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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
at 650°C in comparison with its solubility from phosphate rock (PR). The PR and BB were characterized
diffraction (XRD) and total elemental analysis. Phosphorous was detected in distilled water and dilute sulfu
leachates resulted from columns filled by BB or PR for 30 days. Fractions of water soluble-P (WSP), Olsen
formic acid-P (FAP) and citric acid-P (CAP) extracted from BB and PR were determined before and after
Results showed that all P fractions extracted from raw BB were higher than those from PR and the
concentrations had the order: FAP > CAP > OP > WSP from both sources. Leaching experiments showe
dissolution by water or sulfuric acid from BB was greater than from PR. The released amounts of P from BB by
and water represented 50.0% and 0.85% of total P_2O_5, respectively, while those released from PR represented 2
0.017% of total P_2O_5, respectively. These Results reflected the majority of pH influence on dissolution process.
amounts of P extracted by CA and FA from BB were higher than those extracted from PR after acid leaching
versa after water leaching. Olsen-P fraction increased after acid leaching of PR which reflects improvement bioava
of P after PR acidification. The obtained results may give BB advance over PR as a fast to medium releas
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 ar
acids, organic manure, elemental sulfur (
2011) or plants (Flach et al., 1987; Hinsinger
Hinsinger et al., 2003; Rengel and Ma
2005), but it still less efficient than c
inorganic chemical P fertilizers.

Looking for unusual alternatives of P, fo
as fertilizer to various kinds of soils, b
necessary. The recovery of P from wa
considered one of the recent technologies
compensate the depleted P resources,
recovery from wastewater has receive
attention (Qiu and Teng, 2014). Phos
containing waste streams can range from
wastewater, to separate organic waste fr
including human urine and faeces, grey
animal manure, animal carcasses, det
industrial and food wastes and crop r
Animal manure (and other animal parts
bones and blood) is widely used as a so
phosphorus fertilizer in many regions of th
(Cordell et al., 2011).

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

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^{o}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 ^{o}C/min till reaching to 650 ^{o}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 CuKα 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 c The heating was continued until the forma homogeneous cake. After cooling, the c contents were dissolved with about 30.0 mL HNO_3 and transferred to 250 mL Pyrex bea boiled until complete dissolution. The clear s was transferred to 250 mL Pyrex volumetri and volume completed with distilled water phosphorus in the solutions of BB and I determined spectrometry using vanado-mo yellow method (Chapmann and Pratt, 196 concentrations of Ca and heavy metals (Cd, Cu, Fe, Mn and Cr) were measured by Indu Coupled Plazma ICP-OES Spectrometer (' iCAP 6000 Series, UK).

Phosphate Fractions in BB and PR

Water soluble P (WS-P): One gram of BE was transferred into 250-mL conical flasks mL distilled water was added and the fla shaken on a horizontal shaker (G24 Enviro Incubator Shaker, New Brunswick Scienti USA) for one hour. The suspension was using filter paper Whatman No. 42 concentration was determined in the super Phosphorus was determinate by the ascorb molybdate blue method (Murphy and Riely at wavelength 882 nm using UV/VIS doubl JENWAY spectrophotometer model 6850 .

Olsen P fraction: According to Murphy, J. J.P., 1962, 2.0g sample of BB or PR was S for 30 minutes with 40.0 mL 0.5 mol L^{-1} bicarbonate ($NaHCO_3$) solution adjusted to with 0.01 mol L^{-1} NaOH or 0.01 mol I solutions using pH-meter (WTW inLab pH/I Germany). Suspensions were filtered throug paper Whatmann No. 42 filter paper and measured colorimetrically (Watanabe and 1965) in supernatants.

Formic acid-P fraction (FA-P): A 0.4g sa BB or PR was extracted with 40 mL 2% forn at 23 ^{o}C for 1 hour (Hoffman and Mager 195 samples were then centrifuged at 10,000 rp min, filtered (0.45µm Millipore filter concentration of P in the solution was detern the filtrate by the vanado-molybdate yellow at wavelength 445 nm (Chapmann and Pratt (

Citric acid-P fraction (CA-P): A 0.4g sa BB or PR was extracted with 40 mL 2% cit at 23 ^{o}C for 1 hour. The samples wer centrifuged at 10,000 rpm for 5 min, (0.45µm Millipore filter), and the resid extracted again with 40 mL of 2% fresh citr The concentration of P in the solutic determined in individual filtrates, fo dilution, by the vanado-molybdate yellow m wavelength 445 nm (Chapmann and Pratt (1

Column Leaching Experiment

One hundred grams of BB or PR was pa Pyrex glass column (2.0-cm in diameter an 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 H_2SO_4. 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 ^{o}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

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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 M (Bilali et al., 2005) phosphate rocks.

