Phosphate Sorption of Calcined Materials Used as Components of Soilless Root Media Characterized in Laboratory Studies

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Abstract. Calcined materials may contribute enhanced phosphate (PO₄-P) retention to soilless root media used in container production. Properties of nutrient retention vary greatly depending on the parent clay and calcining treatment. This research characterized PO₄-P sorption of various calcined clay products, including low and regular volatile material (LVM and RVM) 2:1 attapulgite, montmorillonite, and illite clays at various particle sizes; 1:1 kaolin clays in powder form; and diatomaceous earth. Extractable PO₄-P, initial pH, PO₄-P sorption isotherms, amount of P sorbed as a function of solution pH at a fixed total concentration, and degree of phosphorus saturation were determined. Initial pH of the clays ranged from 3.7 to 8.7. Sorption isotherms were conducted with initial adsorbate concentrations ranging from 0 to 200 mg·L⁻¹ PO₄-P from KH₂PO₄. The calcined materials varied in their ability to sorb PO₄-P and generally yielded L-type isotherms, indicating that the adsorbate had relatively high affinity for the calcined material sample surface at low surface coverage. Some 2:1 calcined clays exhibited substantial PO₄-P retention, but 1:1 calcined clays and diatomaceous earth did not. Clays with less moisture (LVM) resulted in greater PO₄-P sorption than those calcined at lower temperatures (RVM). Terra Green montmorillonites had higher PO₄-P sorption than Terra Green attapulgites. Laboratory results indicated potential for substantive PO₄-P retention by several of the calcined clay materials when used in container production. For most materials, PO₄-P sorption did not show pronounced pH dependence, which suggests that PO₄-P retention is not influenced by pH-dependent charge within the pH range of container production.

Small volumes (2% to 20%) of a variety of calcined clay-type products are being used as components of soilless root media because of their potential to increase nutrient retention, air space, water retention, and bulk density of mixes used for container production in the

greenhouse and nursery industries. Properties imparted by these materials are inherited from the parent clay or source, particle size distribution, and calcining process. High calcining temperatures result in expansion of the crushed clay to form a porous structure that is physically and chemically stable. The resulting granules provide aeration to the root medium and hold water internally within their pore structure.

Traditionally, the soil component of root media used for crop production in containers imparted significant PO₄-P retention to the root medium. Marconi and Nelson (1984) showed that over 33% of the total P applied was leached from a soilless root medium containing 1 peatmoss:1 vermiculite, but less than 5% was leached from a 1 sand:1 soil:1 peatmoss mix in a simulated plant-watering scheme. This difference, they concluded, was related to differences in P sorption by the various root medium components. Use of soil in container root media has fallen out of favor with commercial producers because it is relatively expensive compared with other components, variable from source to source, and must be pasteurized before use (Nelson, 2005).

Many types of calcined clay amendments may enhance PO₄-P and water retention of soilless root media. Incorporation of 13% (by volume) of a calcined clay has been shown to reduce the amount of PO₄-P leached from pine bark-based container media by 73% in production of *Loropetalum chinense* var. *rubrum* R. Br. 'Blush' over a 16-week period (Ruter, 2003). Reduction in fertilizer and water use in poinsettia (*Euphorbia pulcherrima* Willd. ex Klotzsch) with incorporation of calcined clays has been shown (Catanzaro and Bhatti, 2005; Catanzaro et al., 2004). Owen et al. (2003) found that amending a pine bark root medium with 8% (by volume) calcined clay led to increased nutrient retention and water-buffering capacity in production of container-grown *Cotoneaster dammeri* C.K. Schneid 'Skogholm'. A root medium of 3 peat:5 compost:2 Turface (calcined arcillite clay; v/v) reduced PO₄-P leaching by 70% compared with a control of 3 peat:5 compost:2 sand in production of black-eyed susan, *Rudbeckia hirta* L. (Bugbee and Eliot, 1998). Because use of calcined clays offers potential to reduce environmental impact from PO₄-P leaching during container production, PO₄-P retention and other properties of a variety of calcined materials should be characterized.

Clay surfaces bear an electrical charge that is a function of permanent charge, variable charge, and inner and outer surface charge. The resultant particle charge is either created through isomorphic substitution, protonation and deprotonation reactions or partial charge as expressed through the polarity of atoms at the clay surface (Essington, 2004). The silicate minerals present in clays develop a pH-dependent charge at the broken edges of the layer structure, which is a phenomenon that occurs in both 1:1 and 2:1 clay soils (Havlin et al., 2003).

Sorption of PO₄ by clay minerals has been attributed to a pH-dependent reaction of PO₄ with calcium, iron (Fe), and aluminum (Al) in the clay (Havlin et al., 2003). Much of the P adsorption by soils can be attributed to chemisorptions involved in ligand exchange between PO₄-P and hydroxyl ions at Fe and Al oxyhydroxides (Parfitt, 1978). pH-dependent PO₄-P sorption by calcined clays has not been systematically investigated and it is not clear how the process of calcining changes the PO₄-P sorption characteristics of clays.

