

Bone Biochar as a Renewable and Efficient P Fertilizer: A Comparative Study

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ABSTRACT

A laboratory study was conducted to investigate phosphate solubility from bone biochar (BB) produced by pyrolysis at 650°C in comparison with its solubility from phosphate rock (PR). The PR and BB were characterized by X-ray diffraction (XRD) and total elemental analysis. Phosphorus was detected in distilled water and dilute sulfuric acid leachates resulted from columns filled by BB or PR for 30 days. Fractions of water soluble-P (WSP), Olsen-P (OP), formic acid-P (FAP) and citric acid-P (CAP) extracted from BB and PR were determined before and after leaching. Results showed that all P fractions extracted from raw BB were higher than those from PR and the extracted concentrations had the order: FAP > CAP > OP > WSP from both sources. Leaching experiments showed that P dissolution by water or sulfuric acid from BB was greater than from PR. The released amounts of P from BB by this acid and water represented 50.0% and 0.85% of total P₂O₅, respectively, while those released from PR represented 29.79 and 0.017% of total P₂O₅, respectively. These Results reflected the majority of pH influence on dissolution process. Residual amounts of P extracted by CA and FA from BB were higher than those extracted from PR after acid leaching and vice versa after water leaching. Olsen-P fraction increased after acid leaching of PR which reflects improvement bioavailability of P after PR acidification. The obtained results may give BB advance over PR as a fast to medium release-P and sustainable source for P fertilizers.

Key words: Bone biochar, phosphate rock, phosphorus solubility, P availability, P-fertilizers.

INTRODUCTION

Phosphorus is considered as one of the major essential nutrients for higher plants and must be applied to soils frequently. Inorganic phosphate is considered as one of the intensive energy consumption industry and depends on the availability of phosphate rock (PR) which currently becomes scarce and depleted in some regions in the world (IFDC, 2010 and USGS, 2010). Besides, intensive application rates of P fertilizers lead to accumulate some heavy metals such as cadmium (Cd) and chromium (Cr) in agricultural soils and may cause some risks in food chain and ground water. For its moderate solubility under acidic conditions, earlier studies showed that PR used as a direct P fertilizer in acid soil but it cannot maintain a sufficiently high phosphorus concentration in the soil solution for high yields of crops with a high initial P demand (Khasawneh and Doll, 1978; Chien and Hammond, 1978a and b). In calcareous soils, PR usually inert and cannot supply adequate rates of P. Several attempts were used to enhance the PR-P solubilization efficiency including using the acidifier microbes (Bianco and Defez, 2010; Vassilev et al., 2013; Sharma et al., 2013; Mendes

et al., 2014), organic acids such as oxalic and citric acids, organic manure, elemental sulfur (Al-Oud, 2011) or plants (Flach et al., 1987; Hinsinger, 2001; Hinsinger et al., 2003; Rengel and Marschner, 2005), but it still less efficient than common inorganic chemical P fertilizers.

Looking for unusual alternatives of P, for using as fertilizer to various kinds of soils, becomes necessary. The recovery of P from wastes is considered one of the recent technologies used to compensate the depleted P resources, and P recovery from wastewater has received great attention (Qiu and Teng, 2014). Phosphorus-containing waste streams can range from mixed wastewater, to separate organic waste fractions, including human urine and faeces, grey water, animal manure, animal carcasses, detergents, industrial and food wastes and crop residues. Animal manure (and other animal parts such as bones and blood) is widely used as a source of phosphorus fertilizer in many regions of the world (Cordell et al., 2011).

In last decade, bone biochar had some attention as a soil amendment for immobilizing heavy metals (Siebers and Leinweber, 2013; Siebers et al., 2013; Rétháti et al., 2014) and as efficient sorbent for

removing contaminants from wastewater (Passman et al., 2014). Bone biochar contains considerable percentage of P and Ca to qualify it as a renewable source of P and can fill the phosphorus fertilizer gap in developing countries (Simons et al., 2014). There are few studies, which covered its solubility and the conditions required to enhance its efficiency as P fertilizer (Warren et al., 2009; Ma and Matsunaka, 2013; Weber et al., 2014). Therefore, the objective of this work was focused on the comparison of P release from BB and PR when these materials are subjected to dissolution by water or acidified water. The comparison between the deferent fractions representing available P in BB and PR was also studied.

MATERIALS AND METHODS

Cattle bone was collected from local market at Alexandria city, rinsed several times by tap and distilled water and oven dried at 105°C for 24 hours. The well dried bone was crushed into pieces of 3.0 - 5.0 cm and prepared for pyrolysis. Known weight of oven-dried bone was sealed by aluminum foil and inserted into muffle furnace (modified to facilitate nitrogen gas to fill the heating room during the pyrolysis). The bone samples were heated at temperature increments of 25 °C/min till reaching to 650 °C. The residence time at this degree was 2 hours. The resulted fumes and gases were ventilated from the upper hole of the muffle furnace. After cooling, the weights of bone biochar (BB) samples were measured and the lose in weight was recorded. The BB was crushed in porcelain mill, passed through 0.5-mm polypropylene sieve and stored in plastic bottles.

Sample of phosphate rock (PR) was purchased from El-Nasr Mining Company, Aswan, Egypt. PR was crushed by hand in porcelain mill, passed through 0.5-mm polypropylene sieve and stored in plastic bottles.

X-ray diffraction of PR and BB

The technique of x-ray diffraction (XRD) has been used to characterize the crystalline structure of mined rock phosphate (Bilali et al., 2005; Lefires et al. 2014) and mineralized bone tissues (Germine and Parsons, 1988; Bigi et al., 1997; Meneghini et al. 2003). The PR and BB used for XRD analysis were thoroughly ground and passed through 90-micron sieve. X-ray diffraction data were measured using Philips Diffractometer using the CuK α radiation produced at 32 kV and 20 mA by a Philips PW 1830/40 X-ray tube.

Elemental Analysis of BB and PR

Total elemental analysis of BB and PR was carried out by fusion method (Pansu and Gautheyrou, 2003), where 1.0 g sample was transferred into platinum crucibles and mixed thoroughly with 5.0 g sodium carbonate. The samples were heated gradually on a direct flame of

Bunsen Burner with gently mixing of the contents. The heating was continued until the formation of homogeneous cake. After cooling, the crucible contents were dissolved with about 30.0 mL 5.0 M HNO₃ and transferred to 250 mL Pyrex beaker and boiled until complete dissolution. The clear solution was transferred to 250 mL Pyrex volumetric flasks and volume completed with distilled water. Total phosphorus in the solutions of BB and PR was determined spectrometry using vanado-molybdate yellow method (Chapmann and Pratt, 1961). The concentrations of Ca and heavy metals (Cd, Pb, Ni, Cu, Fe, Mn and Cr) were measured by Inductively Coupled Plazma ICP-OES Spectrometer (Thermo iCAP 6000 Series, UK).