Elemental analysis and Fractions of P in PR

The elemental analysis of BB and PR, that total content of P_2O_5 (36.068 and 3 respectively) and CaO (38.08 and respectively) for both materials virtually (Table 1). Gafsa rock phosphate contain 28.6% P_2O_5 (Warren et al., 2009) while M contains 31.51% P_2O_5 and 50.19% CaO (al., 2005).

Concentration of heavy metals occurre and PR revealed that chromium (Cr) in PR (kg^{-1}) exceeds about 14 times more than tha contains (6.5 mg kg^{-1}). Knox et al. (2006 close results for total Cr content in mined (kg^{-1}) and processed (101.4 mg kg^{-1}) PR collected from various regions of USA wh found only 4.6 mg Cr kg^{-1} in ground fish Copper was not detected in BB while occu PR (7.75 mg kg^{-1}). The current concentra heavy metals (Cd, Cr, Pb, Cu, Fe, Mn and N are relatively close to those mentioned for East-PR and published by Mortvedt and (1995).

Total carbonate contents in PR and B 10.45 and 6.21%, respectively. These values the idea that calcium phosphate in both m possibly occurred in the form of carbonate a a main component. Calcination of P temperatures higher than 600 ^{o}C) helps in r its carbonate content by decomposition of and formation of CaO (Bilali et al., 2005) results may speculate the low content carbonate and high content of CaO in BB those recorded in PR.

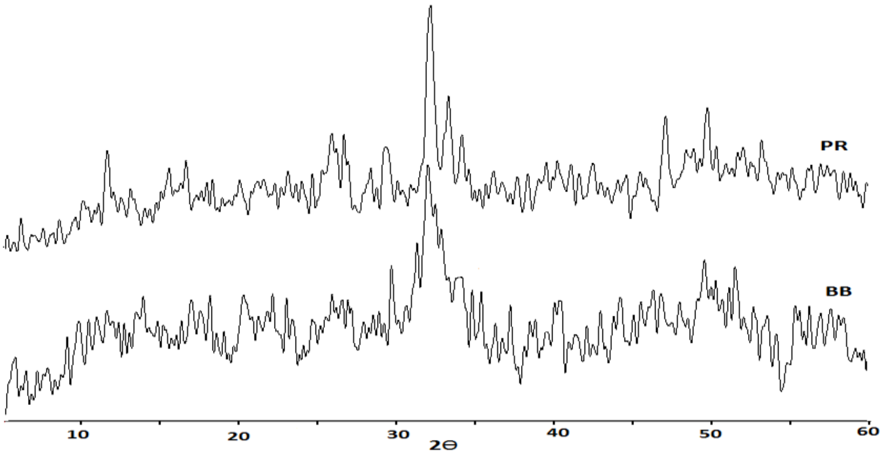

Figure1: XRD patterns of phosphate rock (PR) compared to bone biochar (BB).

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

Measured parameters	BB	PR
Total content		
P_2O_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_2O_5	0.435	0.050
Olsen- P_2O_5	3.435	0.122
FA- P_2O_5	312.951	170.376
CA- P_2O_5	139.301	105.340
P fractions as % of total P		
WS- P_2O_5	0.120	0.015
Olsen- P_2O_5	0.952	0.037
FA- P_2O_5	86.767	51.310
CA- P_2O_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 P_2O_5 kg^{-1}of WS- and Olsen-P were released from BB compared with 50.0 and 122.0 mg P_2O_5 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 P_2O_5 (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 f to 71% and from 21 to 46% of total P, respe Since the formic acid and citric acid ext mainly used for estimation of available fertilizer products (Syers et al. 1986; Braithw al., 1989), the current results of extracte mentioned acids from BB and PR confirm h availability from BB from PR.

