

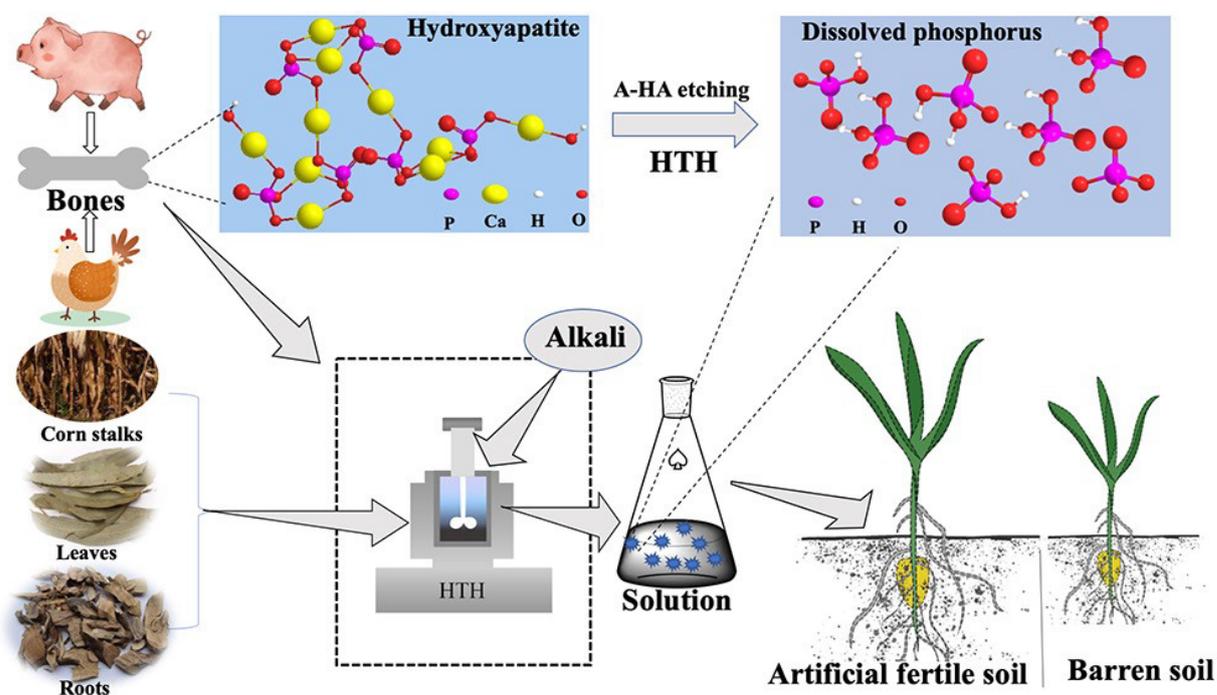


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Sustainable leaching process of phosphates from animal bones to alleviate the world phosphate crisis

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Pot-planting experiments show that the resulting liquids were applied as a fertilizer and led to a significant promotion of the growth of seedlings.

A sustainable leaching process of phosphates from animal bones to alleviate the world phosphate crisis

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ABSTRACT:

Lack of available phosphorus (P) minerals and their very localized regional distribution threatens world food production. Traditional farming methods that recycle various biological wastes and manure for localized fertilization of farmland are our role model, but come with risks such as hygiene, water toxification and passed-on diseases. Here, we present a bran-new hydrothermal process which turns animal bones of kitchen wastes into secondary P sources for fertilization, showing that this hydrothermal humification (HTH) process under 200 °C for 24 h completely disintegrates chemical structure of the biomass, while the simultaneously in-situ prepared artificial humic acid

(A-HA) etches even macroscopic bones. Notably, A-HA can solubilize the insoluble P existing in animal bones partly as directly dissolved phosphorus (DP), accounting for 6.36 % of total phosphorus (TP) in the bone wastes. Characterization methods indicate that oxygen-containing functional groups (i.e., -COOH and phenolic-OH) of A-HA can help to corrode bones, causing $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ to be decomposed into a large number of more active P minerals, furthermore, leading to high DP (96.79 mg/L) content and the formation of new P-based species. Pot planting experiments show that the resulting liquids were applied as a fertilizer and lead to a significant promotion of the growth of seedlings.

KEYWORDS: Animal bones; Artificial humic acid; Phosphorus recovery; Solubilization; Plant growth.

INTRODUCTION

Phosphorus (P) is one of the crucial elements in the biosphere, controlling life activities such as energy conversion and expression of genetic information¹⁻². Every year, China, the United States, Morocco, and other countries mine millions of tons of P from the ground, most of which is turned into fertilizer for food crops³. As the world's population continues to increase, the demand for P grows. However, phosphate deposits with low cadmium/uranium content have been consumed, the available deposits will not be able to meet the urgent needs of humanity⁴⁻⁵. Experts speculate that mineable deposits may disappear within a century^{3, 6}. Therefore, agricultural engineering must address problems such as low utilization rate of P fertilizer and excessive consumption

of P rock resources to promote world food security⁷.