The commercial calcining process results in low volatile material (LVM) or regular volatile material (RVM) moisture contents, depending on calcining temperatures. Calcining, generally, reduces the amount of water trapped between the clay's silicate sheets and also produces a very hard granule that, even when fully saturated with water, does not break apart easily. The first stage of calcining, known as fluid bed drying, reduces the clay moisture level from 40% to 45% down to 6% to 9% using temperatures of ≈120 to 176 °C, resulting in RVM clays. The LVM clays have even lower moisture content of 0% to 3%, which is achieved by secondary calcining at temperatures in the range of 460 to 800 °C (Moll and Goss, 1997). Heating the clays

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causes aggregation of particles that optimizes sorptivity by creating a stable porous internal structure. Calcining reduces the exchange capacity of the clays, but surface binding and internal pores maintain some nutrient retention capacity. X-ray diffraction studies on a 2:1 Ca-montmorillonite clay showed that heat treatment of 200 to 400 °C completely collapsed the interlayer, incorporating interlayer cations into the tetrahedral or unoccupied octahedral sheets (Bray et al., 1998). Noyan et al. (2006) evaluated the specific surface area, specific micromesopore volume, total surface acidity, and adsorption equilibrium constant of original and heated samples of a bentonite clay from Turkey. The specific area, micromesopore volume, and total surface acidity stayed constant as temperature increased to 450 °C and then decreased. Total surface acidity, in general, declined with increasing temperatures. The most acidic sites, however, increased with heating and especially at temperatures of dehydration (100 to 550 °C) and dehydroxylation (550 to 700 °C). Calcining temperatures for maximizing sorptivity, generally, do not exceed the dehydration interval. Noyan et al. (2006) concluded that the decomposition of the 2:1 layers of the clay and collapsing of micro- and mesopores by intra- and interparticle sintering caused a rapid decrease in specific surface area and specific micromesopore volume as the temperature increased.

Diatomaceous earth (DE) is not derived from clay, but consists of granules mined from sedimentary rock deposits resulting from accumulation of amorphous silica comprising the cell walls of dead, single-celled aquatic organisms called diatoms (Handreck and Black, 2002). The usual commercial

function of DE is as an absorbent. Although some commercial growers are using this material as a root medium component, it is not expected to sorb PO₄-P because it lacks charged sorption sites.

Phosphate retention properties of clays after calcining are generally unknown, and the role of pH-dependent edge charge in the PO₄-P retention of calcined materials is untested. In addition, the calcined materials themselves may provide PO₄-P and other nutrients as fertilizer if natural levels are high. Therefore, this research characterizes several calcined clay materials and diatomaceous earth as a basis to evaluate their potential to reduce PO₄-P leached during container production when used as components of soilless root media. Specifically, we 1) determined inherent PO₄-P by extraction and total P present in the mineral; 2) determined initial pH of unaltered samples; 3) characterized PO₄-P sorption at natural pH; 4) developed PO₄-P adsorption envelopes under variable pH conditions to establish the role of pH-dependent edge charge on PO₄-P retention; and 5) determined the initial degree of phosphorus saturation of calcined materials.

Materials and Methods

The tested calcined materials are commercially available (Table 1). The test materials included various particle sizes of 2:1 clays of attapulgite (Attasorb; Engelhard Corp., Quincy, FL) calcined at two temperatures, RVM and LVM: LVM montmorillonite mined in Mississippi and LVM attapulgite mined in Georgia (Terra Green; Oil-Dri Prod. Co., Ripley, MS) and montmorillonite + illite

(Turface; Profile Products LLC, Buffalo Grove, IL); calcined 1:1 clays (Thiele Kaolin Co., Sandersville, GA) in powder form; and diatomaceous earth (Diatomite Eagle-Picher Minerals, Inc., Reno, NV). For ease of reference, the test materials were coded using trade name, temperature treatment, and particle size as mesh size designated by the manufacturer (Table 1). The materials were tested as received from the manufacturer.

Particle size distribution. Particle size distribution was determined by dry sieving. The sieving process was carried out using woven analytical precision sieves (USA standard testing sieves, ASTM specification; Fisher Scientific Co., Columbia, MD). Dry test materials were weighed to 1000 g and passed through a stack of eight sieves ranging from 5 mesh (4.0-mm nominal sieve opening) to 80 mesh (180-μm sieve opening) that were arranged in order of size with the smallest sieve at the bottom of the stack. Samples were uniformly shaken on a circular motion shaker set at 2.2 g_n for 5 min. Sample recovered in each sieve was weighed and the proportions calculated as a percentage of the whole test sample (Table 2) averaged across three replications.

pH measurements. The pH was measured on a slurry consisting of 5 cm³ test material to 10 mL deionized water. Mixtures were thoroughly stirred and allowed to settle for 10 min before reading pH (Oyster pH meter; Extech Instr. Waltham, MA) at 27 °C. The data were analyzed using PROC GLM in SAS ver. 9.1 (SAS Institute, 2002) with three replicates per material.

Phosphorus extraction. Naturally occurring P present in the calcined materials was

Table 1. Calcined material trade names, sample codes, and descriptions of test materials provided by their sources.

