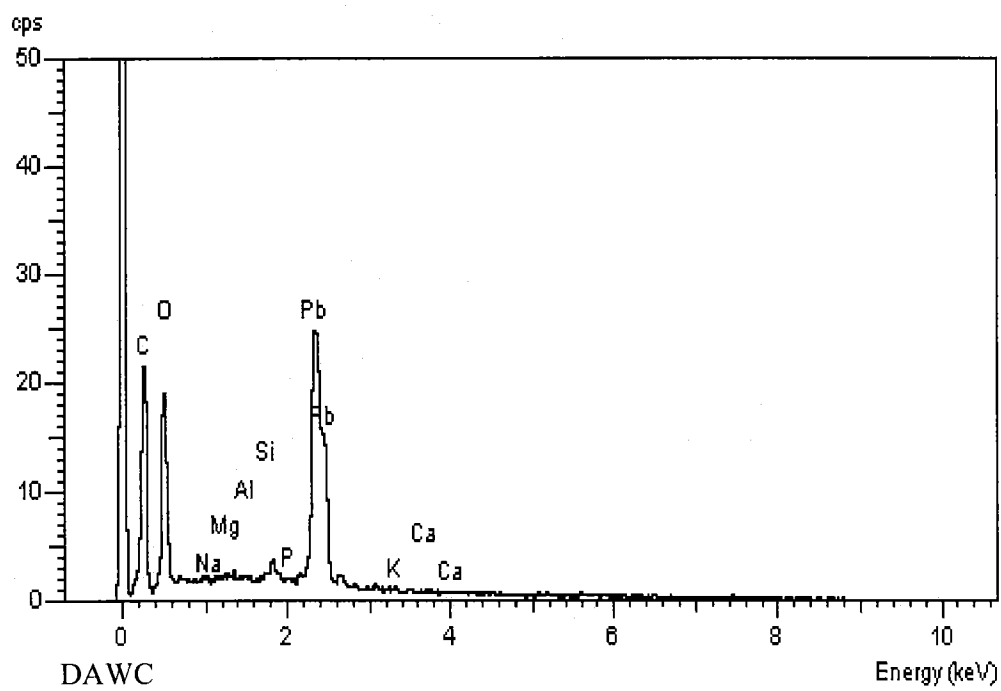
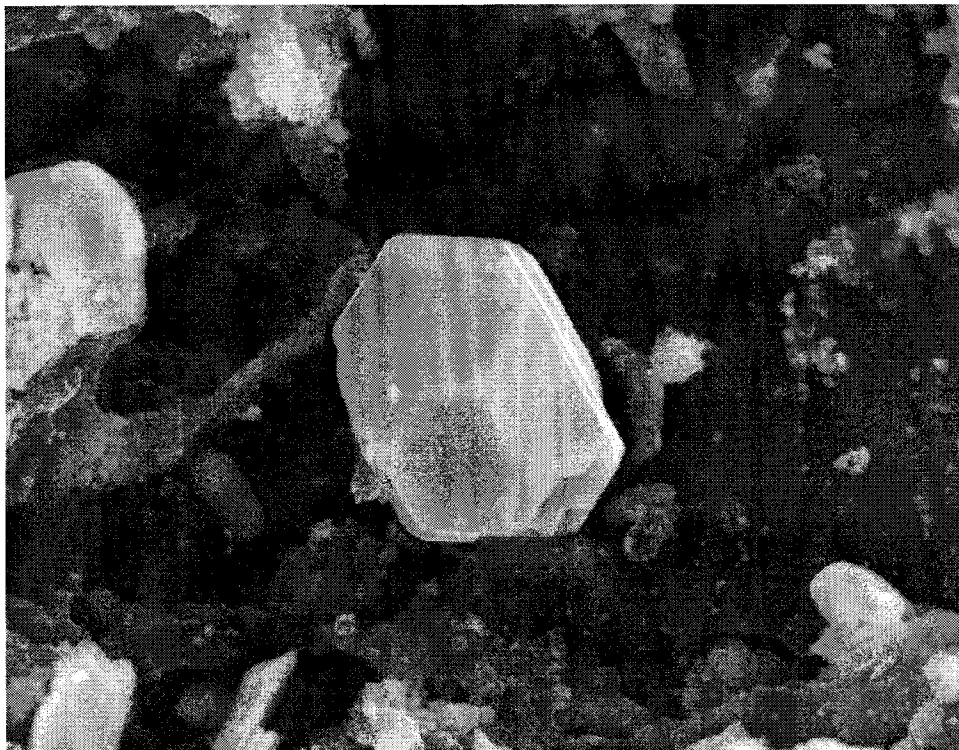


FIG. 1.3A

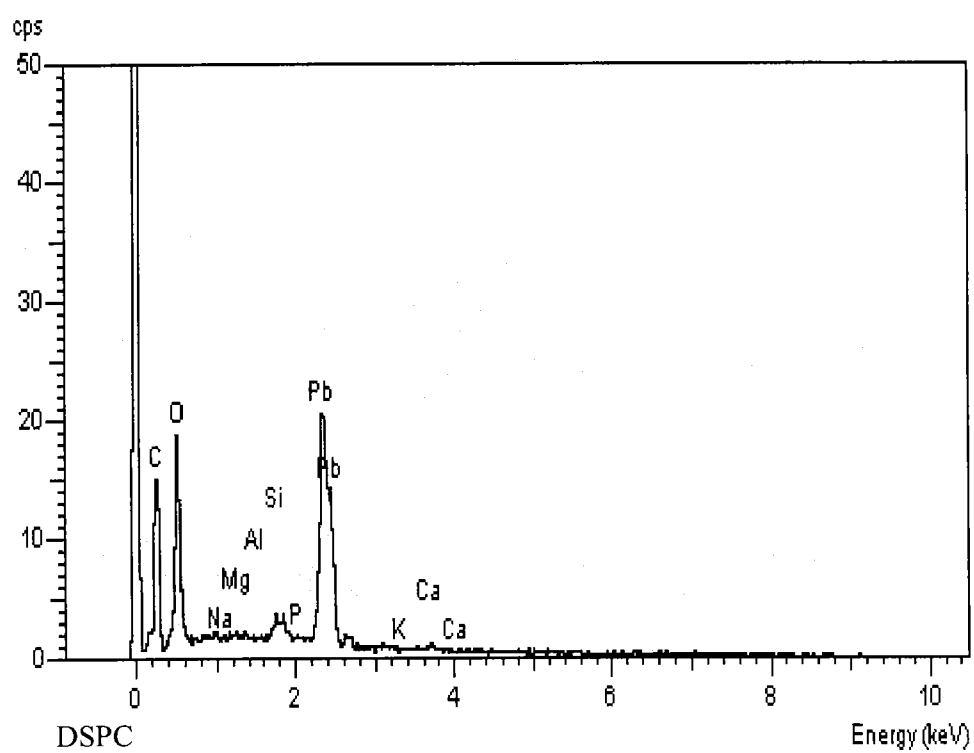
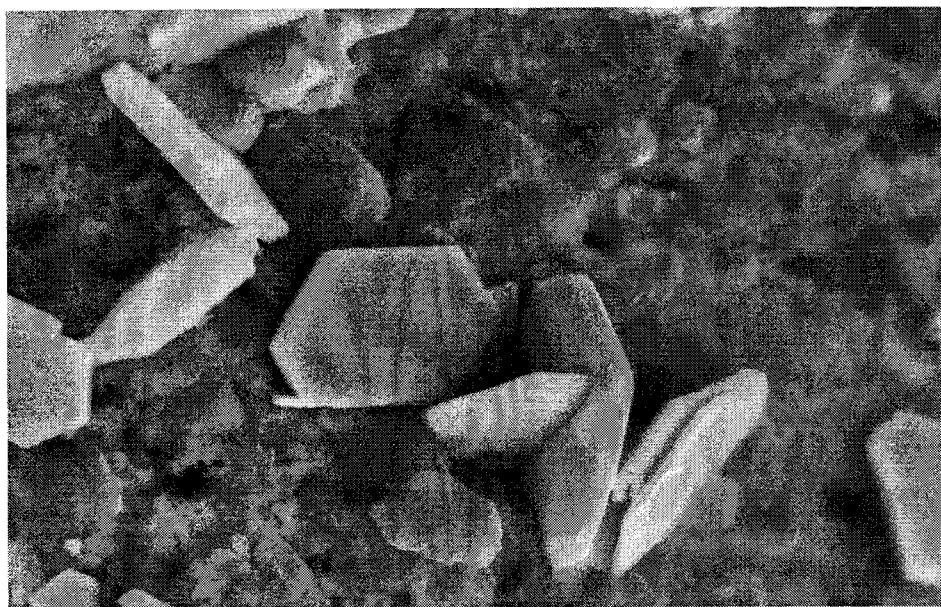