Leaching Experiment

Since pH is the most important soil facto dissolution (Peaslee et al., 1962; Khasawn Doll, 1978) and sulfuric acid is the dissolutio in orthophosphoric acid and superph industry (Schrödter et al., 2011). we simu solubilization through the leaching by sulfuric acid (0.01mol L^{-1}) in compariso distilled water at a constant flow rate to e and compare the release of soluble P from b and PR. The results of cumulative P dissolu water and acid showed great releasing of P fr than from PR (Fig. 2) throughout the c leaching. Within the first 5 days of cumul dissolution by water, there was a sharp increa released from BB (from 0.856 to 2.418 mg P BB). Then the dissolution rate declined (2 3.053 mg P_2O_5 g^{-1} BB) whereas the corresp dissolution from PR was not significant alo 30 days of leaching (from 0.005 to 0.055 mg

^{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 b BB and PR. In BB, a slight augmentatio dissolution was observed within the first fi then increased and became nearly linear u end of experiment (Fig. 2). For PR, t dissolution rate extended to the first 12 da increased where the linear P dissolution ap The amounts of acid-extracted BB-P excee of PR-P by about two folds.

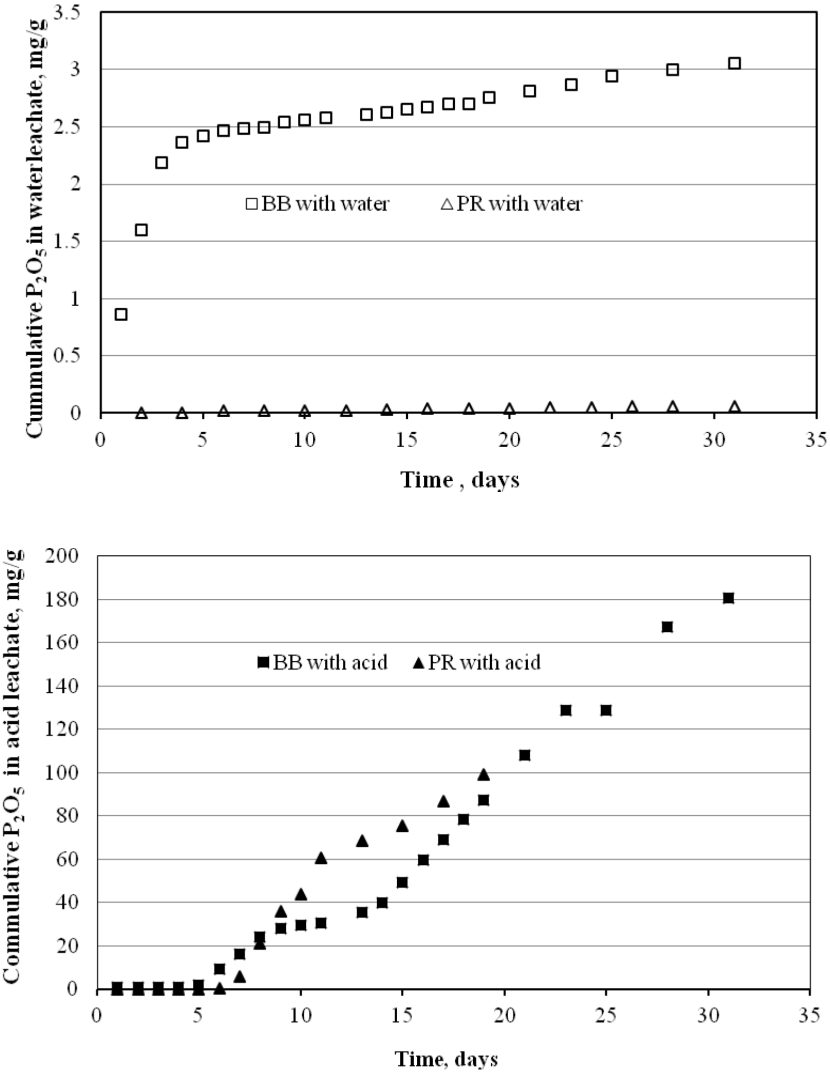

Figure 2: Concentrations of cumulative P_2O_5 in column leachates as a function of dissolution b or by dilute acid (0.01M H_2SO_4) from bone biochar (BB) and phosphate rock (PR).