Trade name	Volatile material characterization ^z	Mesh size (standard US mesh)	Assigned code	Test material description ^y
Attasorb ^x	LVM	8/16	A-LVM-8/16	1% to 10% quartz 90% to 99% Fuller's earth ^w ; is a hydrous magnesium alumina silicate attapulgite; the deposits are on the Florida-Georgia border
Attasorb ^x	RVM	8/16	A-RVM-8/16	
Attasorb ^x	LVM	24/28	A-LVM-24/48	
Attasorb ^x	RVM	24/48	A-RVM-24/28	
Terra Green attapulgite ^v	LVM	24/48	T-A-24/28	10% to 20% quartz 80% to 90% Fuller's earth ^w ; from Georgia mines
Terra Green attapulgite ^v	LVM	16/30	T-A-16/30	
Terra Green attapulgite ^v	LVM	5/20	T-A-5/20	7% to 10% quartz 90% to 93% montmorillonite; from Mississippi mines
Terra Green montmorillonite ^v	LVM	24/48	T-M-24/28	
Terra Green montmorillonite ^v	LVM	16/30	T-M-16/30	
Terra Green montmorillonite ^v	LVM	5/20	T-M-5/20	
Turface ^u			Turface	Product of calcining a smectite clay at temperatures ranging from ≈540 °C to ≈1100 °C
Kaolin Hydrous ^t		Powder	K-Hyd-P	Hydrous kaolin
Kaorock ^t		Powder	K-LSA-P	Low surface area metakaolin
Kaocal ^t		Powder	K-P	Full calcined at 980 °C
Kaocal LA ^t		Powder	K-HSA-P	High surface area metakaolin calcined at less than 980 °C
Diatomite ^s			Diatomite	Diatomaceous earth consists of fossilized remains of diatoms, typical chemical composition of diatomaceous earth is 86% silica, 5% sodium, 3% magnesium, and 2% iron

^zLVM = low volatile material; clays calcined at ≈470 °C; RVM = regular volatile material; clays calcined at ≈180 °C.

^yTest material description was given in material safety data sheets (MSDS) from source unless stated otherwise.

^xEngelhard Corp., Quincy, FL.

^wFuller's earth usually has a high magnesium oxide content. Two varieties of Fuller's earth are mined, mainly in the southeastern states of the United States. These comprise the minerals montmorillonite or palygorskite (attapulgite) or a mixture of the two; some of the other minerals that may be present in fuller's earth deposits are calcite, dolomite, and quartz.

^vOil-Dri Prod. Co., Ripley, MS.

^uProfile Products LLC, Buffalo Grove, IL.

^tThiele Kaolin Co., Sandersville, GA.

^sEagle-Picher Minerals, Inc., Reno, NV.

Table 2. Particle size distribution of the 16 test materials.

	Sieve no.	No. 5	No. 8	No. 10	No. 18	No. 20	No. 35	No. 60	No. 80
Code ^z	Mesh size (standard US mesh)	4.0 mm	2.38 mm	2.00 mm	1.00 mm	0.85 µm	0.5 µm	0.25 µm	0.18 µm
Percent by weight ^y									
A-LVM-8/16	8/16		6	39	55				
A-RVM-8/16	8/16		3	40	57				
A-LVM-24/48	24/48					1	73	26	
A-RVM-24/48	24/48				1	2	71	25	1
T-A-24/28	24/48					1	77	21	
T-M-24/28	24/28				1	4	78	17	
T-A-16/30	16/30				77	11	11	1	
T-M-16/30	16/30				44	20	35	1	
T-A-5/20	5/20	2	37	17	32	2	8	2	
T-M-5/20	5/20	3	52	14	29	1	1		
Turface		1	42	24	29	4			
K-Hyd-P	Powder								100
K-LSA-P	Powder								100
K-P	Powder								100
K-HSA-P	Powder								100
Diatomaceous earth		3	84	8	5				

^zLVM = low volatile material; clays calcined at $\approx 470^\circ\text{C}$. RVM = regular volatile material; clays calcined at $\approx 180^\circ\text{C}$.

^yPercent (by weight) of given particle size.

evaluated with three methods: dilute acid extraction, Mehlich III (M3) extraction, and salicylic-sulfuric digestion. For dilute acid extraction, the weight of 5 cm³ of each test material was determined and measured into 50-mL Erlenmeyer flasks. Thirty milliliters of acid extractant consisting of 0.5 N HCl and 0.2 N H₂SO₄ was added. The flasks were placed on a circular motion shaker at 2 g_n for 10 h at $26.0 \pm 2^\circ\text{C}$, and after 10 h, the supernatant was transferred into 50-mL centrifuge tubes and centrifuged at 310 g_n for 5 min. Solution pH was adjusted by drop-wise addition of 5 M NaOH using p-nitrophenol as the indicator until the color of the sample just changed from colorless to yellow (Bender and Wood, 2000). Phosphate in the supernatant was then analyzed using the colorimetric method of Murphy and Riley (1962) on an ultraviolet/VIS spectrophotometer (Perkin-Elmer, Norwalk, CT). The experimental design was completely random (CRD) and each treatment was replicated three times. The data were analyzed using PROC GLM in SAS ver. 9.1 (SAS Institute, 2002).