FIG. 1.3B

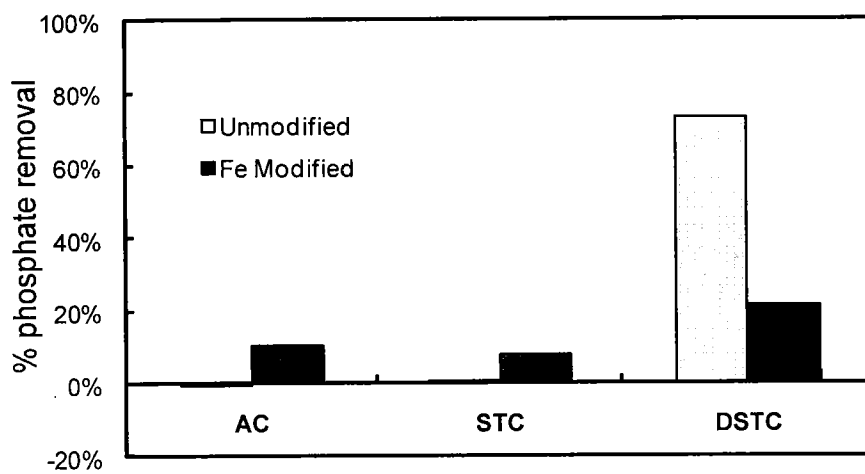
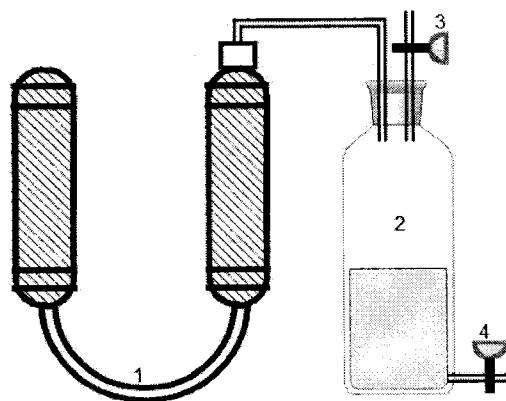


FIG. 1.4



(1) U-tube Gas meter, (2) Anaerobic digester, (3) Gas sampler port, and (4) Drain valve

FIG. 2.1

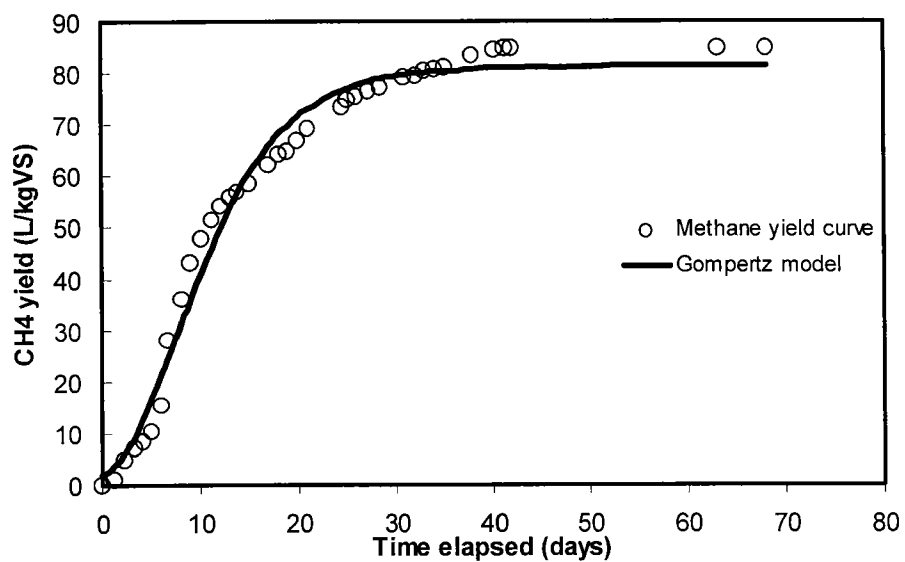
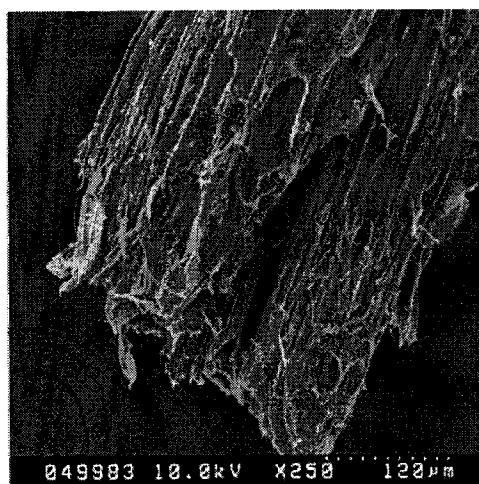
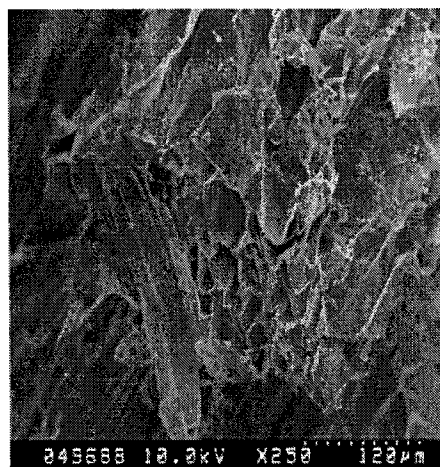