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-
than of PR-P when both applied as a direct s
P fertilizer. In other words, these results
explained by the occurrence of ph
compounds that are more soluble than
consisting in PR. Bone and bone char
characterized by ^{31}P solid state NMR spect
confirmed occurrence of phosphate com
beside hydroxyl-apatite such as, brus
structure ($CaHPO_4.2H_2O$) and phosphor
(Wu et al., 2003). Subjecting bone mate
pyrolysis decreasing protein phosphoryl cont
also a probably destruction of protein pho
Compounds (Novotny et al., 2012). These fa
cause an increase in concentration of water
P released from BB.

Variation in BB- and PR-P dissolution b
sulfuric acid (Fig. 3) might be partially du
concentration of proton (H^+) required b
material to start in P dissolution, and total c
carbonate content accompanied each materi
and 10.45% in BB and PR respectively, T
which will play a significant consumer for pr

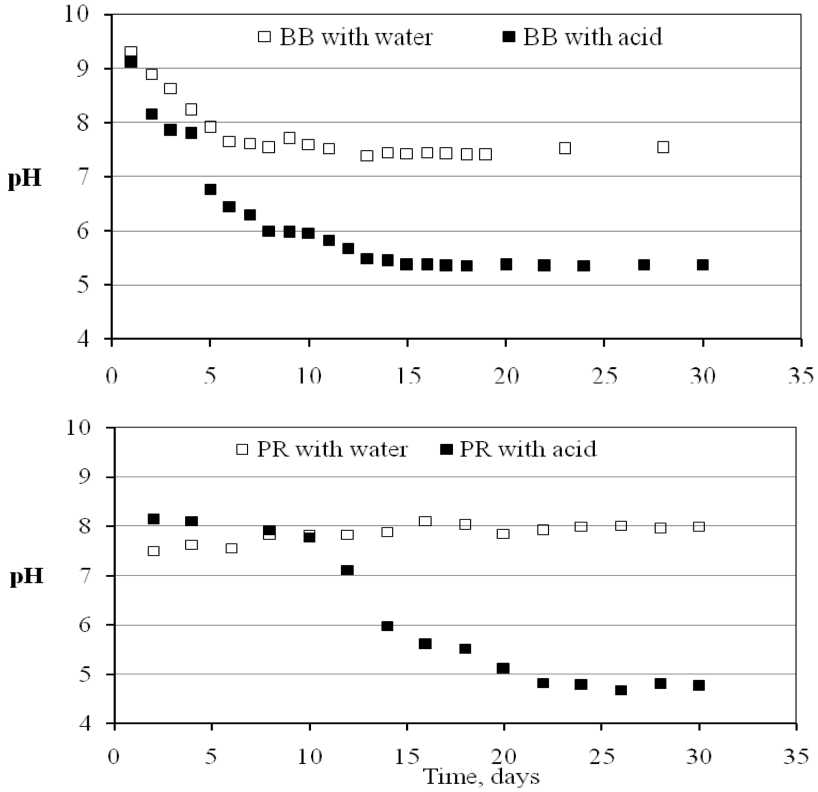

Figure 3: pH values accompanied of P dissolution from bone biochar (BB) and phosphate rock (
fixing flow rate of water or acid throughout 30 day of column leaching experiment.

In the bigening of dissolution reaction, carbontes 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 couse 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) scince 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 form 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 a
leaching processes as significant parts of
Before leaching, P extracted by formic acid
represented about 86 and 51% of total P in
PR, respectively. After leaching, FAP decre
8.9 and 18.9% of total P from BB after leac
water and acid, respectively, while it decre
11.9 and 8.9% of total P from PR (Fig. 4). Si
formic acid extractable P represents the
chemical reactive fraction of PR-P it show
values of agronomic effectiveness of PR (Ma
al., 1984; Rajan et al., 1996). Thus, in the
study, it reflects an advantage of BB over l
slow release P resource. One of the im
observation is the high values of OP
extracted from BB (Fig. 4) comparing wit
from PR. Before leaching, OP represented
0.95% of total P and declined to 0.52 and
after 30 days of leaching by water and
respectively. Non-noteworthy amounts of C
resulted from PR before or after leaching.
observed that leaching of PR by dilut
increased the concentration of OP (0.07% of
than its concentration before leaching (0.
This result revealed that acidification of P
acid increased the bioavailability of PR-P.