On the other hand, P is not exactly a rare element and very abundant in soil, accounting for about 50 mg/kg to 1500 mg/kg of its total composition⁸⁻⁹. However, most of this P is tightly bound to multivalent metal species (i.e., aluminum or iron) to form insoluble phosphates, having low bioavailability in soil¹⁰⁻¹¹. Many studies have pointed out that soil contains abundant organic matters (i.e., humic acid) which contribute to phosphate dissolution and recalcination equilibria¹². Especially in black soils, the amount of highly active organic matter is significant, providing a comfortable growth and reproduction environment for plants¹³⁻¹⁴. Humic acid (HA) contains rich oxygen-containing acidic functional groups (i.e., phenolic-OH, -COOH, etc.)¹⁵⁻¹⁶, which can donate electrons to dissolve the stable multivalent metal phosphate in the soil under the action of photocatalysis or microorganisms¹⁷⁻¹⁸, improving solubility of otherwise insoluble P. Our previous work¹⁹ described a practicable route for solubilization of otherwise insoluble P minerals by application of artificial humic substances in detail. We found that the morpho-synthetic changes were not only due to the classical mechanisms of organic acid etching, but also related to the polymer nature of HA and involved redox processes, all driven by artificial humic substances.

According to the statistics of the Food and Agriculture Organization of the United Nations (FAO), in 2013, the world's total meat consumption was about 3024 million tons, with an annual increase of 2.4 %, with pork and poultry accounting for about 1/2 (<http://www.fao.org/faostat/en/#data>). With the large consumption of meat products,

bones are a hundred million tons waste products, which are usually burned or land filled as kitchen wastes²⁰, leading to potential environmental pollution. Worth noting, bones are made up from hydroxyapatite, a defined P mineral that can be considered as a circular P sources for sustainable P recovery. Currently, Someus and Postma et al²¹⁻²². developed a specific zero emission autothermal carbonization system for recovering phosphorus from animal bones. The solid product obtained is animal bone chars (ABC) concentrated with >30% phosphorus pentoxide (P_2O_5), making it an innovative fertilizer. Darwish et al²³. used acid leaching technology to recover P in waste fish bone ashes for removal of NH_4-N .

Kitchen wastes, in line with the principles of waste utilization, environmental protection and sustainable development, needs to be dealt with in a clean, low energy, highly efficiently engineering process, also excluding biological hazards. The primary intention of this research was to provide new ideas for contributing to the problem of closing the phosphate loop and an analysis on the utilization of such phosphate preparations in agriculture.

MATERIALS AND METHODS

Materials and Reagents

Chicken bones (CB) and pork bones (PB) were collected from the canteens of Northeast Agricultural University. Waste bones were repeatedly cleaned with deionized water to remove impurities, dried at 80 °C for 24 h, and then simply broken into small pieces in order to be able to place them in the reactor. Corn stalks (CS) were collected

on the campus of Northeast Agricultural University, and eucalyptus leaves (L) and tea roots (R) were purchased from Anhui Province, then CS, L, and R were washed with deionized water several times, dried, pulverized, and passed through a 100-mesh sieve to obtain biomass powders. The barren soil was collected in the long-term wasteland on the campus of Harbin Engineering University, air-dried, and removed impurities. Then the barren soil was passed through a 40-mesh sieve, stored for later experiments, and the methods of soil P were listed in Supporting Information. Alkali ash (AA) was collected from a factory in Hubei Province, and potassium hydroxide (KOH), calcium hydroxide ($\text{Ca}(\text{OH})_2$), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and perchloric acid (HClO_4) were purchased by Tianjin Chemical Reagent Co., Ltd., China. All reagents and chemicals were used as received without further purification. Deionized water ($18.8 \text{ M}\Omega \cdot \text{cm}^{-1}$) was used for all experiments.

PROCEDURES

Briefly, 2.4 g plant biomass (L and R) powder, 1.2 g bones (CB and PB) and the required amount of KOH solution were placed in a 100 mL Teflon-lined stainless-steel autoclave at 200 °C for different times (16 h, 24 h, and 48 h). Thereafter, the autoclave was cooled to room temperature, and solids and liquids of the product were obtained and stored separately for further testing and characterizations. In order to further reduce the cost and sustainability of the process, AA and $\text{Ca}(\text{OH})_2$ were used instead of KOH (according to the classical process of caustification) as follows: 2.4 g biomass (CS) powders, 1.2 g bones (CB and PB), and the required AA and $\text{Ca}(\text{OH})_2$ were placed in a

100 mL polytetrafluoroethylene-lined stainless-steel autoclave and then reacted at 200 °C for 48 h (explained below). Thereafter, the autoclave was cooled to room temperature, and solids and liquids of the product were obtained (pH=7~8) and stored separately for testing and characterization, wherein the liquid product was used for direct application to soil samples for pot experiments. All bones extraction P concentrations are shown as the average \pm standard deviation.