Phosphate Fractions in BB and PR

Water soluble P (WS-P): One gram of BB or PR was transferred into 250-mL conical flasks then 50 mL distilled water was added and the flask was shaken on a horizontal shaker (G24 Environmental Incubator Shaker, New Brunswick Scientific Co. USA) for one hour. The suspension was filtered using filter paper Whatman No. 42 and P concentration was determined in the supernatants. Phosphorus was determinate by the ascorbic acid-molybdate blue method (Murphy and Riely, 1962) at wavelength 882 nm using UV/VIS double beam JENWAY spectrophotometer model 6850 .

Olsen P fraction: According to Murphy, J., Riley, J.P., 1962, 2.0g sample of BB or PR was Shacked for 30 minutes with 40.0 mL 0.5 mol L⁻¹ sodium bicarbonate (NaHCO₃) solution adjusted to pH 8.5 with 0.01 mol L⁻¹ NaOH or 0.01 mol L⁻¹ HCl solutions using pH-meter (WTW inLab pH/Ion 735, Germany). Suspensions were filtered through filter paper Whatmann No. 42 filter paper and P was measured colorimetrically (Watanabe and Olsen, 1965) in supernatants.

Formic acid-P fraction (FA-P): A 0.4g sample of BB or PR was extracted with 40 mL 2% formic acid at 23 °C for 1 hour (Hoffman and Mager 1953). The samples were then centrifuged at 10,000 rpm for 5 min, filtered (0.45 μ m Millipore filter). The concentration of P in the solution was determined in the filtrate by the vanado-molybdate yellow method at wavelength 445 nm (Chapmann and Pratt (1961).

Citric acid-P fraction (CA-P): A 0.4g sample of BB or PR was extracted with 40 mL 2% citric acid at 23 °C for 1 hour. The samples were then centrifuged at 10,000 rpm for 5 min, filtered (0.45 μ m Millipore filter), and the residue was extracted again with 40 mL of 2% fresh citric acid. The concentration of P in the solution was determined in individual filtrates, following dilution, by the vanado-molybdate yellow method at wavelength 445 nm (Chapmann and Pratt (1961)

Column Leaching Experiment

One hundred grams of BB or PR was packed in Pyrex glass column (2.0-cm in diameter and 14.0-

cm in height). Glass wool was used to fill the bottom and end of the 2 cm distance columns to maintain and facilitate a continuous flow of leaching solutions. The column was initially flushed with distilled water for 2 h and the volume of flushed water was added to the first-day sample. The column was splitted into two divisions; one was leached by distilled water and the other was leached by 0.01M H₂SO₄. A peristaltic pump (ISMATEC ISM 931, Switzerland) was used at the influent (bottom) of the column to maintain a constant upward flow rate in the column (0.25 mL min⁻¹). Leachates were collected and analyzed daily for pH and P for 30 days. The pH was measured using pH meter WTW inLab pH/Ion 735, Germany. After leaching experiment, the column was evacuated and its contents from BB or PR were oven-dried at 105 °C for 24 hours. Then, the oven-dried BB and PR were crushed and sieved using 0.5-cm polypropylene sieve. The various fractions WSP, OP, FAP and CAP, were determined in BB and PR similarly as mentioned above. Concentration of phosphorus was measured colorimetric using blue method (Murphy and Riley, 1962) or yellow method (Chapmann and Pratt, 1961) depending on the concentration ranges of P as mentioned above.

The data obtained were statistically analyzed by the program of Costat software (Costat, 1985).

RESULTS AND DISCUSSION.

X-ray diffraction of PR and BB

Figure 1 displays the XRD patterns of the PR and BB samples. The Two diffraction patterns display evident similarities and point out the analogy between the structures of PR-apatite and BB-apatite mineral. On the other hand, the obtained diffractograms of PR and BB were similar to those

found for Gafsa (Lefires et al., 2014) and Moroccan (Bilali et al., 2005) phosphate rocks.

Elemental analysis and Fractions of P in BB and PR

The elemental analysis of BB and PR, showed that total content of P₂O₅ (36.068 and 33.205%, respectively) and CaO (38.08 and 35.24%, respectively) for both materials virtually similar (Table 1). Gafsa rock phosphate contains about 28.6% P₂O₅ (Warren et al., 2009) while Moroccan contains 31.51% P₂O₅ and 50.19% CaO (Bilali et al., 2005).

Concentration of heavy metals occurred in BB and PR revealed that chromium (Cr) in PR (91.0 mg kg⁻¹) exceeds about 14 times more than that of BB contains (6.5 mg kg⁻¹). Knox et al. (2006) found close results for total Cr content in mined (111.4 mg kg⁻¹) and processed (101.4 mg kg⁻¹) PR samples collected from various regions of USA while they found only 4.6 mg Cr kg⁻¹ in ground fish bones. Copper was not detected in BB while occurred in PR (7.75 mg kg⁻¹). The current concentrations of heavy metals (Cd, Cr, Pb, Cu, Fe, Mn and Ni) in PR are relatively close to those mentioned for Middle East-PR and published by Mortvedt and Beaton (1995).

Total carbonate contents in PR and BB were 10.45 and 6.21%, respectively. These values support the idea that calcium phosphate in both materials possibly occurred in the form of carbonate apatite as a main component. Calcination of PR (for temperatures higher than 600 °C) helps in reducing its carbonate content by decomposition of calcite and formation of CaO (Bilali et al., 2005). These results may speculate the low content of total carbonate and high content of CaO in BB than in those recorded in PR.