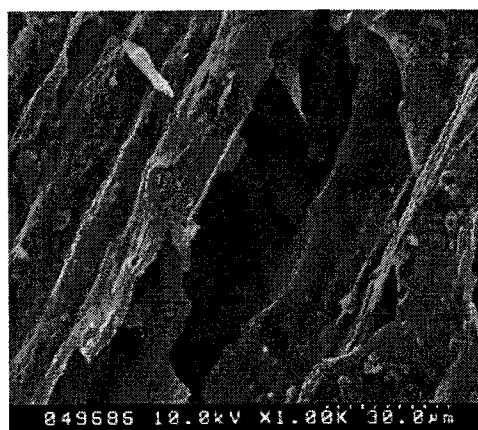
FIG. 2.2



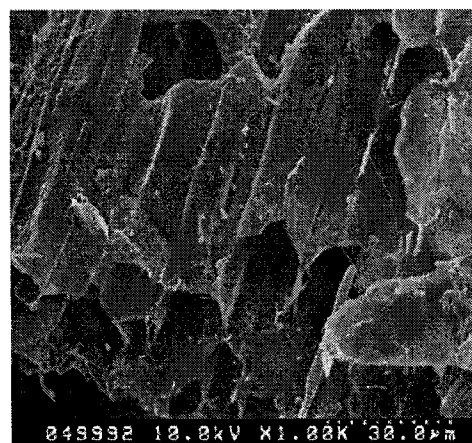
(a) Raw Bagasse



(b) Digested Bagasse Residue



(c) BC



(d) DBC

FIG. 2.3

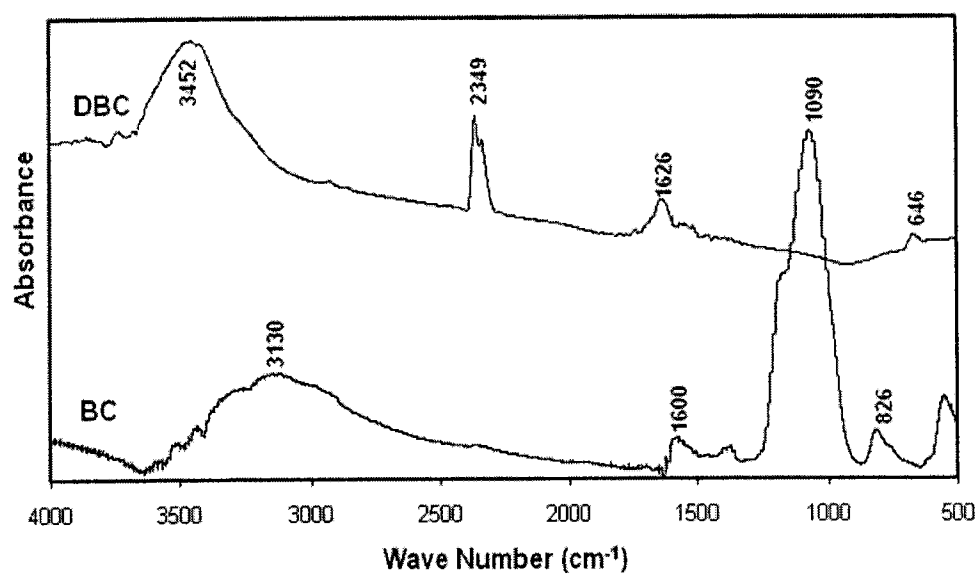


FIG. 2.4