CONCLUSION

The results of XRD for PR and BB ex
matching between the structures of PR-apa
BB-apatite minerals. The used bone biocha
renewable source of P, was characterized
concentrations in heavy metals such as Cr,
Cu than PR and showed a high and fast relea
water soluble P along with the 30 days of l
by water or by diluted acid. The ratio of BB-
released by water reached to 50 whereas it
1.68 for P released by acid. The acid: water
cumulative released BB-P and PR-P represe
and 1750, respectively, which indicated
importance of pH as a major factor for P diss
from its resources. The higher values of va
fractions extracted from BB than those c
from PR characterize its high reactivi
availability as well as this give more prosp
using bone biochar (BB) as efficient and sus
P fertilizer.

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

P fraction	BB	PR	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

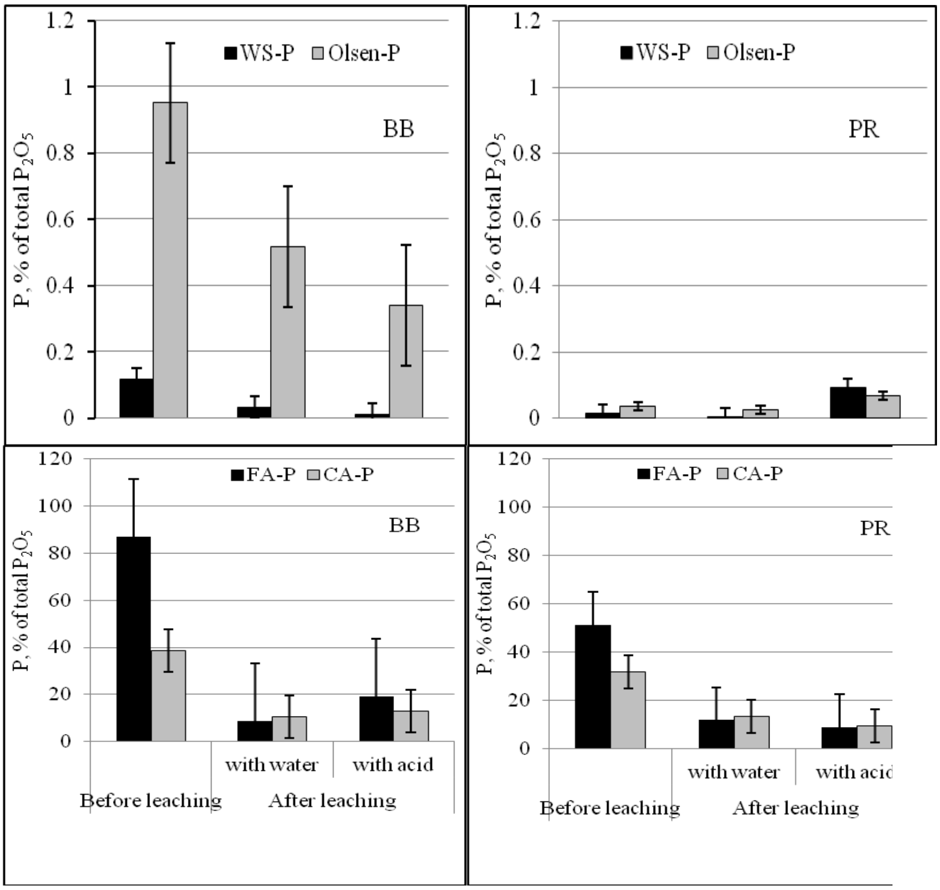

Figure 4: Phosphorus fractions in bone biochar (BB) and phosphate rock (PR) before and after 3 of leaching by water or diluted acid.