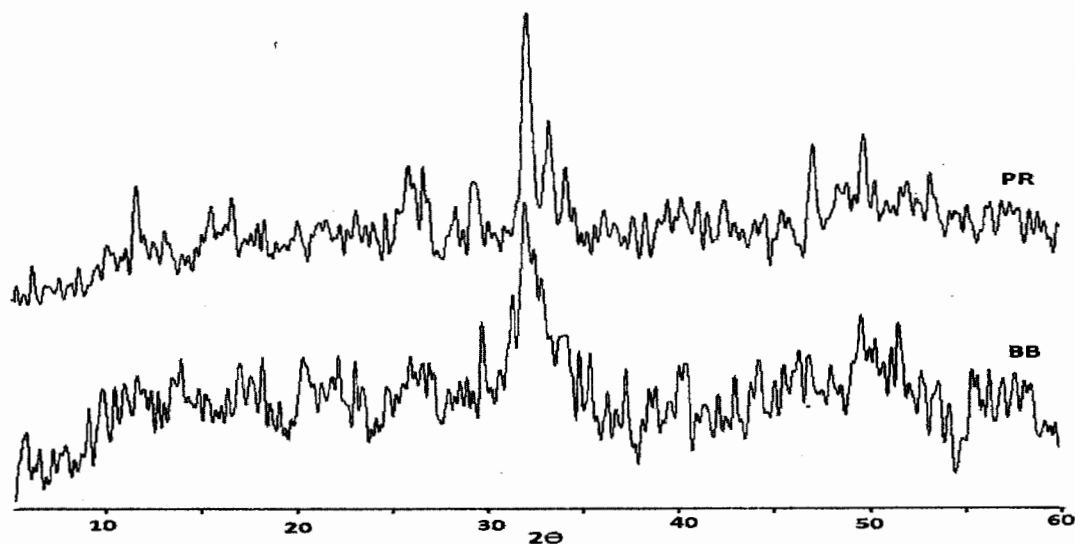


Figure1: XRD patterns of phosphate rock (PR) compared to bone biochar (BB).

Table 1: Elemental analysis and P fractions of bone biochar (BB) and phosphate rock (PR).

Measured parameters	BB	PR
Total content		
P ₂ O ₅ (%)	36.068	33.205
CaO (%)	38.080	35.240
Ca/P ratio	1.727	1.736
C (%)	5.860	0.280
N (%)	1.950	0.180
Total carbonate, %	6.210	10.450
Heavy metals (mg kg⁻¹)		
Cd	2.500	7.200
Cr	6.500	91.000
Pb	nd*	nd
Cu	nd	7.750
Fe	17.000	12.500
Mn	8.000	13.000
Ni	nd	nd
P fractions (mg g⁻¹)		
WS- P ₂ O ₅	0.435	0.050
Olsen- P ₂ O ₅	3.435	0.122
FA- P ₂ O ₅	312.951	170.376
CA- P ₂ O ₅	139.301	105.340
P fractions as % of total P		
WS- P ₂ O ₅	0.120	0.015
Olsen- P ₂ O ₅	0.952	0.037
FA- P ₂ O ₅	86.767	51.310
CA- P ₂ O ₅	38.622	31.724

* nd: not detected

Fractions of P in BB and PR

The concentrations of the tested P fractions in BB and PR indicate that released P from BB was higher than that from PR (Table 1) for all extractable forms. For example; 435.0 and 3435 mg P₂O₅ kg⁻¹ of WS- and Olsen-P were released from BB compared with 50.0 and 122.0 mg P₂O₅ kg⁻¹ from PR, respectively (Table 1). Olsen-P fraction released from BB represented 28.16 times of that obtained from PR (Table 1) and this reflects higher availability of P for plants from BB compared with PR. It is obvious that Olsen-P fraction represent the immediately available soil-P to plants grown in a wide spectrum of soil types particularly basic and calcareous soils, therefore, the high amount of Olsen-P in BB promotes its usage as P fertilizer as a sustainable manner. Warren et al. (2009) found close results of water extractable and Olsen-P in a comparative study on P dissolution from animal bone biochar and Gafsa (Tunisia) phosphate rock. On the other hand, Formic acid-extractable P₂O₅ (FA-P) represented 86.8 and 51.3% of the total P content in BB and PR, respectively, whereas the corresponded values resulted from the extracts of 2% citric acid (CA-P) were 38.6 and 31.7% (Table 1). In a study carried out by Rajan et al. (1992) on the dissolution of P from 11 samples of PR collected from different regions of the world, showed that

fractions of 2% FA-P and 2% CA-P ranged from 22 to 71% and from 21 to 46% of total P, respectively. Since the formic acid and citric acid extractants mainly used for estimation of available P in fertilizer products (Syers et al. 1986; Braithwaite et al., 1989), the current results of extracted P by mentioned acids from BB and PR confirm higher P availability from BB from PR.

Leaching Experiment

Since pH is the most important soil factor in PR dissolution (Peaslee et al., 1962; Khasawneh and Doll, 1978) and sulfuric acid is the dissolution agent in orthophosphoric acid and superphosphate industry (Schrödter et al., 2011), we simulated P solubilization through the leaching by dilute sulfuric acid (0.01 mol L⁻¹) in comparison with distilled water at a constant flow rate to examine and compare the release of soluble P from both BB and PR. The results of cumulative P dissolution by water and acid showed great releasing of P from BB than from PR (Fig. 2) throughout the days of leaching. Within the first 5 days of cumulative P dissolution by water, there was a sharp increase in P released from BB (from 0.856 to 2.418 mg P₂O₅ g⁻¹ BB). Then the dissolution rate declined (2.466 – 3.053 mg P₂O₅ g⁻¹ BB) whereas the corresponding dissolution from PR was not significant along with 30 days of leaching (from 0.005 to 0.055 mg P₂O₅ g⁻¹

¹ PR). The ratio of BB: PR of water soluble P was very high (from 55 to 187). Thus, it reflected a great efficiency of BB as a source of easier available P. It was found that the ratio of water-soluble Bone char:Gafsa PR was 5.8 (Warren et al., 2009). These differences may be related to pyrolysis conditions (temperature and residence time). Leaching of BB and PR by dilute acid showed high dissolution rates than those observed by water (Fig. 2). However, the

behavior of P dissolution by acid differed between BB and PR. In BB, a slight augmentation in P dissolution was observed within the first five days then increased and became nearly linear until the end of experiment (Fig. 2). For PR, the low dissolution rate extended to the first 12 days then increased where the linear P dissolution appeared. The amounts of acid-extracted BB-P exceeded that of PR-P by about two folds.