Mehlich III (M3) extraction solution contained 0.2 N acetic acid, 0.25 N NH₄NO₃, 0.015 N NH₄F, 0.013 N HNO₃, and 0.001 N EDTA (Sen Tran and Simard, 1993). Mehlich III extractable P (1:5 test material:solution ratio) was analyzed with a Lachat-FIA system (Lachat FIA 800 series, Loveland, CO). The M3 procedure uses a strong acid extractant and estimates available P in acid soils. Two replications of each test material were run.

Finally, total P of the test materials was analyzed by colorimetric procedures after salicylic-sulfuric acid digestion (Bremner and Mulvaney, 1982; U.S. Environmental Protection Agency, 1984). The extract was analyzed by colorimetric procedures using the Technicon Auto Analyzer II (Technicon Industrial Systems, Tarrytown, NY). Two replications of each test material were run.

PO₄-P sorption isotherms. To characterize and compare P sorption of the calcined products, sorption isotherms were created for each test material. An amount equal in weight to 5 cm³ volume was measured into a 50-mL Erlenmeyer flask. Samples were equilibrated for 18 h with 30 mL of solution containing initial adsorbate concentrations of 0, 10, 25, 50, 100 and 200 mg·L⁻¹ PO₄-P prepared from KH₂PO₄ using deionized water. Treatment structure was factorial with three replicates of each material for each P concentration and experimental design was CRD. Flasks were placed on a circular motion shaker at 2 g_n for 10 h at $25 \pm 2^\circ\text{C}$ and then centrifuged at 310 g_n for 5 min. Equilibrium P concentration and pH of the supernatant were determined using colorimetric procedures (Chapman and Pratt, 1961; Murphy and Riley, 1962) and the pH meter described previously. The amount of P adsorbed by the clay sample was calculated as follows:

$$Q = v(C_i - C_f)/m \quad (1)$$

where Q is the amount of PO₄-P sorbed (mg·kg⁻¹ P calcined material), v is the liquid sample volume (L), C_i is the initial concentration of PO₄-P in the solution containing adsorbate (mg·L⁻¹), C_f is the final (equilibrium) concentration of PO₄-P in the supernatant solution (mg·L⁻¹), and m is the amount of the test material (kg, dry weight basis; Essington, 2004). Phosphate sorbed, Q , was presented as g·m⁻³ for ease of application to greenhouse container production.

The Freundlich equation, although considered purely empirical in nature, has been extensively used to describe ion adsorption by soils (Aslam et al., 2000; Chaudhry et al., 2003; Obaid-ur-Rehman et al., 2004; Sposito, 1980). The sorption isotherms were examined by modified Freundlich equations proposed by Le Mare (1982). The form of the modified Freundlich model is as follows:

$$P = aC^{b/a} \quad (2)$$

where P is quantity of sorbate (g) per unit volume (m³) of adsorbent, C is equilibrium solution concentration (mg·L⁻¹) of the adsorbate, “ a ” is the amount of PO₄-P sorbed (g·m⁻³) when the concentration C is 1 mg·L⁻¹, and “ b ” is the buffer power defined by the slope of the sorption curve at the point where $P/C = 1 \text{ L} \cdot \text{m}^{-3}$.

The main advantage of this equation is that “ a ” and “ b ” are the amount of P sorbed and buffer capacities, respectively, at the same point on the curve where $C = 1 \text{ mg} \cdot \text{L}^{-1}$, and this point is the same for all the test materials. In our research, the parameters “ a ” and “ b ” were estimated by regression of the logarithmic form of the data obtained from sorption isotherms. Therefore, a plot of $\log P$ (y-axis variable) against $\log C$ (x-axis variable) yields a straight line with slope b/a and y-intercept of $\log a$.

$$\log P = \log a + b/a \log C \quad (3)$$

From the Freundlich equation the parameter, “ a ” could be considered as a capacity factor and was referred to as P sorption capacity; this implies that a material having a larger “ a ” value has a larger sorption capacity than one with a smaller “ a ” value. Therefore, “ a ” value estimates were used to differentiate the P sorption capacities of calcined materials. The Freundlich equation does not predict or include a maximum adsorption capacity, but it is reliable with low solution P concentrations (Havlin et al., 2003). R values were determined for each Freundlich equation.

Adsorption envelopes. Adsorption envelopes were created to determine the amount of P adsorbed as a function of solution pH at the fixed total P concentration of 600 mg·L⁻¹. An amount equal in weight to 5 cm³ volume of eight test materials, A-LVM-8/16, A-RVM-24/28, T-A-24/48, T-M-24/28, T-M-5/20, K-LSA-P, Turface, and Diatomite (Table 1), were equilibrated for 10 h at 25°C with 25 mL KNO₃. A 2.5-mL aliquot of 600 P mg·L⁻¹ from KH₂PO₄ was added and pH adjusted to ranges of 2 to 10 at intervals of one unit using additions of 0.1 M HNO₃ or 0.1 M KOH. Samples were centrifuged as described previously, decanted, filtered, and analyzed for PO₄-P concentration as described previously. The experimental design was CRD with three replications of each treatment. Eight test materials were subjected to nine pH levels.