Small square plastic pots (caliber 7 cm) were used to perform pot experiments in a warm light gradient incubator (simulating the length of the day, the temperature and light intensity were 16 h, 25 °C, and 60 %, respectively. Simulating the length of night, temperature and light intensity are 8 h, 18 °C, and 0 % respectively). Corn as main food crops in the northeast of China was selected because of its fast growth rate, high germination rate, and highly sensitive plant's phosphorus deficiency²⁴. The experimental process was as follows: 200 g sieved barren soils mixed with or without liquid products obtained from HTH reaction (a certain amount of bones, different biomass, KOH or AA and demineralized water in 50 mL hydrothermal reactor) thoroughly to get artificial fertile soil for corn planting. Two corn seeds after being screened and aseptically treated were planted in each pot (setting up 3 parallel groups), and rhizosphere soil were taken at different time points to test soil available phosphorus (AP) (1, 3, 7, and 11 days) and harvested after 22 days. Fresh and dry plant weight were calculated by weighing, and the lengths of roots, stems, and plants were measured by a ruler.

Microstructure, composition, and physicochemical properties of bone-based samples were characterized by Scanning Electron Microscopy (SEM, ZEISS SUPRA40), X-ray Diffraction analysis (XRD, Rigaku TTR III using Cu K α radiation), Fourier Transform Infrared Spectrometry (FTIR, Thermo Fisher Scientific, USA), X-ray Photoelectron Spectroscopy (XPS, Thermo ESCALAB 250) and Elemental Analyzer (Flash Smart NCHS-O). Besides, Inductively Coupled Plasma-Atomic Emission Spectrometry analysis (ICP-AES) was used to detect DP and AP in soil and liquids and P contents in the calculated bone samples after digestion by HNO₃, HF and HClO₄ solutions.

RESULTS AND DISCUSSION

In previous work²⁵, we successfully synthesized artificial humic substances (A-HA and A-FA) having high similarity with natural extracts by a novel HTH technology. In this paper, it is shown that the low-solubility hydroxy-phosphate minerals (i.e., Ca₅(PO₄)₃(OH)) in animal bones are effectively etched and recrystallized to release DP and AP. Characterization of morphologic changes in bones before and after the HTH process are realized by advanced Scanning Electron Microscopy. Comparing Fig. 1a-f with Fig. S1 (supporting information), the surfaces of PB and CB before A-HA etching are smooth and textured, however, after being subjected to HTH treatment, the surfaces became rough, forming velvet-like morphologies. Very worth reporting, the bones become very brittle and could even manually be powdered to fine grains, i.e., the bones lost their complete mechanical cohesion.

In our previous publications^{19, 26-27}, it has been proposed and demonstrated that A-HA was rich in oxygen-containing acidic functional groups such as -COOH, phenolic-OH etc., which can provide a strong etching ability for solubilizing insoluble P. In order to describe the profound difference between diverse biomass species and the ability of their products for etching, originally FePO₄ with a perfect crystal surface were chosen as an example, and the images after HTH reaction with the introduction of different biomass are recapitulated in Fig. S2 (supporting information). As concluded in Table S1 (supporting information), the significant difference in structure is due to the different types and quantities of acidic oxygen-containing functional groups being present in A-HA.

A comparison of EDX patterns (Fig. S3, supporting information) reveals details of the etching mechanisms. In general, the anionic functional groups of A-HA (i.e., -COOH, phenolic-OH, etc.) compete with phosphate ions for the binding of Ca²⁺ ions²⁸, so that we can simultaneously observe bone dissolution A-HA and Ca²⁺ complexes, as well as recrystallization towards new species found as crystals on the surface of bones (Fig. 1). Under the same conditions, A-HA produced from different biomass etched the bones differently, leading to different Ca contents on the bone's surfaces. For instance, the amount of released DP from CB after R-AHA (A-HA from roots) etching is significantly larger than that resulted from L-AHA (A-HA from leaves) sample (96.79 ± 2.54 mg/L *versus* 24.24 ± 1.44 mg/L).