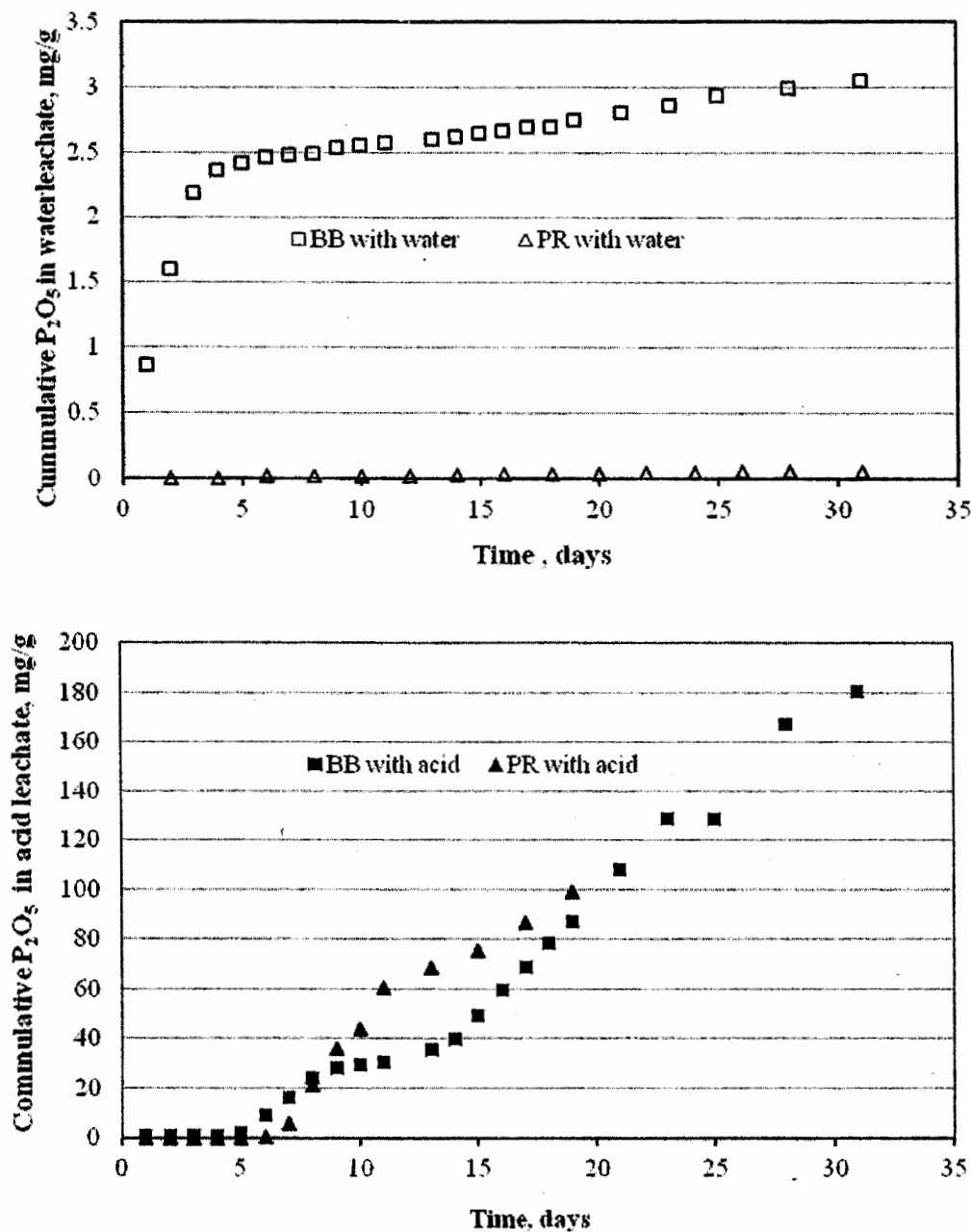


Figure 2: Concentrations of cumulative P₂O₅ in column leachates as a function of dissolution by water or by dilute acid (0.01M H₂SO₄) from bone biochar (BB) and phosphate rock (PR).

The amounts of P released from BB by dilute acid and water represented 50.0% and 0.85% of total P_2O_5 , respectively, while those released from PR represented 29.79 and 0.017% of total P_2O_5 . These results revealed the importance of acidification or acidified amendments combination with applied BB or PR to assure continuous release of P. Figure (2) pointed out that the ratio of cumulative P by dilute acid to cumulative P by water was to 94 for BB and 1730 for PR.

The released amounts of P by water or acid are related to pH effects of leachates. Figure (3) demonstrates the pH changes of water and acid leachates of BB and PR-filled columns. The pH of water leachate of BB markedly decreased during the first 8 days of leaching (from 9.28 to 7.53) then there was no noticeably changed until the end of experiment. The pH values of corresponding water-PR slightly increased (about 0.6 unit) during the first 16 days (7.5 – 8.1) then did not markedly changed. The correlation coefficient (r) values between dissolved P by water and pH were 0.95 ($n=23$) and 0.28 ($n=15$) for BB and PR, respectively. These relationships could reflect the

importance of water-soluble fraction of BB-P rather than of PR-P when both applied as a direct source of P fertilizer. In other words, these results may be explained by the occurrence of phosphate compounds that are more soluble than those consisting in PR. Bone and bone char which characterized by ^{31}P solid state NMR spectroscopy confirmed occurrence of phosphate compounds beside hydroxyl-apatite such as, brushite-like structure ($CaHPO_4 \cdot 2H_2O$) and phosphor protein (Wu et al., 2003). Subjecting bone materials to pyrolysis decreasing protein phosphoryl content and also a probably destruction of protein phosphoryl Compounds (Novotny et al., 2012). These facts may cause an increase in concentration of water soluble P released from BB.

Variation in BB- and PR-P dissolution by dilute sulfuric acid (Fig. 3) might be partially due to the concentration of proton (H^+) required by each material to start in P dissolution, and total calcium carbonate content accompanied each material (6.21 and 10.45% in BB and PR respectively, Table 1) which will play a significant consumer for protons.