~~**1- Yield/ vine:**~~

~~Data in Table (1) clearly show that spraying clusters of Early sweet grapevines with GA$_3$ at 10 to 40 ppm or Sitofex at 2.5 to 10 ppm was significantly effective in improving the yield relative to the check treatment. The promotion on the yield was accompanied with increasing concentrations of each plant growth regulator. Using GA$_3$ at 10 to 40 was significantly preferable than using Sitofex at 2.5 to 10 ppm in improving the yield. A slight and unsignificant promotion on the yield was attributed to increasing concentrations of GA$_3$ from 20 to 40 ppm and Sitofex from 5 to 10 ppm. The maximum yield was produced on the vines that received one spray of GA$_3$ at 40 ppm but the best treatment from economical point of view was the application of GA$_3$ at 20 ppm (since no measurable promotion on the yield was recorded between 20 and 40 ppm of GA$_3$). Under such promised treatment, yield/ vine reached 13.6 and 14.0 kg during both seasons, respectively. The control vines produced 9.1 and 9.6 kg during 2013 and 2014 seasons, respectively. The percentage of increase on the yield application of GA$_3$ at 20 ppm over the treatment reached 49.5 and 45.8 % durin seasons, respectively. The beneficial effects on the yield might be attributed to their action on increasing cluster weight. The pr effects of GA$_3$ on the yield was supported results of Dimovska *et al*., (2011) and Abu and Salameh (2012) on different grapevine c~~

~~The results regarding the beneficial ef Sitofex on enhancing the yield are in harmo those obtained by Juan *et al*. (2009); Abdel *et al*., (2010) and Al- Obeed (2011).~~

~~**2- Harvesting date:**~~

~~It is clear from the data in Table (1) that and Sitofex treatments had significantly del the harvesting date of Early Sweet grapevine than the control treatment. The degree of d on harvesting date was correlated to the inc the concentrations of both GA$_3$ and Sitofex GA$_3$ significantly delayed harvesting comparing with using Sitofex. In~~

~~concentrations of GA_3 from 20 to 40 ppm and Sitofex form 5 to 10 ppm failed to show significant delay on harvesting date. A considerable advancement on harvesting date was observed on untreated vines the great delay on harvesting date was observed on the vines that received GA_3 at 40 ppm during both seasons. GA_3 and Sitofex were shown by many authors to retard the release of ethylene and the disappearance of pigments such as chlorophylls and carotenoids and onest of maturity start. Also they were responsible for prolonging pre-maturity stages Nickell (1985). These results regarding the delaying effect of GA_3 and Sitofex on harvesting date were in harmony with those obtained by Wassel *et al*., (2007), Kassem *et al*. (2011), Abu- Zahra and Salameh (2012) and Refaat *et al*. (2012).~~

~~3- Cluster weight and dimensions:~~

~~It is evident from the data in Table (1) that treating clusters with GA_3 at 10 to 40 ppm or Sitofex at 2.5 to 10 ppm was significantly accompanied with enhancing weight, length and width of cluster relative to the control treatment.~~

~~The promotion was significantly associated with increasing concentrations of GA$_3$ and Sitofex. Using GA$_3$ was significantly favourable than using Sitofex in this respect. The maximum values were recorded on the vines that received one spray of GA$_3$ at 40 ppm. Meaningless promotion was detected with increasing concentrations of GA$_3$ from 20 to 40 ppm and Sitofex from 5 to 10 ppm. The untreated vines produced the minimum values during both seasons. The positive action of GA$_3$ on cluster weight and dimensions might be attributed to its essential role on stimulating cell division and enlargement of cells, the water absorption and the biosynthesis of proteins which will lead to increase berry weight. Dimovska *et al*., (2011); Abu Zahra and Salameh, (2012) and Dimovska *et al*., (2014).~~

~~The previous essential role of CPPU on cluster weight was attributed to its higher content of cytokinin when applied to plants (Nickell, 1985).~~

~~4- Shot berries %:~~

~~Data in Table (2) obviously reveal that percentage of shot berries in the clusters of Early Sweet grapevines was significantly controlled with spraying GA$_3$ at 10 to 40 ppm or Sitofex at 2.5 to 10 ppm relative to the check treatment. Using GA$_3$ was preferable than using Sitofex in reducing the percentages of shot berries. There was a gradual reduction on the percentage of shot berries with increasing concentrations of GA$_3$ and Sitofex. There was a slight reduction on such unfavourable phenomenon with increasing concentrations of GA$_3$ form 20 to 40 ppm and Sitofex from 5 to 10 ppm. The minimum values of shot berries (7.3 and 6.9 % during both seasons, respectively) were recorded on the clusters harvested from vines treated with GA$_3$ at 40 ppm. The maximum values of shot (12.0 & 12.5 %) during both seasons were r on the untreated vines during both seaso reducing effect of GA$_3$ on shot berries m attributed to its important role on enhanci division and the biosynthesis of proteins (1985). These results were supported by the of wassel *et al*. (2007) and Abu-Zahra and (2012).~~