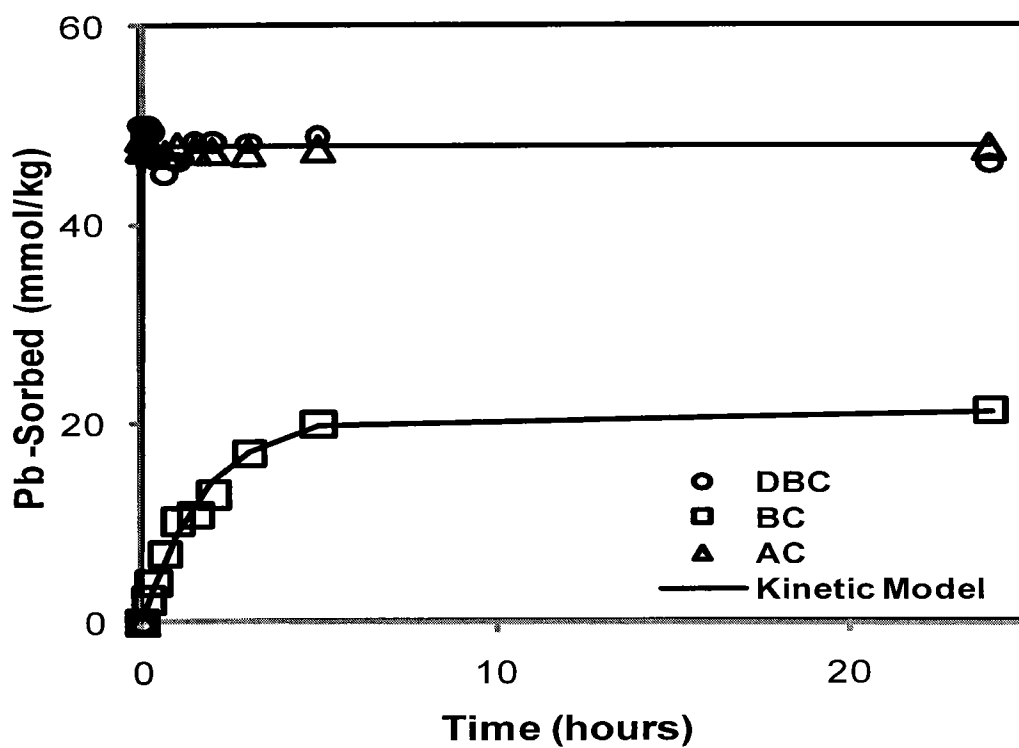


FIG. 3.1A

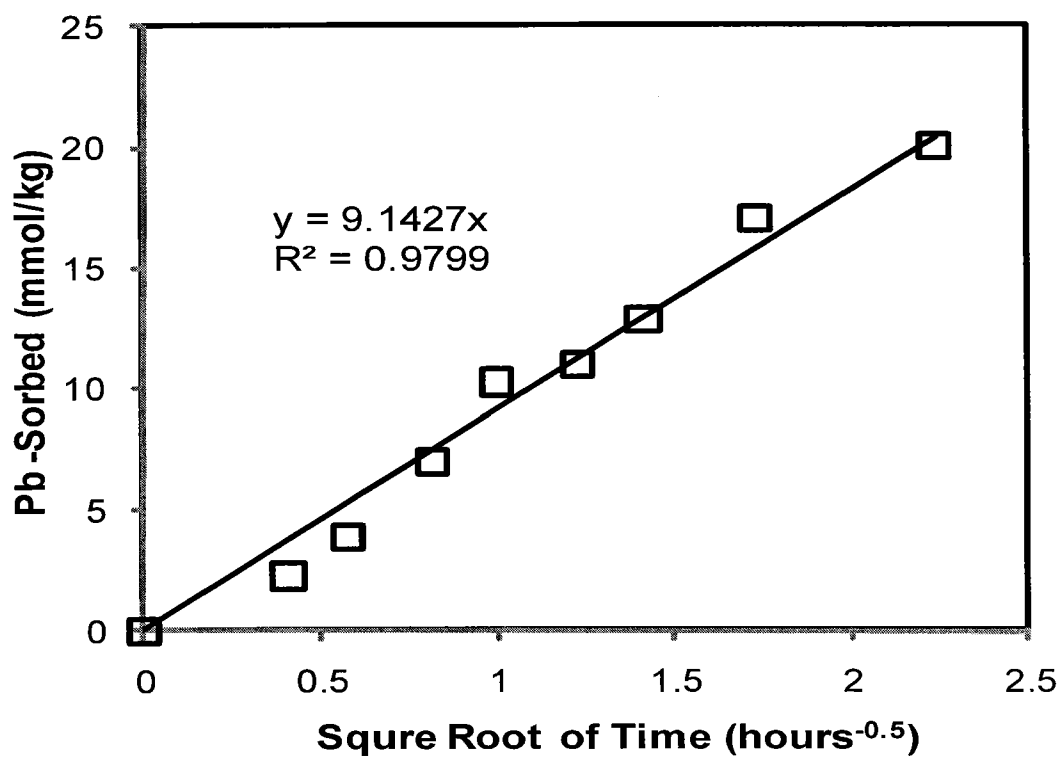


FIG. 3.1B

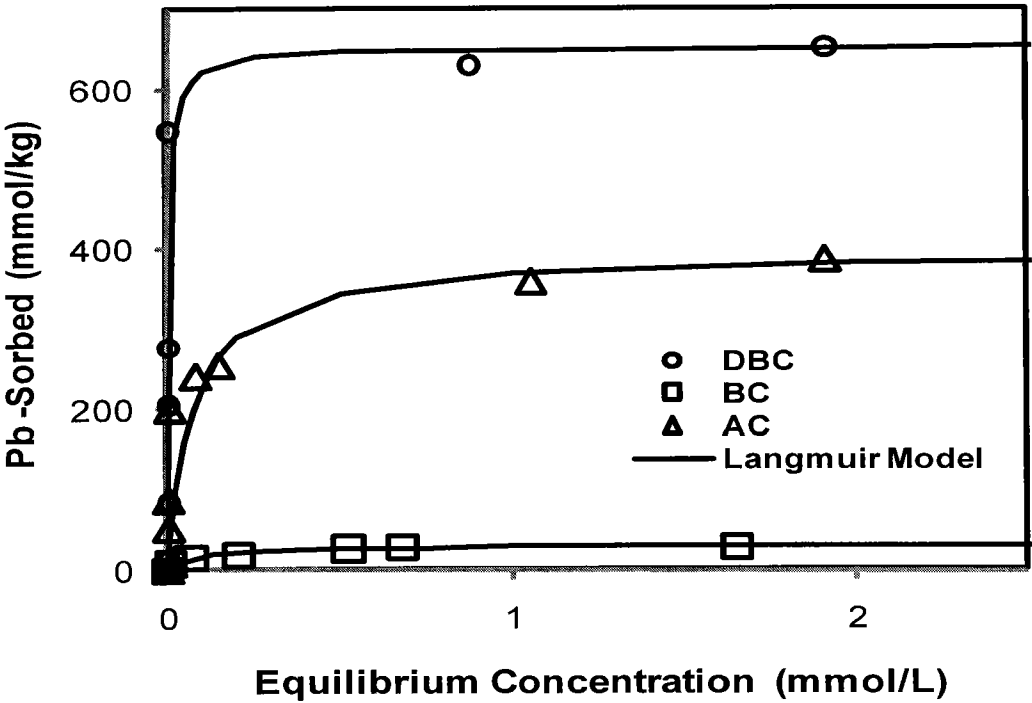


FIG. 3.2

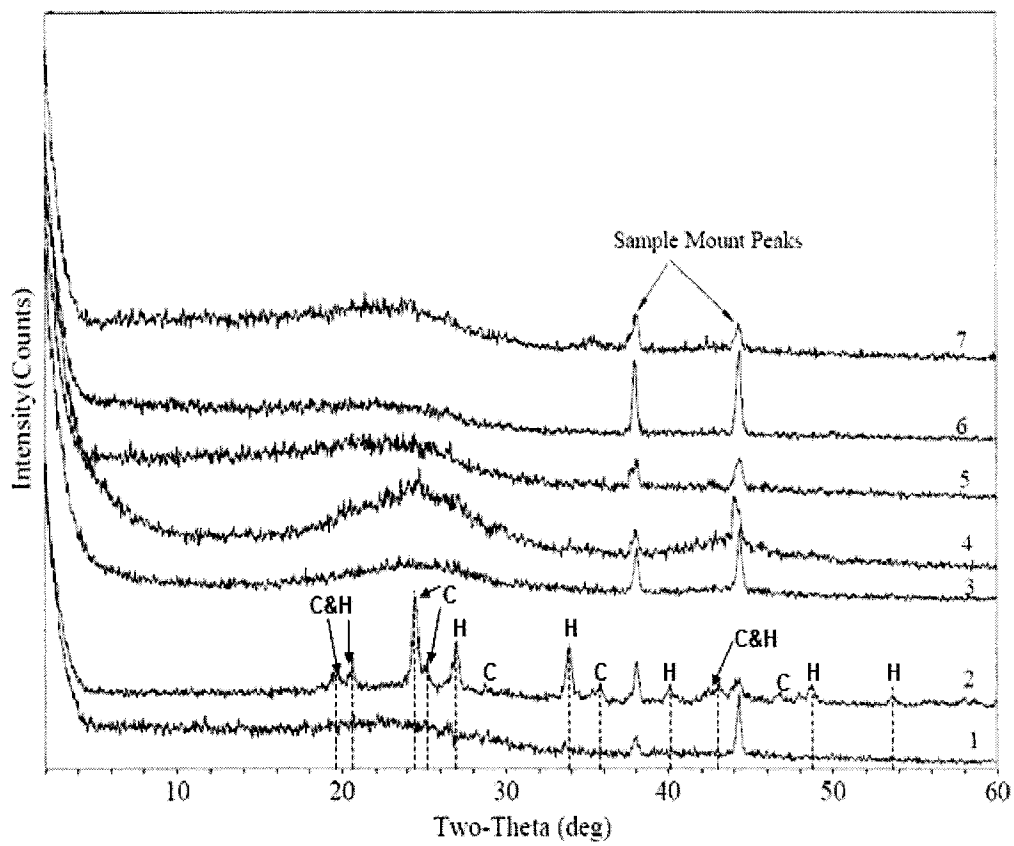


FIG. 3.3

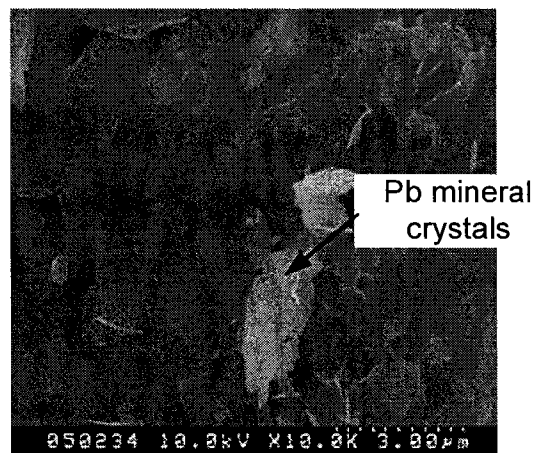