Degree of phosphorus saturation. Degree of P saturation (DPS) estimates how close the test material is to being saturated with PO₄-P (Sharpley, 1995). The DPS of the calcined materials was determined to compare the level of initial saturation with PO₄-P of each material's exchange sites. A DPS index (Pote et al., 1999) was created from soil test phosphorus (STP) determined by M3 extraction and a phosphorus sorption index (PSI) calculated from a single point isotherm (Bache and Williams, 1971; Sims et al., 2002). To establish the PSI, 30 mL of a 500

mg·L⁻¹ PO₄-P sorbate solution from KH₂PO₄ was added to 5 cm³ of test material, equilibrated on a shaker for 18 h at 25 ± 2 °C, and centrifuged as described previously. Phosphate was determined as described previously (Murphy and Riley, 1962). The PSI was calculated using the equation:

$$PSI = q(\log C)^{-1}$$

where q is the amount of P sorbed (mg·kg⁻¹) and C is the equilibrium solution P concentration (mg·L⁻¹). The second step involved estimating DPS_{STP} using the ratio of STP to (PSI + STP) and multiplying by 100: DPS_{STP} (%) = {STP(mg·kg⁻¹)/[PSI + STP(mg·kg⁻¹)]} × 100.

Results and Discussion

Particle size distribution, pH, and bulk density. Characterization of particle size distribution of the test materials is summarized in Table 2. Results follow U.S. standard mesh sizes.

Attasorb materials were alkaline with pH ranging from 8.2 to 8.7 (Table 3). Terra Green montmorillonites were acidic with pH ranging from 3.8 to 4.3, whereas Terra Green attapulgites were less acidic with pH ranging from 5.6 to 6.2. Turface and diatomite had pH values of 6.1 and 5.1, respectively (Table 3). The various calcined materials exhibited a wide range of pH. It is important for

a grower to be aware of the pH levels that root medium components contribute to a mix because they may influence nutrient retention and management during production.

Calcined materials have lower bulk density (less than 1 g·cm³) compared with most mineral soils, which have bulk densities between 1 and 2 g·cm³ (Hillel, 2004). Lower bulk densities after calcining indicate increased porosity of the test material. Compared with Attasorb and Terra Green materials, DE exhibited greater porosity (Table 3). Compared with clay soils, the granular test materials have the advantage of adding stable pore space to soilless root media, which contributes to beneficial physical properties in container production.

Phosphorus content of calcined materials. Total native P present in the materials was relatively high in the Attasorb and Terra Green attapulgites (700 to 2800 mg·kg⁻¹; Table 3). This significant amount of PO₄-P may provide some P fertilizer during production and/or remain in the container after the production cycle concludes. Kaolin test materials contained between 580 and 670 mg·kg⁻¹ P, whereas diatomite and Terra Green montmorillonite had the least native P at between 250 and 370 mg·kg⁻¹ P (Table 3). High levels of native P in the calcined materials might be expected to reduce PO₄-P sorption capacity.

Phosphorus was extracted from the test materials using two procedures, an acid ex-

traction and the M3 test, which was developed in North Carolina for routine analysis of P, potassium, calcium, magnesium, sodium, and micronutrients in acid soils. The two extraction methods yielded substantially different P contents (Table 3). Different chemical extractants are designed for soils depending on their chemical characteristics. Attapulgite test materials from two sources, which have pH ranging from 5.6 to 8.7, resulted in greater P extracted by 0.5 N HCl + 0.2 N H₂SO₄ than the M3 procedure, but the opposite was true for kaolinite test materials, which had pH of 4.5 to 5.3. The evolution of carbon dioxide during acid extraction of the Attasorb materials indicated a possible presence of free CaCO₃, which, in combination with the higher pH, suggested that the M3 test is not ideal for these calcareous clays. Results of the M3 test showed the influence of particle size on available PO₄-P with smaller sizes of the same material yielding more PO₄-P. Kaolinite materials KLSA and K-P yielded the most PO₄-P, 460 and 116 mg·kg⁻¹ PO₄-P, respectively, from the M3 procedure. Attasorb RVM materials yielded more available PO₄-P compared with LVM materials (45 to 92 mg·kg⁻¹ P and 6 to 14 mg·kg⁻¹ P, respectively).

PO₄-P isotherms. The isotherms, which are L-type according to classification of sorption isotherms by shape, indicate monomolecular adsorption of PO₄-P (Figs. 1A, 2A,

Table 3. Bulk density, pH, amount of P extracted from test materials from three different extraction procedures, degree of phosphorus saturation, P sorption index, and P sorption capacity, and buffer capacity calculated from the modified Freundlich equation.