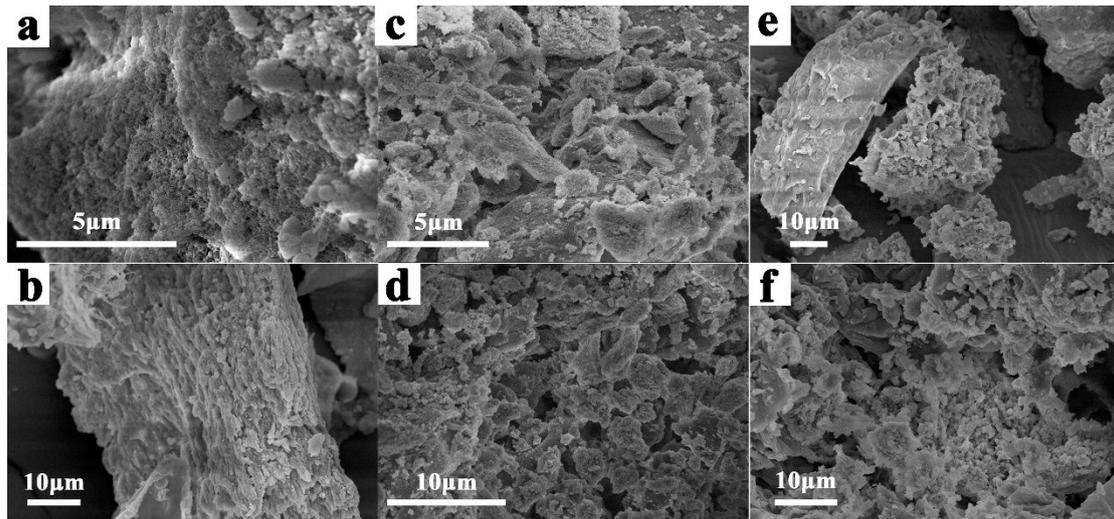


Fig. 1. SEM images of PB (a, c, e) and CB (b, d, f) etched with A-HA from roots, leaves and corn stalks, respectively.

To further analyze the process of A-HA decay and etching of animal bones, XRD analysis was applied to reveal details of a series of bone-based residues obtained at different conditions including bones (CB and PB), biomass (R, L, and CS), and reaction time (16 h, 24 h, and 48 h). We intend to describe the strong interaction between A-HA and animal bones and the dynamics of the structural rearrangements; the relative results are shown in Fig. 2. In the CB + L/R + KOH series, five strong diffraction peaks appeared on the etched bones: 25.88° , 31.77° , 39.81° , 46.71° , and 49.47° , corresponding to diverse planes of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ (0 0 2), (2 1 1), (3 1 0), (2 2 2), and (2 1 3) (JCPDS, No.09-0432)²⁹⁻³⁰, respectively. Three strong diffraction peaks at 29.55° , 31.82° , and 37.93° correspond to the crystal planes of CaCO_3 (2 2 0), (2 2 1), and (2 3 0) (JCPDS, No.17-0763)³¹, respectively. In addition, with the increase of reaction time, the peak intensity assigned to $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ existed in the bone gradually decreased, suggesting dissolution of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, which was attributed to the strong interaction

between A-HA and bones. The detection of a large amount of soluble P in the solution after the HTH reaction furthermore proved the conversion of insoluble P minerals into dissolved or amorphous P species, which will be reported later in this article. Notably, other new P species such as $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ can be found according to their strong diffraction peaks located at 25.88° , 31.94° , 32.90° , 46.79° and 49.50° (JCPDS, No. 18-0303). In addition, the application of alternative, more sustainable raw materials (CS, AA, and $\text{Ca}(\text{OH})_2$) as a strategy for etching bones also released a large amount of soluble P. This shows that etching bones with A-HA in general converts insoluble P in the bones into soluble P, and as such the P can be sustainably cycled, which has great significance and a wide applicability.

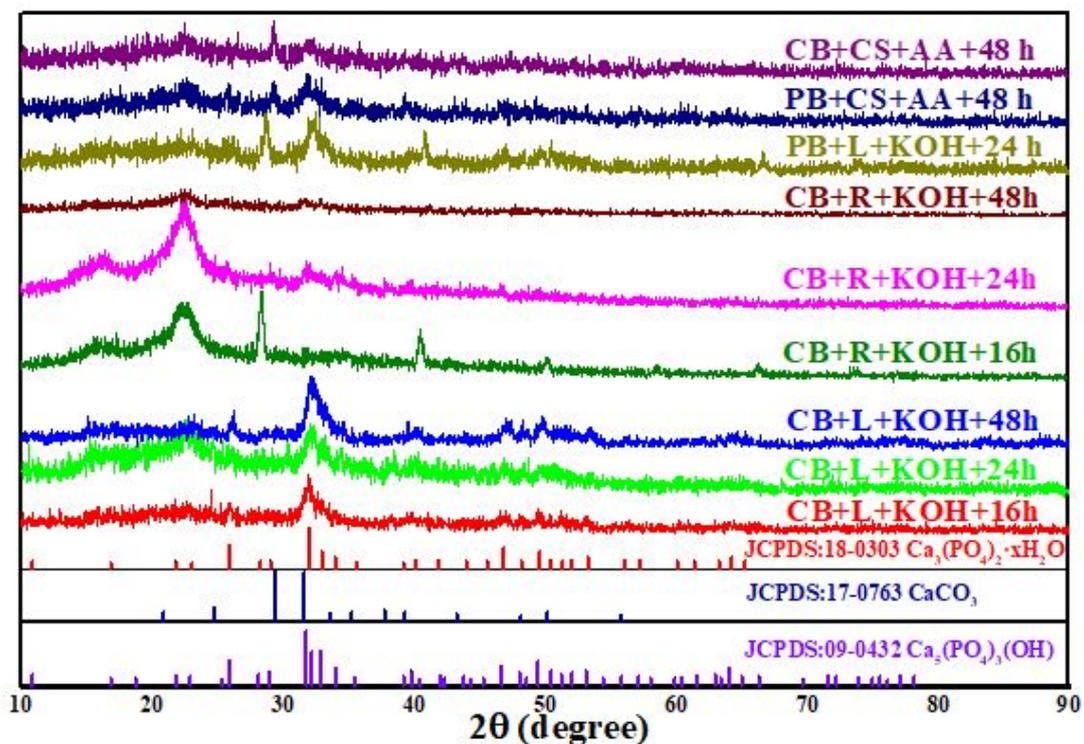


Fig. 2. XRD comparison of different bones (CB and PB) etched by A-HA from different biomass (leaves, roots, corn stalks)