FIG. 3.4

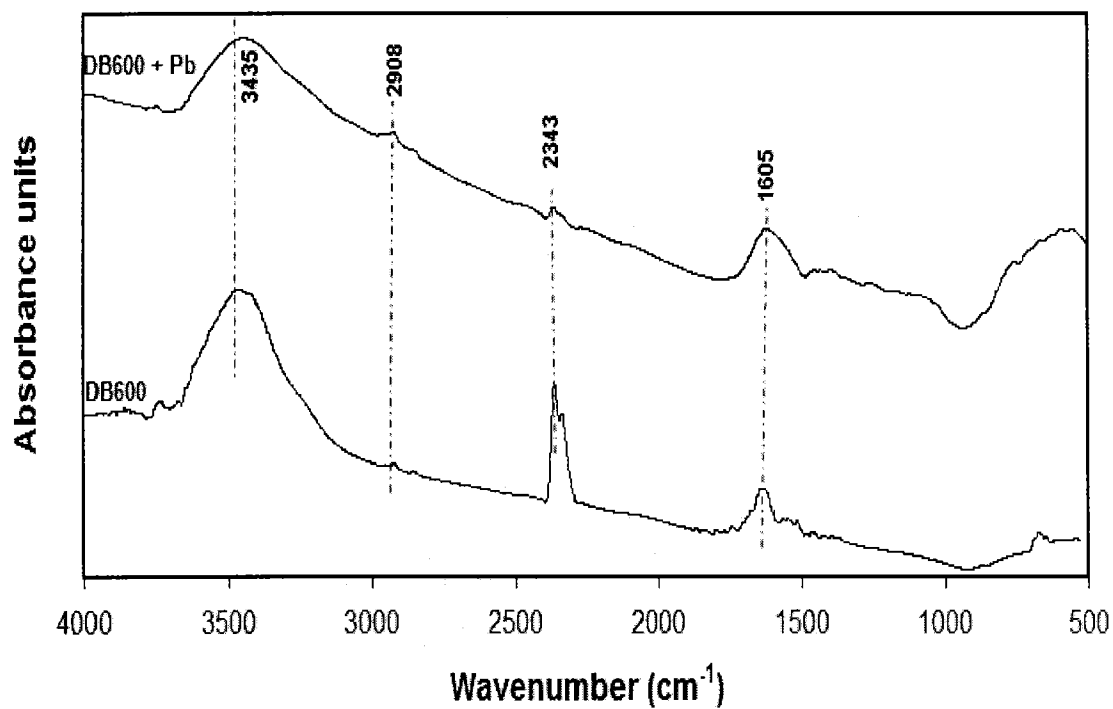


FIG. 3.5A

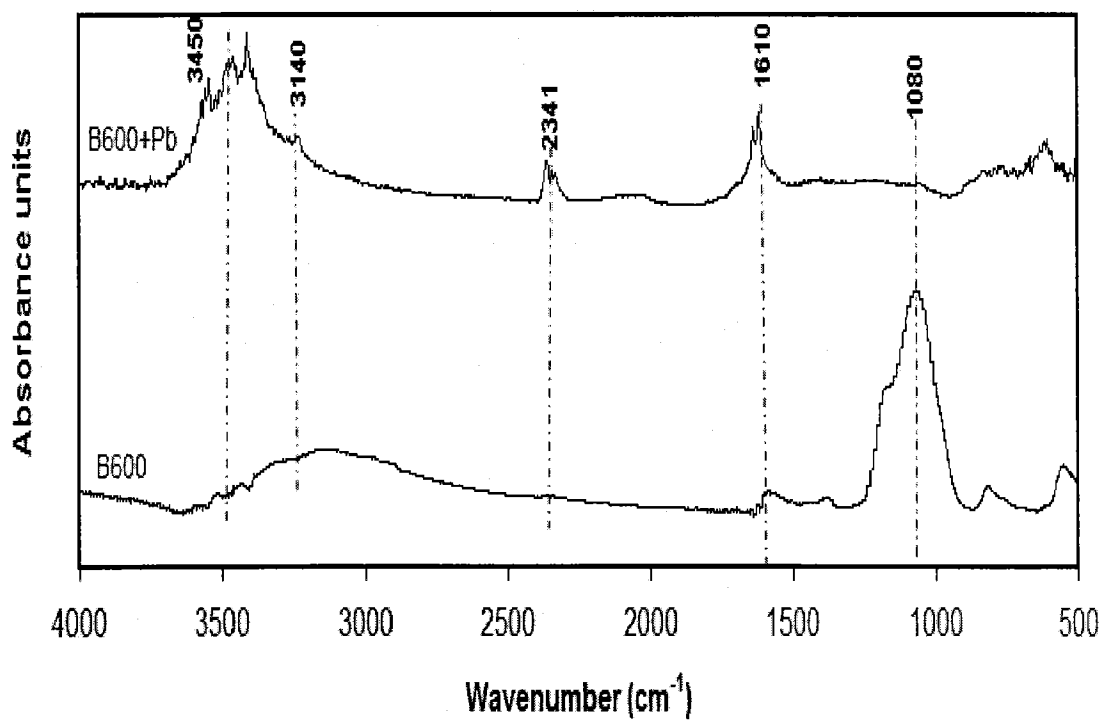


FIG. 3.5B

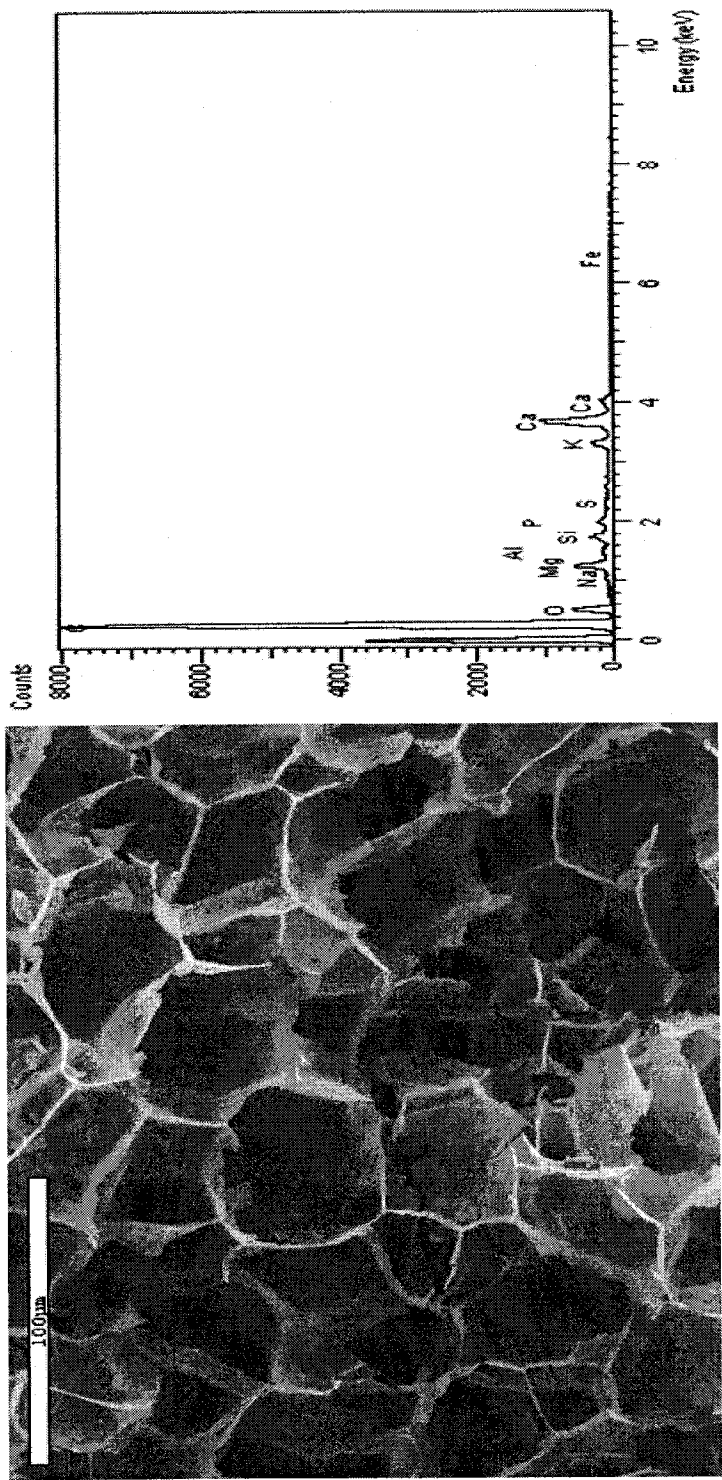


FIG. 4.1A

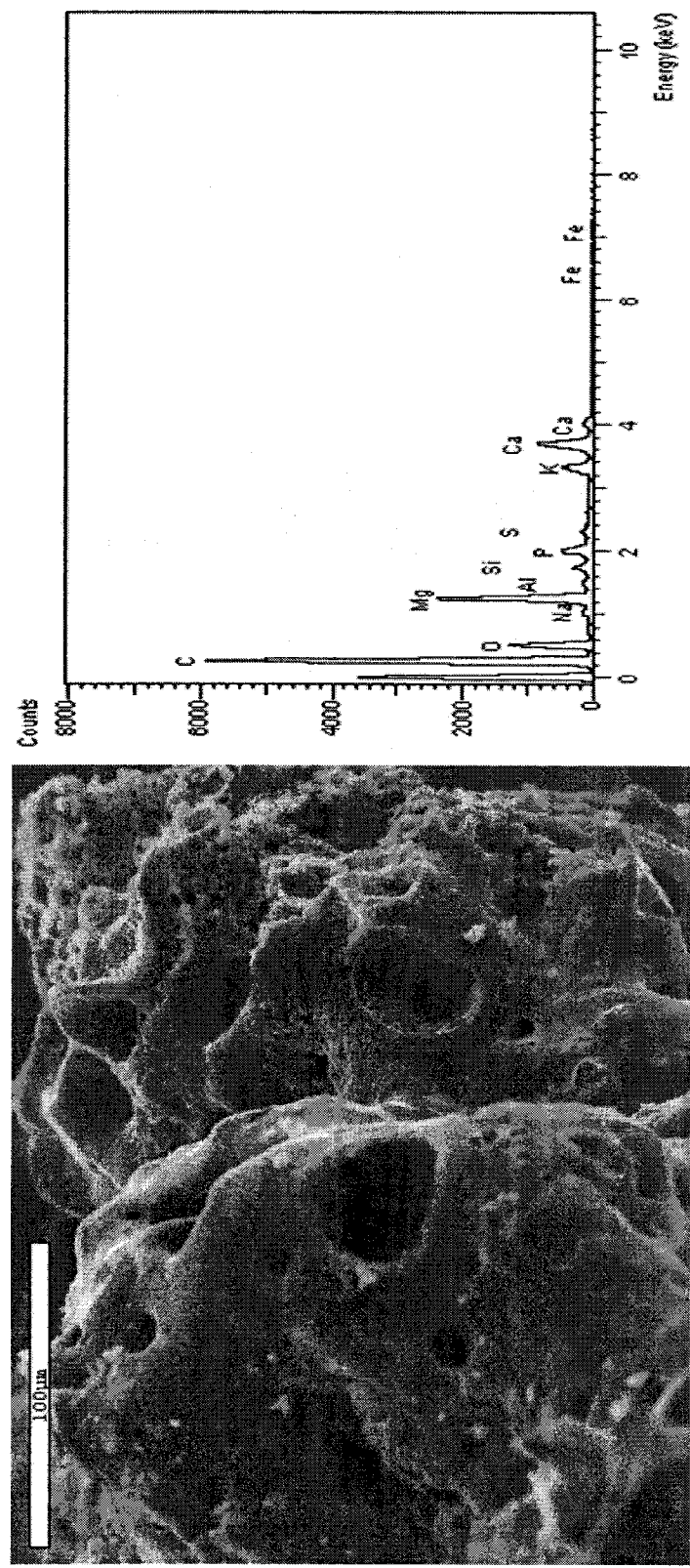