Test material code name	pH ^z	Bulk density (g·cm ⁻³)	Total P ^{y,x} (mg·kg ⁻¹)	P ^w (mg·kg ⁻¹)	P ^{v,x} (mg·kg ⁻¹)	Degree of phosphorus saturation (DPS; %) ^a	P sorption index (PSI) ^t (q* ¹⁰ log C ⁻¹)	Amount adsorbed (P sorption capacity) "a" (g·m ⁻³) ^s	Buffer capacity "b" (L·m ⁻³) ^r
A-LVM-24/48	8.4	0.75	1,076 ± 198	306	14 ± 0.5	0.9	1,476	495	241
A-RVM-24/28	8.5	0.76	737 ± 156	534	92 ± 0.5	6.8	1,265	230	106
A-LVM-8/16	8.2	0.76	2,790 ± 147	231	6 ± 0.5	0.4	1,231	320	150
A-RVM-8/16	8.7	0.80	1,770 ± 14	146	45 ± 0.5	3.8	1,140	220	102
A-LVM-5/25	8.4	0.76	1,227 ± 150	245	20 ± 0.5	1.4	1,354	—	—
T-A-24/28	5.7	0.58	1,739 ± 212	166	70 ± 0.5	7.2	893	210	97
T-A-16/30	5.6	0.52	1,560 ± 97	250	34 ± 0.5	2.9	1,130	240	103
T-A-5/20	6.2	0.67	1,947 ± 88	60	39 ± 0.5	3.2	1,156	250	114
T-M-24/28	4.3	0.72	377 ± 11	37	107 ± 2.0	7.7	1,285	425	202
T-M-16/30	4.0	0.71	263 ± 31	19	65 ± 2.0	4.0	1,556	590	295
T-M-5/20	3.8	0.77	351 ± 21	78	35 ± 3.5	1.8	1,838	700	357
Turface	6.1	0.22	345 ± 22	22	27 ± 3.0	4.1	637	115	48
K-Hyd-P	4.2	0.19	264 ± 40	0.1	4 ± 0.0	0.5	736	100	36
K-LSA-P	4.6	0.15	656 ± 17	47	460 ± 20	27.7	1,199	120	48
K-P	5.3	0.12	652 ± 15	7	116 ± 0.5	13.9	725	70	25
K-HSA-P	4.5	0.26	581 ± 21	23	93 ± 1.0	4.8	1,832	130	53
Diatomite	5.1	0.37	259 ± 52	34	24 ± 3.0	4.8	475	28	10
Diatomite (calcined)	5.4	0.34	179 ± 4	28	20 ± 1.5	4.7	398	—	—
LSD _{0.05} ^q	0.44	0.014		36.7				56.5	71.3

^zpH measurements were taken on 1:2 (v/v) test material:deionized water.

^yFrom salicylic-sulphuric acid digest.

^xMean ± SD (n = 2).

^wFrom extract with 0.5 N HCl and 0.2 N H₂SO₄. Data are means of three replications; SE = 12.7.

^vFrom Mehlich III extraction procedure.

^aDegree of phosphorus saturation (DPS) estimated from PSI and Mehlich III P.

^tCalculated from a single-point isotherm based on 500 mg·L⁻¹ PO₄-P concentration.

^sFrom modified Freundlich model; "a" value estimates P sorption capacity.

^rFrom modified Freundlich model; "b" value estimates buffer power defined by the slope of the sorption curve at the point where quantity of sorbate (P)/equilibrium solution concentration (C) = 1 L·m⁻³.

^qLSD = least significant difference. Differences between means greater than the LSD indicate significant differences at P < 0.05. Different letters indicate statistically significant differences.

Fig. 1. $\text{PO}_4\text{-P}$ isotherms for Terra Green test materials (A) and pH of solution at various equilibrium P concentrations (B).

Fig. 2. $\text{PO}_4\text{-P}$ isotherms for Attasorb test materials (A) and pH of solution at various equilibrium P concentrations (B).

3A, and 4A). Using the parameter “a” from the Freundlich equation as a capacity factor, Terra Green montmorillonites had the highest $\text{PO}_4\text{-P}$ sorption (425 to 700 g m^{-3}). Terra Green attapulgites had lower $\text{PO}_4\text{-P}$ sorption (210 to 250 g m^{-3}) as shown in Table 3 and Figure 1A. Information obtained from the manufacturer of the Terra Green calcined materials indicated differences in the clays mined in Georgia versus Mississippi. The montmorillonites from Mississippi contained more Fe, whereas the product mined in Georgia had higher magnesium and calcium

content, which were capable of forming surface or solution precipitates with oxyanions. Differences in surface area may have influenced $\text{PO}_4\text{-P}$ sorption; however, the specific surface area provided by the suppliers ranged from $98 \text{ m}^2 \text{ g}^{-1}$ for Attasorb materials and 102 to $122 \text{ m}^2 \text{ g}^{-1}$ for Terra Green materials based on the standard Brunauer, Emmett and Teller procedure (Brunauer et al., 1938), which did not appear to be different enough to explain difference in $\text{PO}_4\text{-P}$ sorption.

Phosphate sorption levels of Terra Green materials increased with increasing initial pH. The T-M-16/30 and T-M-5/20 had the highest sorption with the initial pH range of 3.8 to 4.0 , whereas T-A-16/30, T-A-24/28, and T-A-5/20 had comparatively lower $\text{PO}_4\text{-P}$ sorption with initial pH ranging from 5.6 to 6.2 (Table 3). The high $\text{PO}_4\text{-P}$ sorption under lower pH could have involved the dissolution of Al in the clay lattice in the formation of AlPO_4 crystals. In acidic solutions, the mineral surface has a net (+) charge, although both (+) and (−) sites exist. The predominance of (+) charges readily attracts $\text{H}_2\text{PO}_4^{2-}$ (Havlin et al., 2003).