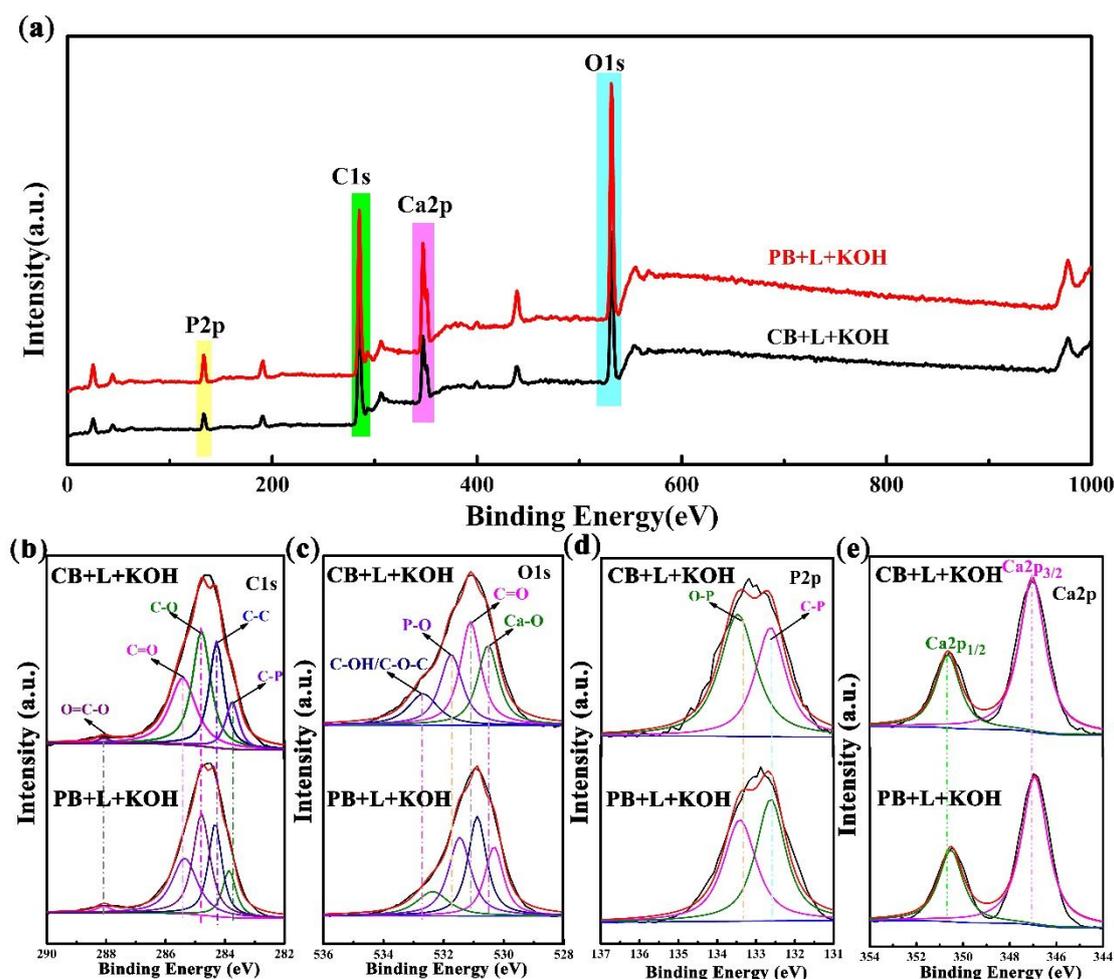


Fig. 3. Full spectrum (a) and high-resolution spectra of C1s (b), O1s (c), P2p (d), and Ca2p (e)

after chicken and pig bones were etched by A-HA from leaves.

XPS and FTIR data also confirm the existence of a strong chemical interaction between A-HA and bones, in which the dissolution of bones and the morphological transformation of phosphorus is driven by thermodynamics, sufficient reaction time between organic and inorganic phases assumed. As shown in Fig. 3a and Fig. S4 (supporting information), four main strong peaks with binding energies of 290.98 eV, 539.18 eV, 139.58 eV, and 356.18 eV are easily assigned to the C1s, O1s, P2p, and Ca2p orbitals, respectively, indicating that the main elements contained in the powders are C, O, P, and Ca. The proportion of each atom is listed in Table S2 (supporting