FIG. 4.1B

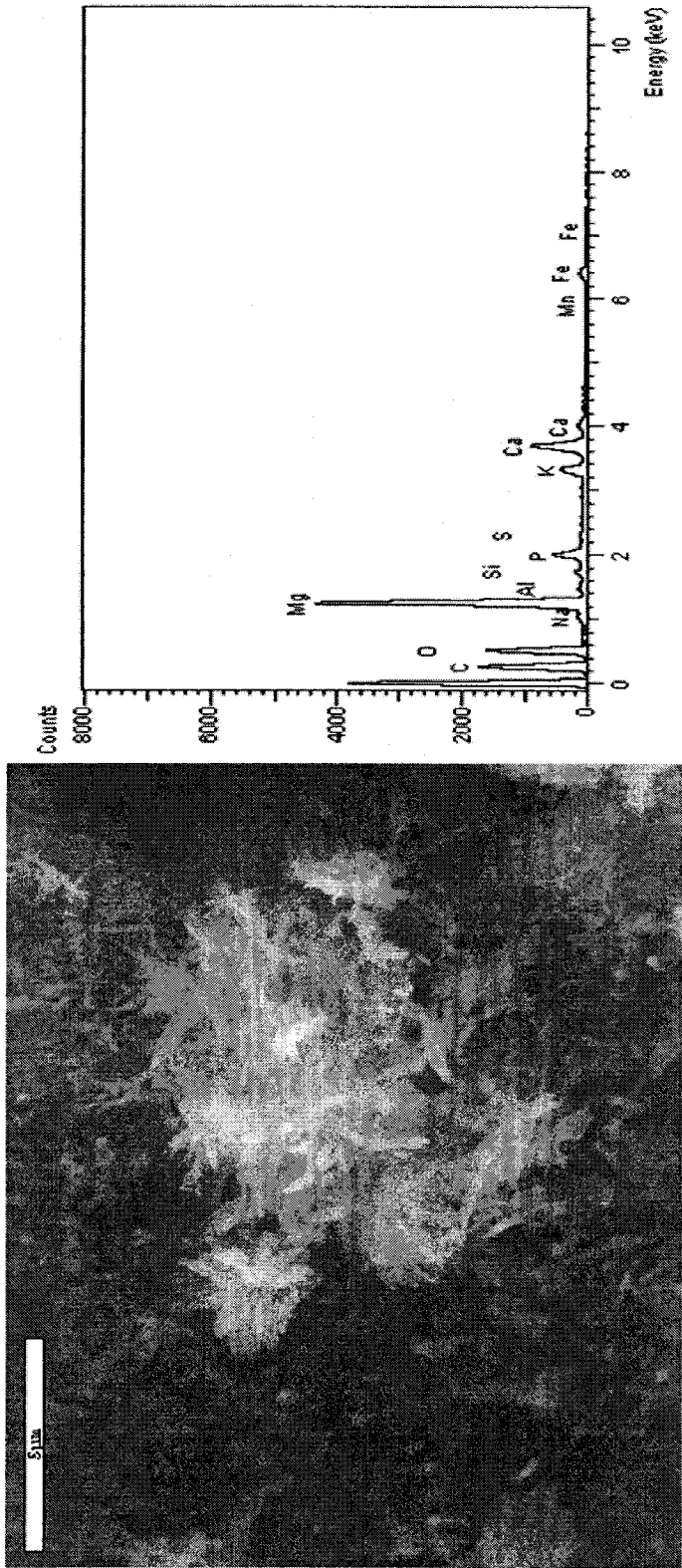


FIG. 4.1C

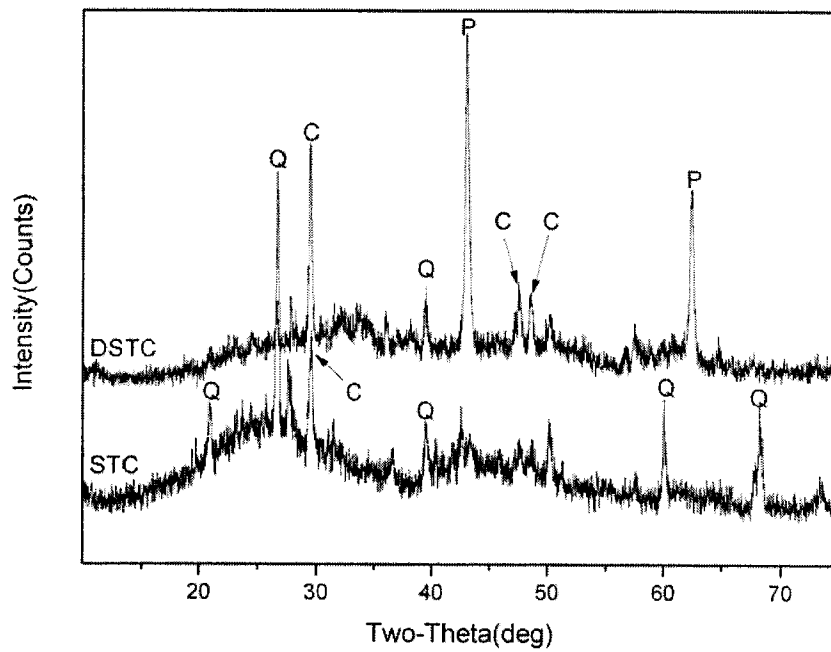


FIG. 4.2

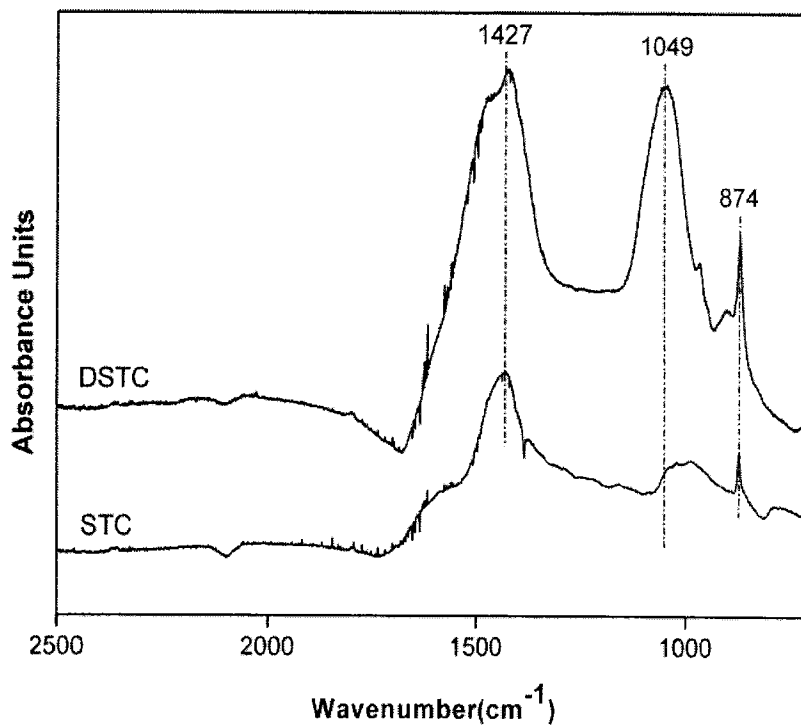


FIG. 4.3

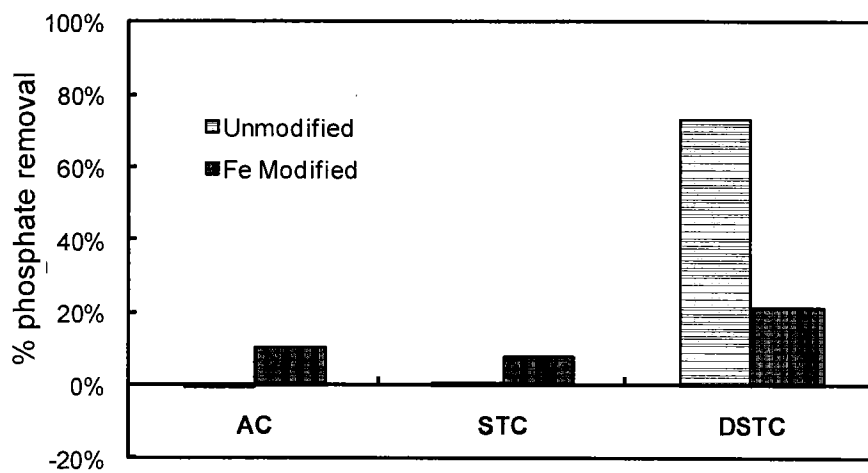


FIG. 4.4