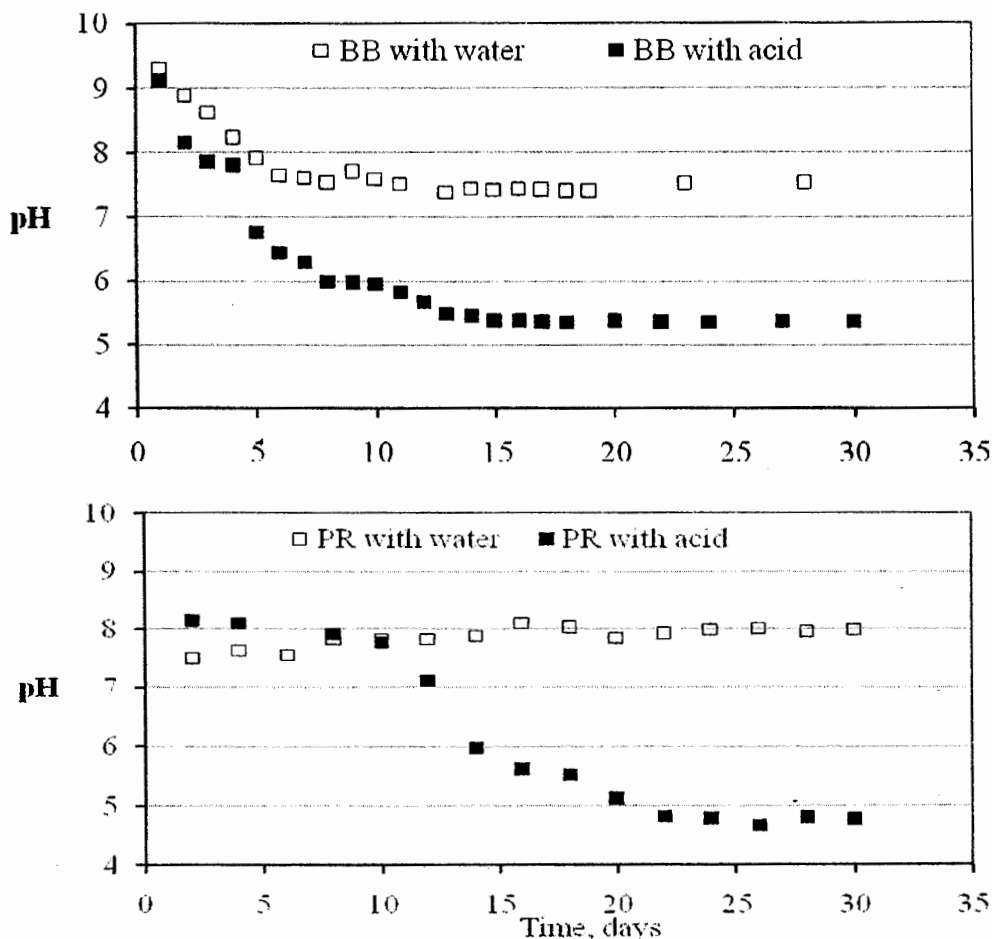


Figure 3: pH values accompanied of P dissolution from bone biochar (BB) and phosphate rock (PR) by fixing flow rate of water or acid throughout 30 day of column leaching experiment.

In the bigening of dissolution reaction, carbonates will initially consume the H^+ ions before the phosphates dissolution, consequently and therefore, PR delayed (12 days) than BB (5 days) in releasing of P. Mowo et al. (2014) explained the variation in P dissolution rate from PR samples collected from various regions according to factors such as calcium carbonate content and availability of enough protons. The kind and structure of phosphate compounds occurred with hydroxy apatite can also a cause of this variation between BB and PR. One of the important factors affecting P solubility of BB is the thermochemical conditions (temperature of pyrolysis and residence time) since Novotny et al. (2012) concluded that swine bones, pyrolyzed under different conditions, can show a great diversity of solubility properties, which is an important characteristic for phosphate fertilizers.

Residual P Fractions after leaching

The amounts of residual P fractions after leaching of BB and PR with water or diluted acid were detected in the forms of OP, FAP and CAP (Table 2). It is obvious that the variation in the used extraction solutions (FA, CA and Olsen) is dependent on extraction of certain forms of P associated with available P in phosphate-bearing materials (such as PR and BB). This reflects the agronomic effectiveness of these materials and which is related to some criteria such as soil types (regions) and its physic-chemical properties (Rajan et al., 1992; Wang et al., 2012). The residual amounts of P extracted by FA and CA from PR leached by acid were less than the leached by water and vice versa with respect to BB. The residual amounts of P extracted by CA was significantly higher than those extracted by FA from BB and PR columns that leached by water while it was lower than those extracted by FA only from BB. Residual amounts of Olsen-P extracted from BB were higher than those extracted from PR in both leaching processes (Table 2). A comparison between the amounts of various P fractions (WSP, OP, FAP and CAP) before and after leaching by water or dilute acid, expressed as percent of total P_2O_5 content, are illustrated in Fig. (4). The amounts of WSP and OP fractions represented the mild part in the two tested P materials but it is worthy to consider its residual

amounts extracted from BB during and after the leaching processes as significant parts of total P. Before leaching, P extracted by formic acid (FAP) represented about 86 and 51% of total P in BB and PR, respectively. After leaching, FAP decreased to 8.9 and 18.9% of total P from BB after leaching by water and acid, respectively, while it decreased to 11.9 and 8.9% of total P from PR (Fig. 4). Since the formic acid extractable P represents the major chemical reactive fraction of PR-P it shows high values of agronomic effectiveness of PR (Mackay et al., 1984; Rajan et al., 1996). Thus, in the current study, it reflects an advantage of BB over PR as a slow release P resource. One of the important observation is the high values of OP fraction extracted from BB (Fig. 4) comparing with those from PR. Before leaching, OP represented about 0.95% of total P and declined to 0.52 and 0.34% after 30 days of leaching by water and acid, respectively. Non-noteworthy amounts of OP were resulted from PR before or after leaching. It was observed that leaching of PR by dilute acid increased the concentration of OP (0.07% of total P) than its concentration before leaching (0.037%). This result revealed that acidification of PR with acid increased the bioavailability of PR-P.

CONCLUSION

The results of XRD for PR and BB exhibited matching between the structures of PR-apatite and BB-apatite minerals. The used bone biochar, as a renewable source of P, was characterized by low concentrations in heavy metals such as Cr, Cd and Cu than PR and showed a high and fast releasing for water soluble P along with the 30 days of leaching by water or by diluted acid. The ratio of BB-P: PR-P released by water reached to 50 whereas it reached 1.68 for P released by acid. The acid: water ratio of cumulative released BB-P and PR-P represented 94 and 1750, respectively, which indicated to the importance of pH as a major factor for P dissolution from its resources. The higher values of various P fractions extracted from BB than those obtained from PR characterize its high reactivity and availability as well as this give more prospects for using bone biochar (BB) as efficient and sustainable P fertilizer.

Table 2: Concentration of P fractions from bone biochar (BB) and phosphate rock (PR) after leaching by water or diluted acid.