The Attasorb LVM materials had higher $\text{PO}_4\text{-P}$ sorption (“a” = 320 to 495 g m^{-3}) than Attasorb RVM materials (“a” = 220 to 230 g m^{-3}) as shown in Table 3 and Figure 2A. Particle size played a part in enhancing $\text{PO}_4\text{-P}$ sorption in Attasorb LVMs with the smallest particle size having higher sorption than larger particle sizes. It was observed that RVM materials had a tendency to disintegrate into smaller particles when in solution compared with the LVM materials; therefore, the difference between the eventual surface area of RVM clay particles was not as great, which explained the lack of effect of particle size on $\text{PO}_4\text{-P}$ sorption. The LVM materials demonstrated better aggregate stability than RVM materials and would be preferred for use as soilless root medium components. Owen et al. (2007) compared the use of two temperature treatments (RVM and LVM) of a Georgian palygorskite–bentonite calcined clay at 8% by volume of a bark-based root medium; the mix with LVM clay leached 35% less $\text{PO}_4\text{-P}$ than the mix containing RVM clay.

The Terra Green attapulgites that originated from Georgia, T-A-5/20, T-A-16/40, and T-A-24/48, resulted in $\text{PO}_4\text{-P}$ sorption capacity, “a”, of 250 , 240 and 210 g m^{-3} , respectively, showing no influence across these particle sizes on amount of $\text{PO}_4\text{-P}$ sorbed (Table 3). Ruter (2003) investigated the influence of three particle sizes of calcined clay (Sud-chemie, Meigs, GA) on $\text{PO}_4\text{-P}$ retention. He concluded that particle size had limited influence on amount of $\text{PO}_4\text{-P}$ sorbed when particle sizes were greater than 3.36 mm and less than 1.00 mm (24/48 US mesh) and within the range of 1.00 to 3.36 mm (5/20 and 16/30 US mesh), 61%, 76%, and 74% reduction of PO_4 leached occurred, respectively.

The slopes of the isotherms are indicators of buffer capacity with steeper slopes indi-

Fig. 3. The $\text{PO}_4\text{-P}$ isotherms for kaolin test materials (A) and pH of solution at various equilibrium P concentrations (B).

Fig. 4. $\text{PO}_4\text{-P}$ isotherms for diatomaceous earth and Turface test materials (A) and pH of solution at various equilibrium P concentrations (B).

cating higher buffering capacity (Ozanne and Shaw, 1968). Such plots can be used to estimate the quantity of P to be applied to maintain the soil solution concentration at the desired level (Fox and Kamprath, 1970). Material with high $\text{PO}_4\text{-P}$ sorption like Terra Green montmorillonites continued to sorb $\text{PO}_4\text{-P}$ at even the highest levels of added $\text{PO}_4\text{-P}$ (200 mg L^{-1} ; Fig. 1A). The higher $\text{PO}_4\text{-P}$ buffer capacity of these materials would necessitate greater P addition to achieve 0.2 mg L^{-1} soluble $\text{PO}_4\text{-P}$, which is considered optimum for most plants (Beckwith,

Fig. 5. Adsorption envelopes of PO₄-P in suspensions containing 50 PO₄-P mg·L⁻¹ in 0.01 M KNO₃ solution for the various test materials (A–B). Sorption is expressed as the fraction of the average PO₄-P adsorbed (mg·kg⁻¹) and maximum total PO₄-P concentration (mg·kg⁻¹).

1965), but ensures that the level of soluble PO₄-P is maintained for a longer period. As PO₄-P is removed from solution by the plant, there would be a less dramatic change in intensity (root medium solution PO₄-P concentration) in the more highly buffered media.

The buffer index from the slope of the Freundlich equation indicated that the kaolinite materials had very low buffer capacity (25 to 53 L·m⁻³; Table 3 based on Fig. 3A); they also had the lowest bulk density (Table 3). The kaolins are processed to achieve a low permeability, a property that would curtail sorption capability. Among the kaolin samples, K-HAS-P had the highest bulk density (0.26 g·cm⁻³) as shown in Table 3.

The relatively low PO₄-P sorption exhibited by Turface (Fig. 4A) could be as a result of high calcining temperatures of over 550 °C leading to the collapse of micro- and mesopores. Calcining temperatures play an important role in determining the sorptivity of the test materials.

Diatomaceous earth resulted in the lowest PO₄-P sorption. If diatomaceous earth increased PO₄-P retention after incorporation into soilless root media, the mechanism would not appear to be of a chemical nature.

pH. The pH of the supernatant after sorption remained fairly stable above the equilibrium concentration of ≈0.5 mg·L⁻¹ PO₄-P for all test materials (Figs. 1B, 2B, 3B, and 4B). This was an indication that the calcined clays could help stabilize pH of soilless root media, which often contribute to problems of pH drift because of their poor buffer capacity. In peat-based soilless root media, lack of cation exchange capacity and base saturation of peatmoss had been implicated as contributors to pH drift phenomena (Rippy et al., 2005). However, calcined clays would need to comprise a significant volume of the total root medium to stabilize problems with pH drift during production.