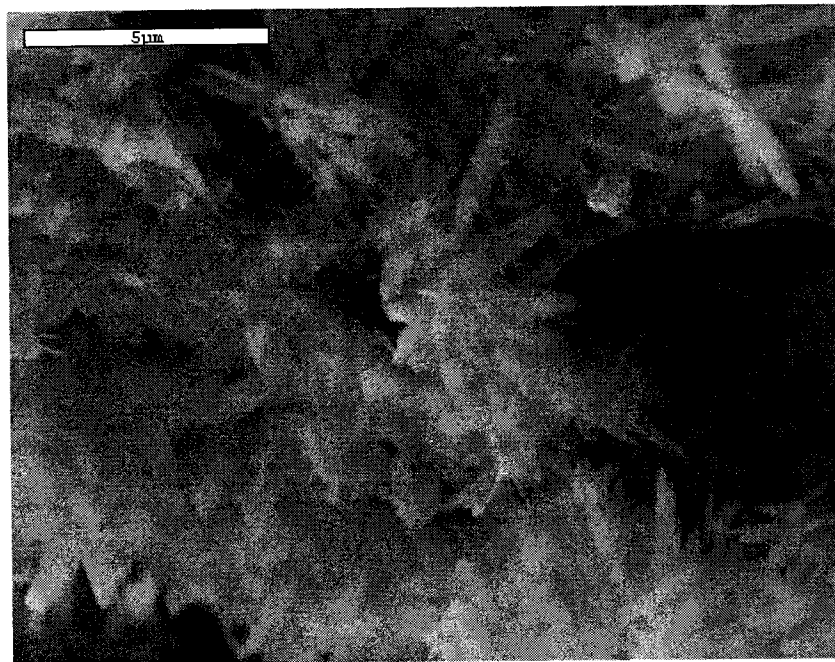


FIG. 5.1A

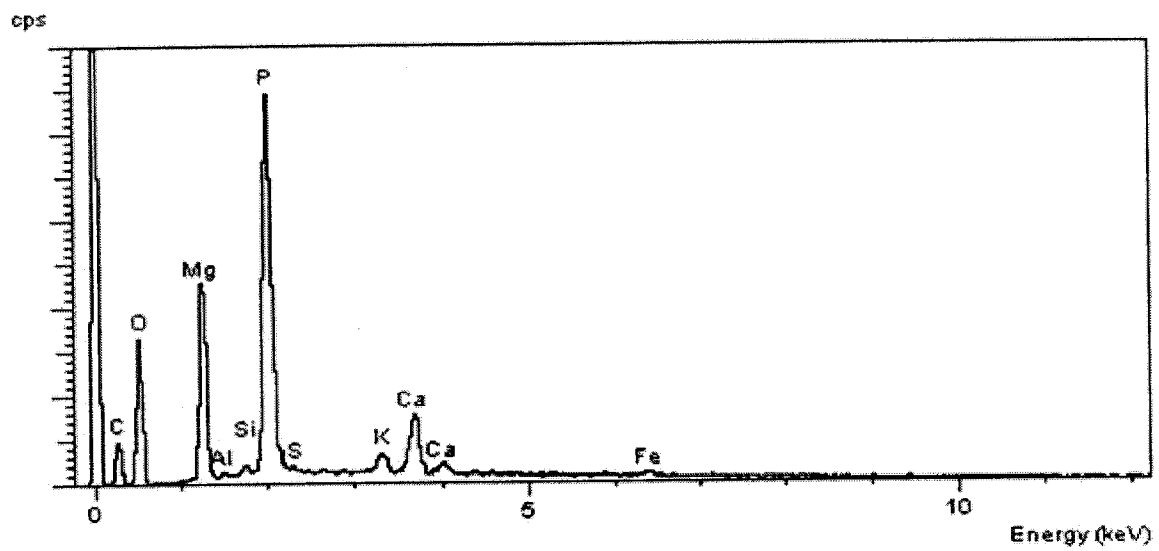


FIG. 5.1B

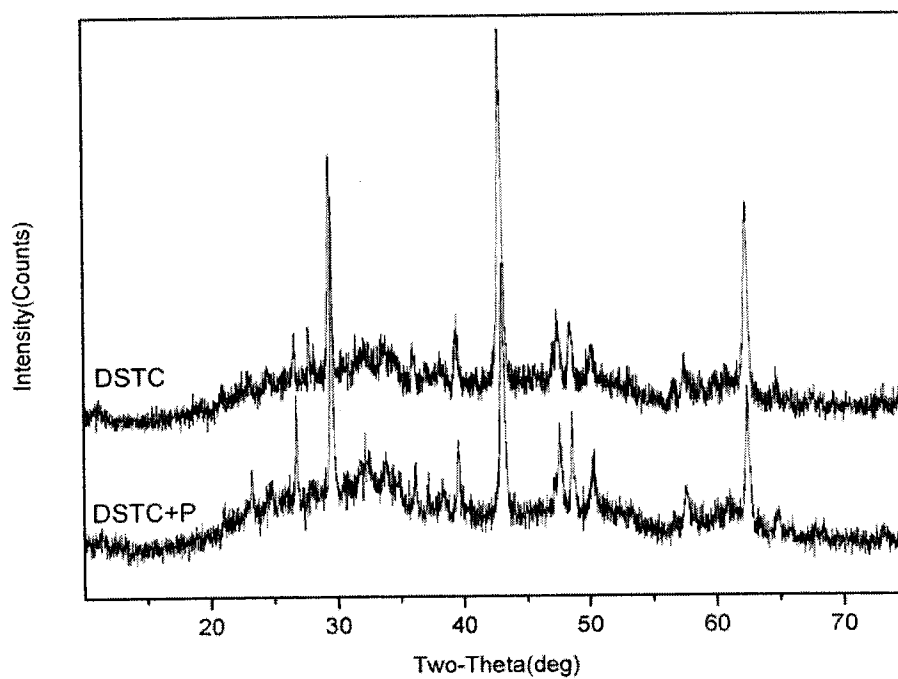


FIG. 5.2A

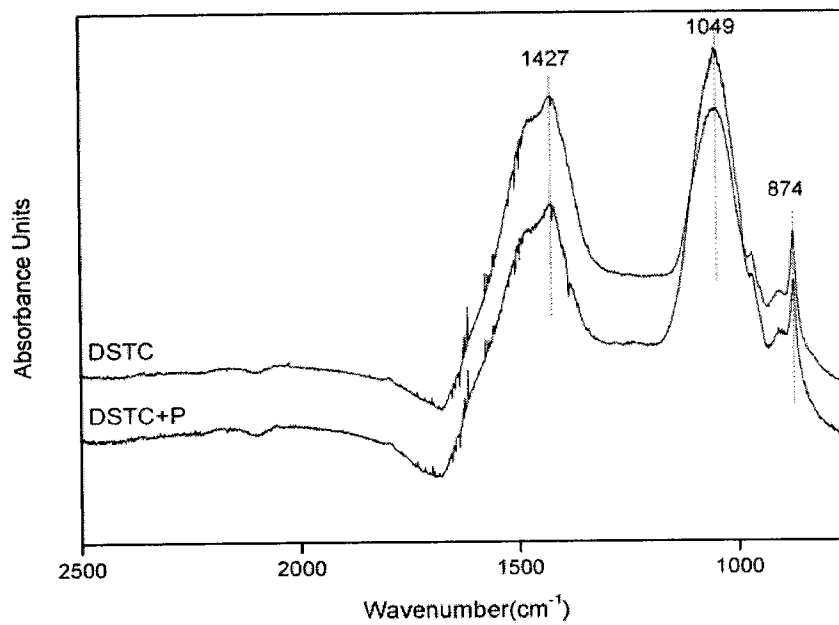


FIG. 5.2B

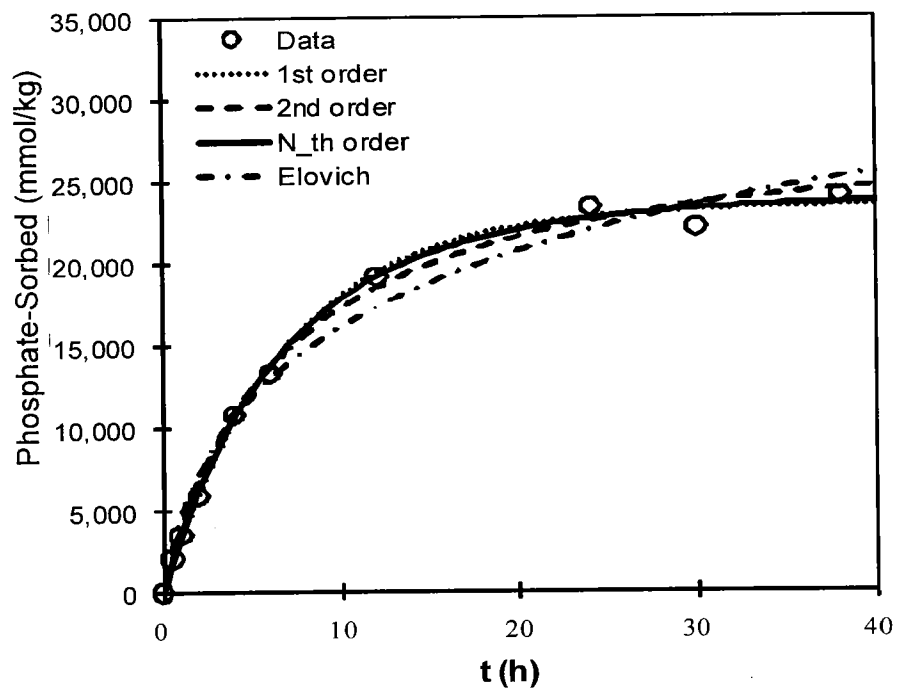