P fraction	BB		PR	
	mg P_2O_5 g ⁻¹ Raw material			
	Leached by water		Leached by acid	
Water-soluble P (WSP)	0.124	0.007	0.048	0.308
Olsen-P (OP)	1.870	0.089	1.230	0.232
Formic acid-P (FAP)	32.188	39.500	68.500	29.625
Citric acid-P (CAP)	37.500	44.350	47.350	31.125

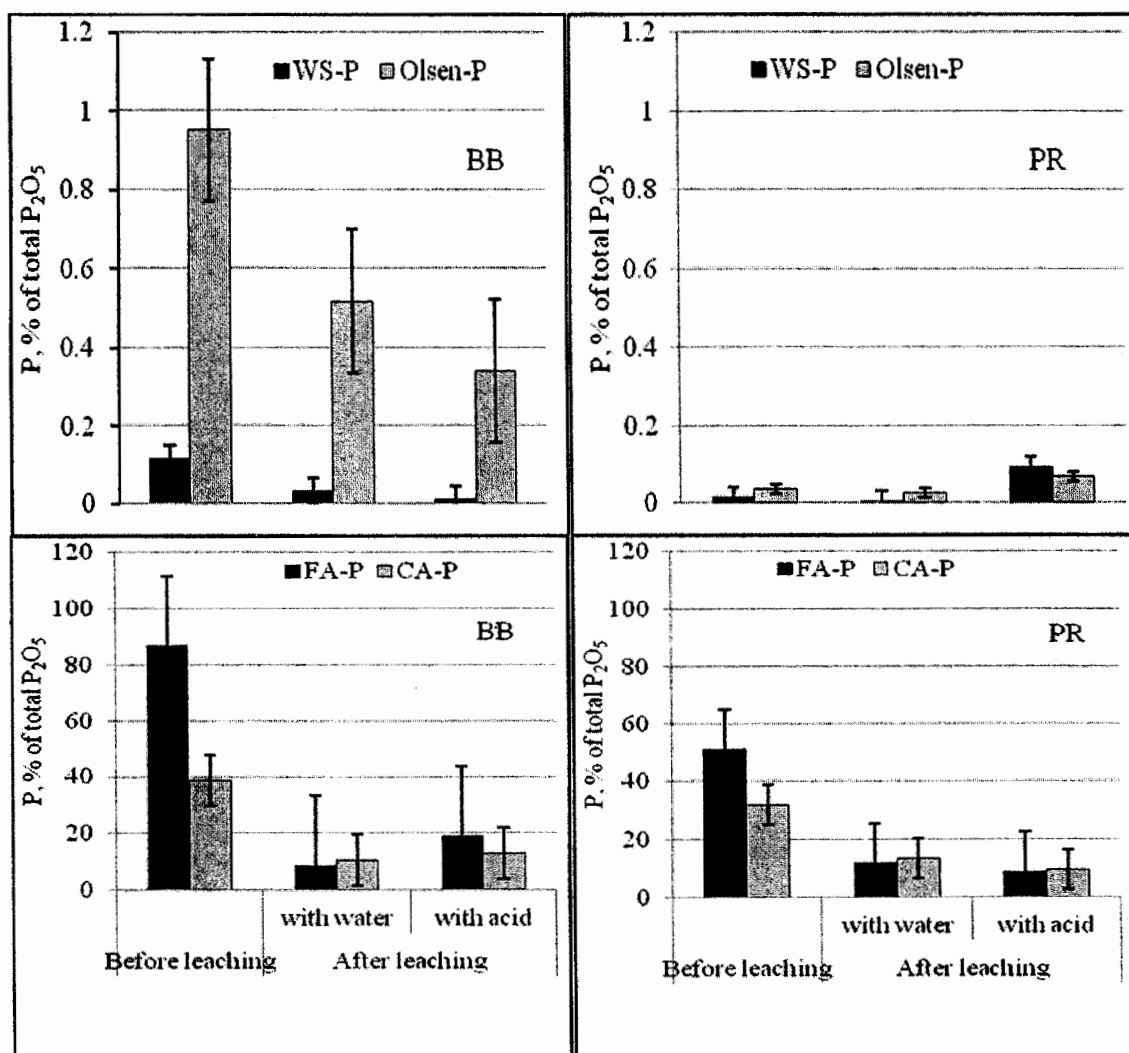


Figure 4: Phosphorus fractions in bone biochar (BB) and phosphate rock (PR) before and after 30 days of leaching by water or diluted acid.

REFERENCES

- Al-Oud, S.S., 2011. Improving phosphorus availability from phosphate rock in calcareous soils by amending with: organic acid, sulfur, and/ or organic manure. *J. Applied Sci.*, **4**, 227-235.
- Bianco, C., Defez, R., 2010. Improvement of Phosphate Solubilization and Medicago Plant Yield by an Indole-3-Acetic Acid-Overproducing Strain of *Sinorhizobium meliloti*. *Appl. Environ. Microbiol.* **76**, 4626-4632. doi:10.1128/AEM.02756-09
- Bigi, A., Cojazzi, G., Panzavolta, S., Ripamonti, A., Roveri, N., Romanello, M., Suarez, N., Moro, L. 1997. Chemical and structural characterization of the mineral phase from cortical and trabecular bone. *J. inorganic Biochemistry* **68**,45-51. doi:10.1016/S0162-0134(97)00007-X.
- Bilali, L., Benchanaa, M., El harfi, K., Mokhlisse, A., Outzourhit, A., 2005. A detailed study of the microwave pyrolysis of the Moroccan (Yousoufia) rock phosphate. *J. Analytical and Applied Pyrolysis* **73**, 1-15. doi:10.1016/j.jaap. 2004. 08.004
- Braithwaite, A. C., Eaton, A.C., Groom, P.S., 1989. Some factors associated with the use of the extractants 2% citric acid and 2% formic acid as estimators of available phosphorus in fertilizer products. *Fertilizer research* **19**,175-181. doi:10.1007/BF01054459
- Chapman, H.D., Pratt, P.F., 1961. *Methods of Analysis for Soils, Plants and Waters*. Div. Agric. Sci., Univ. of California, Berkeley.
- Chien S. H., Hammond, L.L. 1978-b. A comparison of various laboratory methods for predicting the agronomic potential of phosphate rocks for direct application. *Soil Sci. Soc. Am. J.* **42**,935-939. doi:10.2136/sssaj1978.03615995004200060022x