information). Fig. 3b presents the high-resolution fitting spectra of C1s of solid residues from bones etched by A-HA, and O-C=O (288.1 eV), C=O (285.4 eV), C-O (284.8 eV), C-C (284.3 eV), and C-P (283.7 eV) were deconvoluted into five peaks³²⁻³⁶. Obviously, a large number of oxygen-containing functional groups are found on the former bone surface (Table S3 in supporting information, 63.0 % for PB and 64.0 % for CB) (i.e., -C-O, C=O, and -COOH). The morphological changes may be caused by the large amount of A-HA etched into the bones, while the insoluble complex of A-HA and Ca²⁺ deposits on the bones surface. This is confirmed by Fig. S5 (supporting information): in the FTIR spectra of the original bones (CB and PB), a significant vibration of the -OH peak in Ca₅(PO₄)₃(OH) was found at 3565 cm⁻¹³⁷⁻³⁸, while this peak disappeared for the etched bones, indicating that the stable structure of Ca₅(PO₄)₃(OH) is destroyed by A-HA and reconstructed into new compounds. In addition, bones etched by A-HA have larger peaks corresponding to -C=O/ -COOH in 1613 cm⁻¹ than the original bones³⁹⁻⁴⁰. The raw bones samples have common peaks of P-O stretching at 589 cm⁻¹, which are significantly stronger than those of the A-HA etched ones³⁷, indicating that the anionic functional group in A-HA has a strong chemical interaction with the P-O in the bones. Combined with the results of XRD analysis, we can conclude that phosphate ions may have exchanged in the reaction with the anionic functional groups of A-HA. There are however still some Ca₅(PO₄)₃(OH) compounds left in the solid residues after HTH reaction, and other new phosphate species such as Ca₃(PO₄)₂ · xH₂O can be postulated from XPS and XRD analysis, indicating that as-liberated phosphate ions then

recrystallize on the surface with Ca^{2+} and other bone components to form new P minerals. This recrystallization-after-etching were already observed in the SEM images, and we also remember that the bones were converted into mechanically easy-to-break powder aggregates. In addition, elemental analysis of the raw and A-HA etched bones revealed that the percentage of C, H, and O elements in the etched bones was significantly higher than the corresponding values in raw bone (Table S4 in supporting information).

Further experiments were preformed to determine the content of P in bones (CB and PB), and the measurements after digesting the bones showed that the content of total phosphorus (TP) in chicken bone (17.0 mg/g in solution) and pork bone (15.4 mg/g in solution) (details shown in Supporting Information). This relatively high P content in the bones can be advantageously used for fertilizer production. As shown in Fig. 4, for the series of CB + L + KOH samples, the amount of etching soluble P gradually increases as the reaction time increases. Interestingly, the resultant bone residues gradually decreased as reaction time was prolonged (16-48 h), even completely digested. In general, protein after HTH reaction is not protein anymore (200 °C, 16-48 h). Protein firstly hydrolyses at 180 °C, then generates amino acides which will recombine with lignin to form humic acid or condense into heterocycles. The maximum values in these standard solutions are 24.24 ± 1.44 mg/L for DP, and 11.68 ± 0.84 mg/L for AP after 24 h. When compared to CB + R + KOH samples, the amount of soluble P resulted from the bones was the largest after 24 h. We find their considerable P

dissolution (DP, AP, and DP recovery rates were 96.79 ± 2.64 mg/L, 77.69 ± 0.10 mg/L, and 6.36 %, respectively). For PB + L + KOH samples, after 24 h, DP value in these standard solutions was 15.25 ± 0.92 mg/L and AP value was 7.96 ± 0.23 mg/L. Worth noting, amount of soluble P produced by PB + R + KOH samples was dominant (DP, AP, and DP recovery rates were 63.81 ± 5.78 mg/L, 42.05 ± 4.20 mg/L, and 4.77 %). The above results indicate that the A-HA derived from root has a stronger ability to etch bone than the A-HA derived from leaf. The DP recovery rates for all samples are listed in Table S5 (supporting information).

In order to expand experiments to a widely applicable plant biomass source, the former model biomasses (leaves and roots) and the alkaline additive (KOH) in the experiment were replaced by typical waste corn stalks (CS), available in huge amounts as waste about 300 million tons per year in China⁴¹, and combustion waste alkaline ash (AA) to realize a whole sustainable solid waste starting situation. Since the alkali produced by the action of AA and $\text{Ca}(\text{OH})_2$ is relatively weak, the hydrothermal reaction time was set to 48 h. Even under such real-life conditions, a large amount of P was dissolved (Chicken bone: DP is 15.25 ± 0.92 mg/L, AP is 6.85 ± 1.01 mg/L; Pork bone: DP is 18.08 ± 1.04 mg/L, AP is 2.86 ± 0.04 mg/L), implying that combustion ashes and chalk are suitable candidates to replace KOH.