FIG. 5.3A

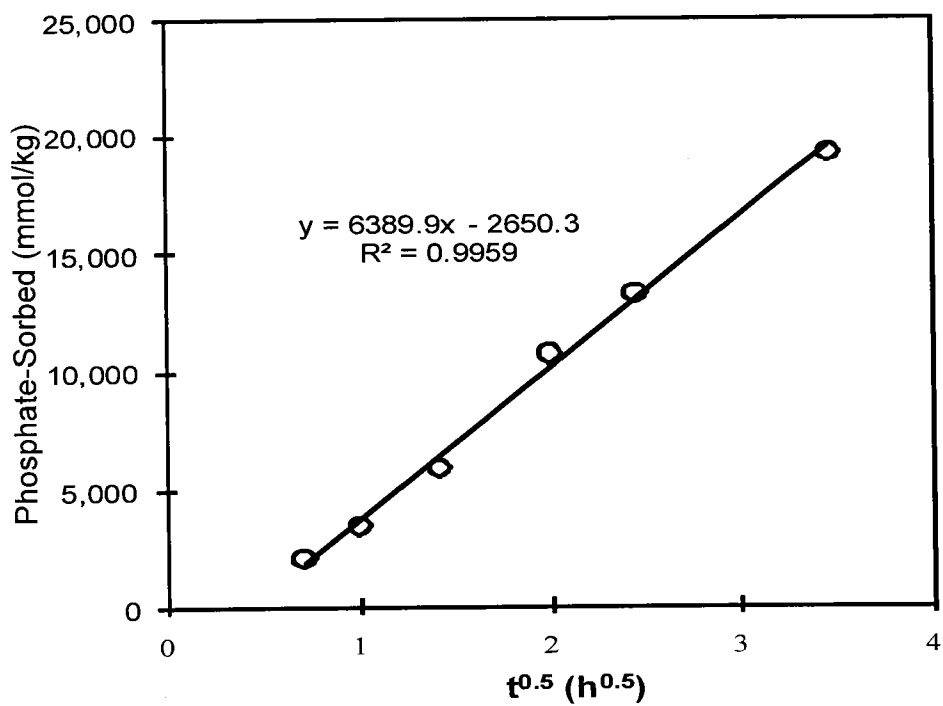


FIG. 5.3B

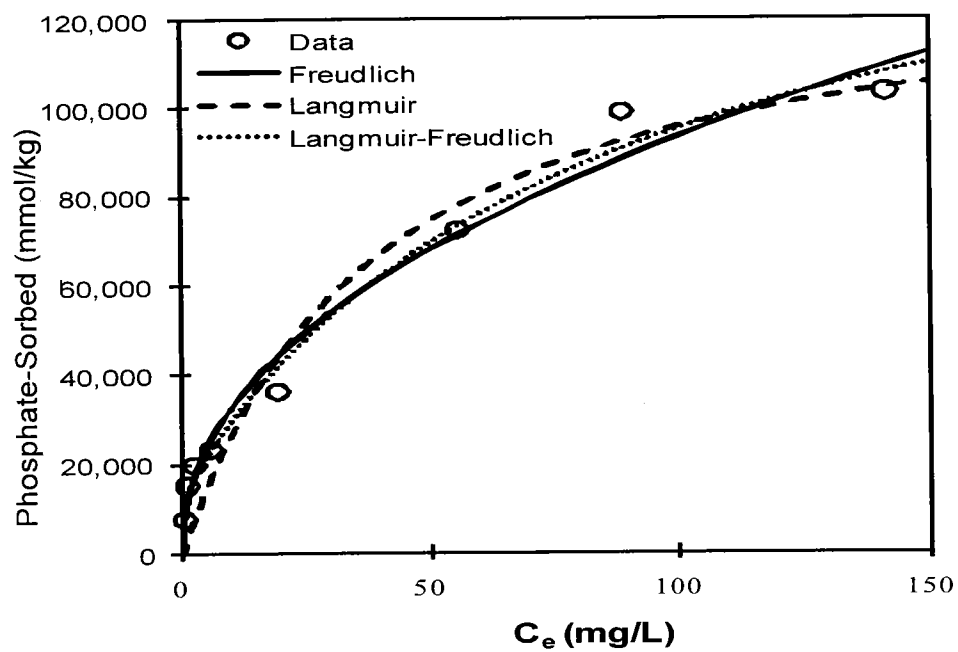


FIG. 5.4

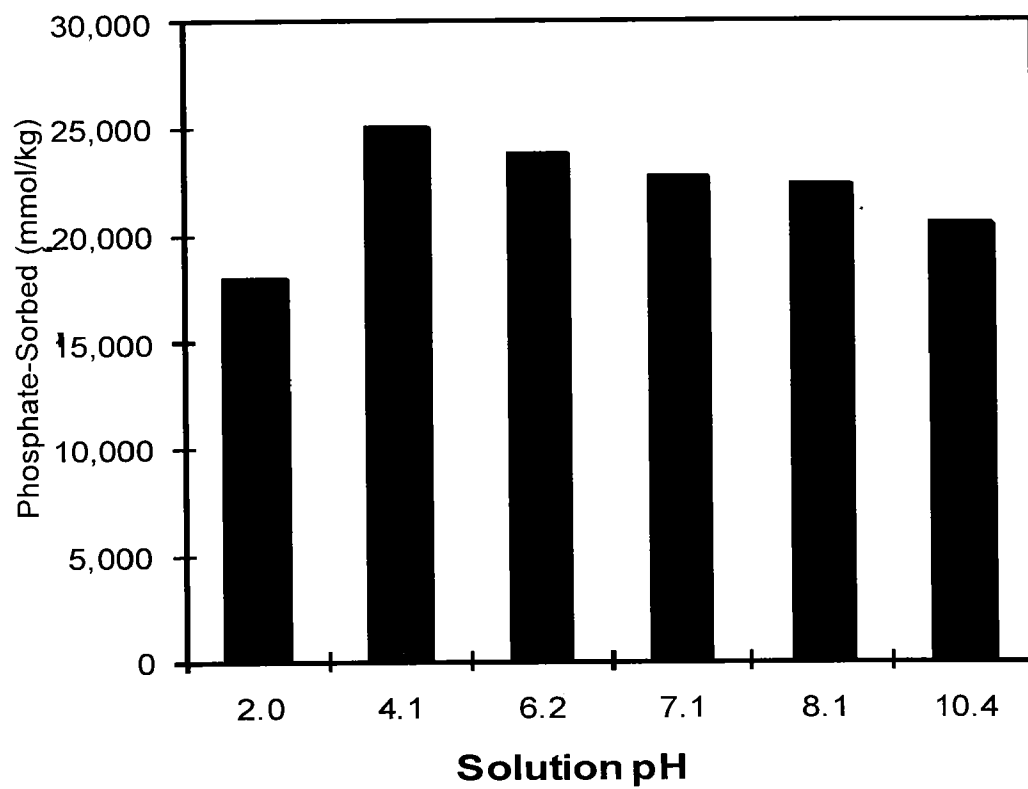


FIG. 5.5A

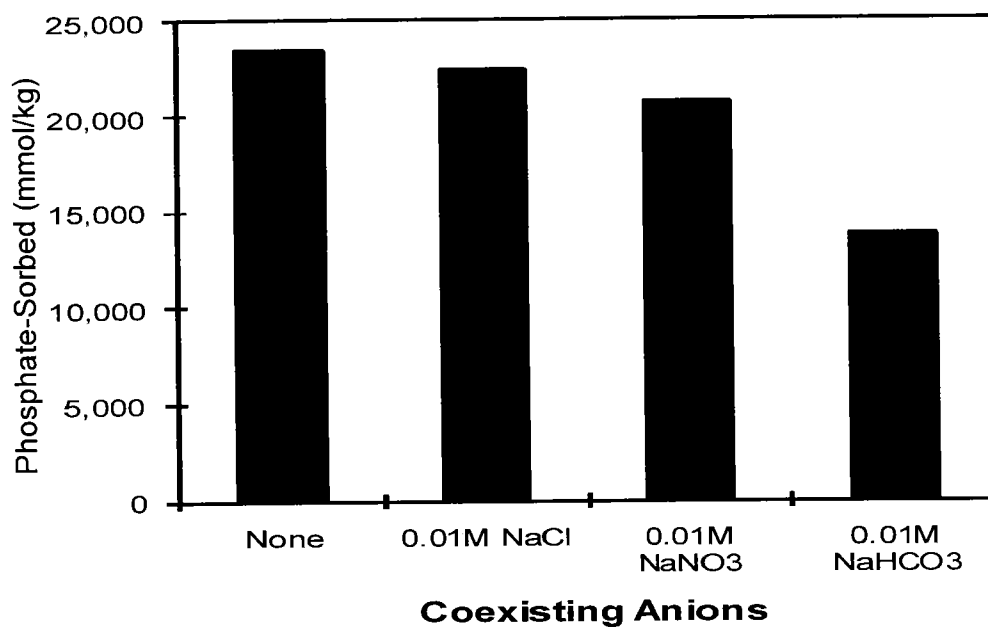


FIG. 5.5B