- Chien, S.H., Hammond, L.L. 1978-a. A simple chemical method for evaluating the agronomic potential of granulated phosphate rock. *Soil Sci. Soc. Am. J.*, **42**: 615-617. doi:10.2136/sssaj1978.03615995004200040016x
- Cordell, D., Rosemarin, A., Schröder, J.J., Smit, A.L., 2011. Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. *Chemosphere* **84**, 747-758. doi:10.1016/j.chemosphere.2011.02.032
- Costat 1985. User's Manual. Version 3, Cohort. Tucson, Arizona, USA. Development Center, Muscle Shoals, AL 35662, USA.
- Flach, E. N., Quak, W., Van Diest, A. 1987. A comparison of the rock phosphate-mobilizing capacities of various crop species. *Trop Agric.* **64**, 347-352.
- Germine, M., Parsons, J. R. 1988. Deconvoluted x-ray diffraction analysis of bone and mixtures of bone and particulate hydroxyapatite. *J. Biomedical Materials Research, (Suppl: Applied Biomaterials)* **22**, 55-67.
- Hinsinger, P. 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant Soil* **237**, 173-195. doi:10.1023/A:1013351617532
- Hinsinger, P., Plassard, C., Tang, C., Jaillard, B., 2003. Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: A review. *Plant Soil* **248**, 43 - 59. doi:10.1023/A:1022371130939
- Hoffman, E., Mager, D. 1953. Solubility of phosphoric acid and phosphate rocks. *Zeitschrift für pflanzenernahrung, düngung und bodenkunde* **62**, 262-264. doi:10.1002/jpln.19530620308
- IFDC 2010. World Phosphate Rock Reserves and Resources. International Fertilizer
- Khasawneh, F. E., Doll, E.C., 1978. The use of phosphate rock for direct application to soils. *Advanc. Agron.* **30**, 159-206.
- Knox, A.S., Kaplan, D.I., Paller, M.H., 2006. Phosphate sources and their suitability for remediation of contaminated soils. *Science of the Total Environ.* **357**, 271-279. doi:10.1016/j.scitotenv.2005.07.014
- Lefires, H., Medini H., Megriche, A., Mgaidi, A., 2014. Dissolution of Calcareous Phosphate Rock from Gafsa (Tunisia) Using Dilute Phosphoric Acid Solution. *International J. Nonferrous Metallurgy.* **3**, 1-7. doi:10.4236/ijnm.2014.31001
- Ma, Y. L., Matsunaka, T., 2013. Biochar derived from dairy cattle carcasses as an alternative source of phosphorus and amendment for soil acidity. *Soil Sci. Plant Nutrit.*, **59**, 628-641, doi:10.1080/00380768.2013.806205
- Mackay, A.D., Syers, J.K., Gregg, P.E.H., 1984. Ability of chemical extraction procedures to predict the agronomic effectiveness of phosphate rock materials. *NZJ Agric Res.* **27**, 219-230. doi:10.1080/00288233.1984.10430424
- Mendes, G.O., Zafra, D.L., Vassilev, N.B., Silva, I.R., Ribeiro, J. J.I., Costa, M.D., 2014. Biochar enhances *Aspergillus niger* rock phosphate solubilization by increasing organic acid production and alleviating fluoride toxicity. *Appl. Environ. Microbiol.* **80**, 3081-3085. doi:10.1128/AEM.00241-14
- Meneghini, C., Dalconi, M. C., Nuzzo, S., Mobilio, S., Wenk, R. H., 2003. Rietveld Refinement on X-Ray Diffraction Patterns of Bioapatite in Human Fetal Bones. *Biophysical Journal* **84**, 2021-2029. doi:10.1016/S0006-3495(03)75010-3
- Mortvedt, J.J., Beaton, J.D. 1995. Heavy metal and radionuclide contaminants in phosphate fertilizers. In SCOPE 54-Phosphorus in the Global Environment -Transfers, Cycles and Management. Scientific Committee on Problems of the Environment. International Council of Scientific Unions. SCOPE, John Wiley & Sons Ltd.
- Mowo, J.G., Janssen, B., Oenema, O., Masuki, K., Mrema, J., 2014. The importance of proton supply in phosphate rock dissolution: Comparative study of three phosphate rocks from sub-Saharan Africa. *J. Soil Sci. Environ. Manage* **5**, 44-51. doi:10.5897/JSSEM12.070
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* **27**, 31-36. doi:10.1016/S0003-2670(00)88444-5
- Novotny, E.H., Aucaise, R., Velloso, M.H.R., Corrêa, J.C., Higarashi, M.M., Abreu, V. M. N., Rocha, J.D., Kwapinski, W., 2012. Characterization of phosphate structures in biochar from swine bones. *Pesq. agropec. bras., Brasília* **47**, 672-676.
- Pansu, M., Gautheyrou, J., 2003. Handbook of Soil Analysis. New York, USA. Springer.
- Passman, S.D., White, T.J., Lewis, R.D., 2014. Point-of-Use Water Filtration for Arsenic: A Sustainable and Simple Solution in Resource-poor Settings. *International Journal for Service Learning in Engineering*, **9**, 79-91.