~~5- Fruit quality:~~

~~Data in Tables (2, 3 & 4) clearly sh spraying clusters with GA3 at 10 to 40 Sitofex at 2.5 to 10 ppm significant accompanied with enhancing weight, long and equatorial of berry, total acidity%, pro and percentages of P, K and Mg and T. reducing sugars %, T.S.S. / acid an carotenoids relative to the check treatme effect either increase or decrease was as with increasing concentrations of each auxi GA$_3$ significantly changed these paramete using Sitofex. A slight effect was recorded quality parameters with increasing concentra GA$_3$ from 20 to 40 ppm and Sitofex from ppm. From economical point of view, t results with regard to fruit quality were o due to treating clusters with GA$_3$ at 2 Untreated vines produced unfavourable eff fruit quality. These results were true duri seasons. The effect of GA$_3$ on increasin weight and dimensions might be attribute effect in promoting cell division and enlarge cells, water uptake and the biosynthesis of Nickell (1985). These results were in conc with those obtained by Williams and Ayars and Dimovska *et al*., (2014).~~

~~The higher content of Sitofex from cy surly reflected on enhancing cell division elongation of berries Nickell (1985). These were in agreement with those obtained b Zahra (2013) and Retamales *et al*. (2015).~~

~~CONCLUSION~~

~~Treating Early Sweet grapevines once w average berries reached 6mm with GA$_3$ at was responsible for promoting yield an quality.~~

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الملخص العربى

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

~~**رش حامض الجبريليك والسيتوفكس فى تحسين المحصول وجودة حبات العنب الايرلى سويت فى منطقة المنيا– مصر**~~

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دراسة معملية لبحث ذائبية الفوسفات الموجود فى الفحم الحيوى لعظم الحيوانات والمنتج بطريقة الترميد
على درجة حرارة 650 درجة مئوية ومقارنة ذلك بذائبية الفوسفات من صخر الفوسفات. تم دراسة خواص كلا
باستخدام الأشعة السينية والتحليل العنصرى الكلى. وتم تقدير الفوسفات الذائب بواسطة الماء المقطر والماء
والمارين خلال عمود محتوى على فحم العظم أو صخر الفوسفات على مدار 30 يوم وذلك بمعدل احلال
رة 0.25 ملليلتر فى الدقيقة باستخدام مضخة ثمانية القنوات. كذلك تم تقدير صور الفوسفور المستخلص بالماء
أو بيكربونات الصوديوم(OP) أو حامض الستريك(CAP) أو حامض الفورميك(FAP) قبل تجربة الذوبان
وقد أوضحت النتائج أن تركيز كل صور الفوسفور المستخلص من فحم العظام كان أعلى من المستخلص من
فوسفات وكان ترتيب التركيزات المستخلصة من كلا المصدرين هو: FAP>CAP>OP>WSP. أوضحت تجارب
ى الأعمدة أن الفوسفور الذائب بواسطة الماء أو الحامض المخفف من الأعمدة المحتوية على فحم العظام
ن الأعمدة المحتوية على صخر الفوسفات وأن الكميات المستخلصة بالحامض المخفف تمثل 50% من
الكلى(المقدر فى صورة خامس أوكسيد الفوسفور) والكمية المستخلصة بالماء فقط تمثل 0.85% من الفوسفور
نما تمثل الكمية المستخلصة من صخر الفوسفات بالحامض تمثل29.79% وبالماء فقط 0.017% من
الكلى وبالتالى نجد أن تلك النتائج تعكس تأثير ال pH على عملية الإذابة. من ناحية أخرى بينت النتائج أن
المتبقية من الفوسفور والمستخلصة من فحم العظام بواسطة حامض الستريك وحامض الفورميك كانت أعلى من
تخلصة من صخر الفوسفات والعكس صحيح بالنسبة للكميات المستخلصة من الأعمدة المغسولة بالماء فقط.
ركيز الفوسفور المستخلص بمحلول بيكربونات الصوديوم من أعمدة صخر الفوسفات بعد الغسيل بالحامض مما
حسن مستوى تيسر الفوسفور بعد تحميضه. وتبين النتائج المتحصل عليها أهمية استخدام الفحم الحيوى للعظام
سريع التيسر للفسفور على المدى القصير والمتوسط وكمصدر للأسمدة الفوسفاتية.

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