Adsorption envelopes. The Attasorb RVM material sorbed more PO₄-P with increasing pH with 0% sorbed at pH 2 to 3 and up to ≈90% sorbed at pH 10; ≈40% to 60% was sorbed at a pH range of 5 to 8 (Fig. 5B). The Attasorb LVM material, on the other hand, had 60% to 80% sorption over the pH range of 2 to 10, and the fraction generally increased as pH increased (Fig. 5B). The LVM materials (A-LVM-8/16, T-A-24/28) compared with an RVM material (A-RVM-24/28) showed yet another desirable characteristic of pH stability: sorption increased with increasing pH up to 6, and no significant change in PO₄-P sorption was observed from pH 6 to 9. Three possible mechanisms are proposed to explain the increasing PO₄-P sorption with increasing pH exhibited by Attasorb: precipitation of Ca phosphates, Ca-induced P sorption, or coadsorption of Ca and H₂PO₄⁻ or HPO₄²⁻ as ion pairs or complexes (Essington, 2004).

Terra Green montmorillonite of 5/20 mesh had a stable, high PO₄-P sorption of 98% over the entire pH range, whereas the smaller particle size of this material, 24/28 mesh, had a high sorption fraction of 85% to 90% between pH 2 and 8 with a sharp decrease in sorption after pH 8 to approximately only 20% PO₄-P sorption at pH 10 (Fig. 5B).

Turface had a stable PO₄-P sorption of ≈60% over the pH range of 3 to 10 (Fig. 5A). Diatomaceous earth had a small fraction of PO₄-P sorbed (15% to 30%), which decreased with increase in pH. Low surface area metakaolin (K-LSA-P) had a high PO₄-P sorption of 98% at pH 2 and 3, which decreased with increasing pH to 40% PO₄-P adsorbed at pH 10 (Fig. 5A).

The adsorption envelopes indicate that pH-dependent charge of the calcined materials is not a critical mechanism of PO₄-P sorption in greenhouse production. Laboratory results from various calcined clays demonstrate that the mechanism by which PO₄-P attaches to the surface of a calcined material is generally not pH-dependent within the pH ranges of 5.0 to 7.0 maintained during container production.

Degree of phosphorus saturation. The DPS was calculated using the ratio of M3 PO₄-P to the experimentally determined PSI (Bache and Williams, 1971; Pote et al., 1999; Sims et al., 2002; Table 3). The DPS of the calcined materials generally suggested that they possess significant capacity to sorb PO₄-P with DPS less than 7.7% for all materials except two of the 1:1 kaolinites (Table 3). The low STP and high PSI values associated with several of the calcined materials, namely Attasorb LVM and Terra Green attapulgites and montmorillonites, suggest that a large quantity of vacant sites exist for PO₄-P sorption.

In summary, several of the calcined materials that we characterized could be used as a component of soilless media to decrease PO₄-P leaching. Results of isotherm and DPS calculations indicated that the most promising materials were Terra Green montmorillonites and attapulgites and Attasorb LVM

attapulgites. The least promising materials were diatomaceous earth and kaolinites. The PO₄-P adsorption envelopes indicated that PO₄-P sorption was not strongly pH-dependent within the pH range of commercial production, indicating that pH-dependent charge is not a critical means of PO₄-P retention during greenhouse production. Calcining temperature affected optimal PO₄-P sorption: LVM attapulgites had better sorption than the RVM attapulgites that were calcined at lower temperatures, but Turface, which is also a 2:1 clay and calcined at a very high temperature, did not match the PO₄-P sorption potential of LVM Attasorb and LVM Terra Green attapulgites. Finally, the high level of native total P in some of the materials may provide some PO₄-P as fertilizer to crops.

Benefits of using calcined materials beyond PO₄-P retention may include increased water retention because the calcined products have significant moisture sorption properties, which are related to their primary commercial use as absorbents. The temperatures of calcining are crucial in determining the extent to which the hardened aggregates maintain internal porosity.

Limitations of using calcined products as soilless root medium components include the high cost of purchase and shipping, especially if used at high enough percentages in soilless root media to impart adequate benefit such as buffering against pH drift. Because the materials are mined, natural variability occurs at different mines and even mining depths within the same mine; this would contribute to lack of uniform and consistent quality attributes in the materials. Finally, if calcined materials with very high PO₄-P sorption capacity are used, the materials themselves may remove PO₄-P from root medium solution when used in tandem with very low rates of PO₄-P fertilization.

Future research should investigate optimal percentages of incorporation of calcined products into soilless media, especially under conditions of greenhouse production. The mechanism of PO₄-P sorption by the calcined materials is ambiguous and further research could elucidate these mechanisms. Phosphate desorption of the materials should be further evaluated. Finally, the economic benefits of reduced PO₄-P runoff in greenhouse effluent and reduced water use during production should be evaluated to help growers make decisions about using calcined materials.

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