- Peaslee, D. E., Anderson, C.A., Burns, G.R., Black, C.A., 1962. Estimation of Relative Value of Phosphate Rock and Superphosphate to Plants on Different Soils. *Soil Sci. Soc. Am. Proc.*, **26**, 566-570. doi:10.2136/sssaj1962.03615995002600060016x
- Qiu, G., Ting, Y. P., 2014. Direct phosphorus recovery from municipal wastewater via osmotic membrane bioreactor (OMBR) for wastewater treatment. *Bioresource Technol.*, **170**, 221-229. doi: 10.1016/j.biortech. 2014. 07.103
- Rajan, S.S., Brown, M.W., Boyes, M.K., Upsdell, M.P. 1992. Extractable phosphorus to predict agronomic effectiveness of ground and unground phosphate rocks. *Fertilizer Res.* **32**, 291-302. doi:10.1007/BF01050366
- Rengel, Z., Marschner, P., 2005. Nutrient availability and management in the rhizosphere: exploiting genotypic differences. *New Phytologist* **168**, 305-312. doi: 10.1111/j.1469-8137.2005.01558.x
- Rétháti, G., Vejzer, A., Simon, B., Benjared, R., Füleky, G., 2014. Examination of zinc adsorption capacity of soils treated with different pyrolysis products. *Acta Universitatis Sapientiae Agriculture and Environment*, **6**, 33-38. doi: 10.2478/ausae-2014-0010
- Schrödter, K., Bettermann, G., Staffel, T., Klein, T., Hofmann, T., 2011. Phosphoric Acid and Phosphates. In *Ullmann's Encyclopedia of Industrial Chemistry*. 7th ed. Pp, 14106-14128. Wiley-VCH.
- Sharma, S.B., Sayyed, R.Z., Trivedi, M.H., Gobi, T.A., 2013. Phosphate solubilizing microbes: sustainable approach for managing phosphorus deficiency in agricultural soils. *Springer Plus*, **2**, 587. doi: 10.1186/2193-1801-2-587
- Siebers, N., Leinweber, P., 2013. Bone Char: A Clean and Renewable Phosphorus Fertilizer with Cadmium Immobilization Capability. *J.E.Q.* **42**, 405-411. doi:10.2134/jeq2012.0363
- Siebers, N., Kruse, J., Leinweber, P., 2013. Speciation of Phosphorus and Cadmium in a Contaminated Soil Amended with Bone Char: Sequential Fractionation and XANES Spectroscopy. *Water Air Soil Pollut.* **224**, 1564-1576. doi: 10.1007/s11270-013-1564-7
- Simons, A., Solomon, D., Chibssa, W., Blalock, G., Lehmann, J., 2014. Filling the phosphorus fertilizer gap in developing countries. *Nature Geoscience* **7**, 3. doi:10.1038/ngeo2049
- Syers, J.K., Mackay, A.D., Brown, M.W., Currie, L.D. 1986. Chemical and physical characteristics of phosphate rock materials of varying reactivity. *J. Sci. Food Agric.* **37**, 1057-1064. doi: 10.1002/jsfa.2740371102
- USGS 2010. Phosphate Rock. World Mine Production and Reserves. http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/mcs-2010-phosp.pdf (April, 2015).
- Vassilev, N., Martos, E., Mendes, G., Martos, V., Vassileva, M., 2013. Biochar of animal origin: a sustainable solution to the global problem of high grade rock phosphate scarcity? *J. Sci. Food Agric.* **93**, 1799-1804. doi: 10.1002/jsfa.6130
- Wang, T., Camps-Arbestain, M., Hedley, M., Bishop, P., 2012. Predicting phosphorus bioavailability from high-ash biochars. *Plant Soil* **357**, 173-187. Doi: 10.1007/s11104-012-1131-9
- Warren, G.P., Robinson, J. S., Someus, E., 2009. Dissolution of phosphorus from animal bone char in 12 soils. *Nutr Cycl Agroecosyst* **84**, 167-178. doi: 10.1007/s10705-008-9235-6
- Watanabe, F. S., Olsen, S.R., 1965. Test of an ascorbic acid method for determining phosphorus in water and NaHCO₃ extracts from soil. *Soil Sci. Soc. Am. Proc.* **29**, 677 - 678. doi:10.2136/sssaj1965.03615995002900060025x
- Weber, B., Stadlbauer, E.A., Schlich, E., Eichenauer, S., Kern, J., Steffens, D., 2014. Phosphorus bioavailability of biochars produced by thermo-chemical conversion. *J. Plant Nutr. Soil Sci.* **177**, 84-90. doi: 10.1002/jpln.201300281
- Wu, Y., Ackerman, J.L., Strawich, E.S., Rey, C., Kim, H.M., Glimcher, M.J., 2003. Phosphate ions in bone: identification of a calcium-organic phosphate complex by 31P solid state NMR spectroscopy at early stages of mineralization. *Calcif Tissue Int* **72**, 610-626. doi: 10.1007/s00223-002-1068-8.

المخلص العربي

الفحم الحيوى لعظم الحيوانات كمصدر متجدد وكفاء للسماد الفوسفاتى: دراسة مقارنة

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فى دراسة معملية لبحث ذاتية الفوسفات الموجود فى الفحم الحيوى لعظم الحيوانات والمنتج بطريقة الترميد اللاهوائى على درجة حرارة ٦٥٠ درجة مئوية ومقارنة ذلك بذائبية الفوسفات من صخر الفوسفات. تم دراسة خواص كلا المادتين باستخدام الأشعة السينية والتحليل العنصرى الكلى. وتم تقدير الفوسفات الذائب بواسطة الماء المقطر والماء المحمض والمارين خلال عمود محتوى على فحم العظم أو صخر الفوسفات على مدار ٣٠ يوم وذلك بمعدل احلال ثابت وقدرة ٠,٢٥ مليلتر فى الدقيقة باستخدام مضخة ثمانية القنوات. كذلك تم تقدير صور الفوسفور المستخلص بالماء (WSP) أو بيكربونات الصوديوم (OP) أو حامض الستريك (CAP) أو حامض الفورميك (FAP) قبل تجربة الذوبان وبعدها. وقد أوضحت النتائج أن تركيز كل صور الفوسفور المستخلص من فحم العظام كان أعلى من المستخلص من صخر الفوسفات وكان ترتيب التركيزات المستخلصة من كلا المصدرين هو: WSP > CAP > OP > FAP. أوضحت تجارب الذوبان فى الأعمدة أن الفوسفور الذائب بواسطة الماء أو الحامض المخفف من الأعمدة المحتوية على فحم العظام أعلى من الأعمدة المحتوية على صخر الفوسفات وأن الكميات المستخلصة بالحامض المخفف تمثل ٥٠% من الفوسفور الكلى (المقدر فى صورة خامس أو كسيد الفوسفور) والكمية المستخلصة بالماء فقط تمثل ٠,٨٥% من الفوسفور الكلى بينما تمثل الكمية المستخلصة من صخر الفوسفات بالحامض تمثل ٢٩,٧٩% وبالماء فقط ٠,١٧% من الفوسفور الكلى وبالتالي نجد أن تلك النتائج تعكس تأثير ال pH على عملية الإذابة. من ناحية أخرى بينت النتائج أن الكميات المتبقية من الفوسفور والمستخلصة من فحم العظام بواسطة حامض الستريك وحامض الفورميك كانت أعلى من تلك المستخلصة من صخر الفوسفات والعكس صحيح بالنسبة للكميات المستخلصة من الأعمدة المغسولة بالماء فقط. وقد زاد تركيز الفوسفور المستخلص بمحلول بيكربونات الصوديوم من أعمدة صخر الفوسفات بعد الغسيل بالحامض مما يعكس تحسن مستوى تيسر الفوسفور بعد تحميضه. وتبين النتائج المتحصل عليها أهمية استخدام الفحم الحيوى للعظام كمصدر سريع التيسر للفوسفور على المدى القصير والمتوسط وكمصدر للأسمدة الفوسفاتية.