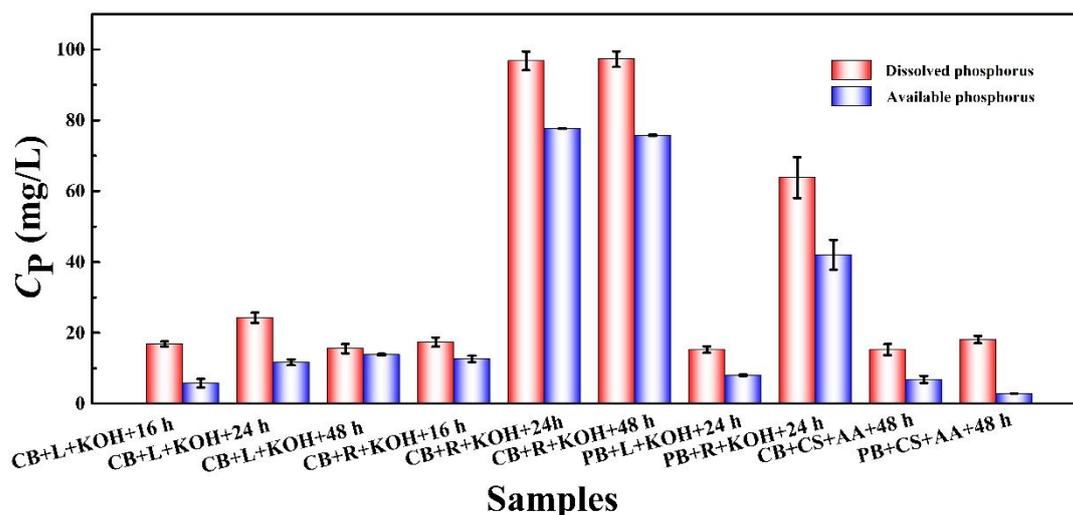


Fig. 4. Comparison of dissolved phosphorus and available phosphorus after different A-HA

(leaves, roots and corn stalks) etched different animal bones (CB and PB).

Release of DP and AP creates a new, sterile, non-unpleasant smelling system for fertilization which is derived from kitchen waste. To further study the effect of soluble P extracted from bones on soil fertility and plant growth, samples of CS + B (chicken and pig bones) + AA were chosen as examples for further pot experiments. The products were applied in planting experiments on barren soil collected from abandoned land. From previous studies we know that this standard barren soil has a TP content of 474.9 mg/kg (27.0 mg/kg for AP), which is less than that of natural fertile black soil, which is 900.0 mg/kg (180.0 mg/kg for AP)^{19, 42}. This may be due to soil P mineralization, less soil organic matter, and poor P cycles in the ecosystem⁴³. In pot experiments, adding bones P fertilizer containing a certain amount of AP to this soil significantly promotes the growth of seedlings. As shown in Fig. 5a, after 22-day cultivation, the corn seedlings were cultivated for a total of 22 days. After the corn seeds were planted, the growth status of the corn seedlings was photographed regularly

(intervals of 3, 8, 11, and 22 days), indicating that growth on bone-reinforced soil was significantly better than barren soil (control group). After 22 days, the corn seedlings were pulled out and the lengths of corn seedling roots, stems and plants, and their fresh and dry weights were measured (Fig. 5b-d). The results showed that the growth of corn biomass is significantly better on artificial fertile soil than those of the control group. The average height of seedlings grown on the two artificial fertile soils was 50.0 cm (pig bone) and 44.5 cm (chicken bone), which is much larger than the average height of the plants grown on control group (35.3 cm). In addition, the root length, fresh plant weight, and dry plant weight of plants grown on artificial fertile soils showed obvious improvements (Fig. 5b-d), quantifying that the restructured P extracts from bones have in these experiments a positive effect on plant growth. Artificial fertile soils contain considerable AP 40.0 mg/kg (CB extracted P modified soil) and 41.6 mg/kg (PB extracted P modified soil), which are much higher than the poor soil 27.0 mg/kg (control) and artificial fertile soils, continuously providing nutrients to plants (Fig. 5e). As shown in Fig. 5e, after 11 days of corn growth, AP content still remained at 29.2 mg/kg (CB extracted P modified soil) and 25.8 mg/kg (PB extracted P modified soil), i.e. there is a continuous P-transformation activated and ongoing.

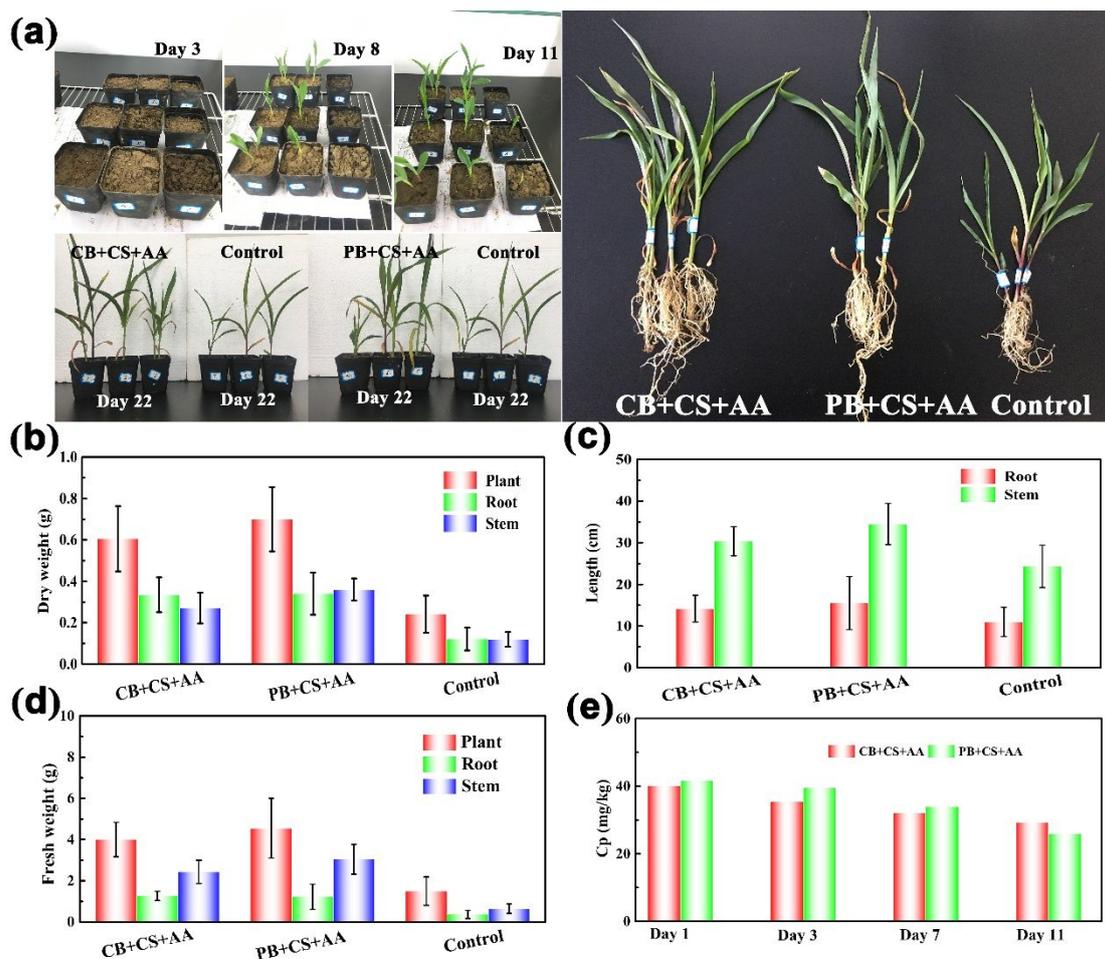


Fig. 5. Comparison of 22 days of seeding growth before and after modification of artificial fertile soil.

(including recording changes in AP (b) in artificial fertile soil for 11 day)

CONCLUSION

Ahead of the background that the world's phosphate mineral deposits become depleted in the near future, as well as there are large amounts of animal bones from food production and kitchen wastes treated unreasonably, we propose a feasible approach to transform the insoluble P present in animal bones via artificial humic acid (A-HA) treatment into a remineralized dispersion for plant cultivation. Various analytical techniques were applied to study the etching mechanisms of the bones by A-HA samples. We found that the morphological changes of bones and the amount of

phosphorus released are not only due to ion exchange with the anionic functional groups of A-HA, but also massively due to remineralization into new, more soluble calcium phosphate species, stabilized by A-HA.

In addition, the practicability of this “closing-the-phosphate-cycle” approach was confirmed by planting experiments. The introduction of the newly obtained digestible phosphate- and available phosphate in experiments analyzing the growth of corn seedlings gave significant promotion of plant growth. The average height of seedlings grown on the two reinforced soils were 50.0 cm and 44.5 cm, which was much larger than the average height of the seeding grown on control group (35.3 cm). Obviously, the proposed technique is not only simple and convenient, but also hygienic and chemically save, and may contribute to improved food safety in the future. The current data of course only set the base for more stringent farmland tests, which also may reveal some long term advantages of the added humic acid for farmland texture and agriculture.

SUPPORTING INFORMATION

Details of fabrication of A-HA and data analysis of soil and bone phosphorus; Images of original bones; Images of FePO_4 treated by HTH progress with the corresponding elemental mapping; Images of chicken bone etched with A-HA and the corresponding elemental mapping; Full spectrum and high-resolution XPS spectra of C1s, O1s and P2p of solid residues from bones etched by A-HA; FTIR spectra of bones and resultant residues etched by A-HA; Content of acidic functional groups of A-HA extracted from different biomasses; Atomic ratios of resultant residues from bones etched by A-HA;

Area ratios of each component in resultant residues from bones etched by A-HA; Elemental analysis of original bones and the corresponding solid residues after HTH progress; DP recovery rate of bones etched by different A-HA under different conditions.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

A-HA, artificial humic acid; A-FA, artificial fulvic acid; HTH, hydrothermal humification; DP, soluble phosphorus; TP, total phosphorus; AP, available phosphorus; CB, chicken bones; PB, pork bones; CS, corn stalks; L, eucalyptus leaves; R, tea roots; AA, alkali ash; R-HA, artificial humic acid from roots; L-HA, artificial humic acid

from leaves; W-HA, artificial humic acid from wood; CS-HA, artificial humic acid from corn straw;

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