

A Novel Phosphate Sorbent to Reduce Non-point Source Pollution and Increase Plant Production

Progress report for LNE19-387R

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Grant Recipient: West Virginia University

Region: Northeast

State: West Virginia

Project Leader:

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Project Information

Project Objective:

1. Determine if heavy metals present in some AMD sources would be incorporated into the coating and characterize their leaching potential;
2. Determine the operational parameters for the use of coated sand in the horticultural industry; and
3. Quantify any additional benefits from using coated sand in potting media such as improved root structure, increased flowering and improved post-production success.

Research

Hypothesis:

Coated sand, made from AMD, is a cost-effective phosphate sorbent that will allow the capture and reuse of dissolved phosphate in the greenhouse/nursery industries. This will result in reduction in fertilizer application and non-point source phosphate inputs to aquatic systems while reducing the amount of AMD sludge to be disposed of. It will also provide a constant source of phosphorus during production and post-production that will lead to increased profits for the growers.

Materials and methods:

Leaching of AMD coating

Coated sand is made using acid mine drainage (AMD) which may contain toxic heavy metals such as lead, copper or arsenic. The procedure used to make coated

sand will exclude many of the toxic heavy metals. Additionally, heavy metals that are in the coating could be bound to the sand and are not at risk of leaching into aquatic and terrestrial environments. However, it is essential that we understand which, if any, of the toxic heavy metals in the AMD might be present in coated sand and whether they can be leached from the coating. In this experiment we added any of the heavy metals not already present in the AMD to the highest concentrations found in the literature and followed our standard coating procedure. Both the sand and leachate were evaluated for heavy metal concentrations.

Seventy-five liters of raw AMD was collected from the Omega mine site south of Morgantown. The raw AMD was spiked with heavy metals at concentrations found in the literature. The pH was adjusted and the precipitated metals allowed to settle overnight. The supernatant was siphoned off and the precipitated was applied to sieved sand in the standard coating procedure. Supernatant and sludge samples were analyzed for aluminum (Al), arsenic (As), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), and zinc (Zn) via ICP-OES to determine the partitioning of metals.

Coated sand (250 ml/414 g) was placed in each of six 2 inch pots and watered with 250 ml tap water to thoroughly wet the sand. On subsequent days the sand was watered daily with 100 ml tap water. Leachate was collected on day 1, 14, 28, and 42 and analyzed for the metals listed above. Tap water was also analyzed for the same metals to differentiate between the contribution from the sand and what existed in the tap water.

A second leaching experiment was done with both coated sand spiked with heavy metals (n=2) and coated sand that had not been spiked (n=3). In this experiment we monitored leachate pH, sulfate, Fe, Al, Ca, Mg, and Mn concentrations.

Phosphate Sorption

Two experiments were performed to assess the efficacy of using coated sand to reduce phosphorous (P) concentrations in horticultural effluents: outside-pot-sorption (objective 2) and in-pot sorption (objective 3). The first, outside pot sorption, evaluated how well the coated sand removed P from pot leachate. In the second, in-pot sorption, coated sand was incorporated into the potting mix. In both experiments, plain sand was used as a control, and for the in-pot sorption, an additional control without any sand was included.

Outside-Pot Sorption



Phosphate sorption of leachate by coated sand was assessed by placing a tray of plain or coated sand beneath a pot planted with pansy, petunia, or chrysanthemum. Each tray was filled with 1 L (1,400g) of either plain or coated sand and covered with landscape fabric to prevent plant roots from colonizing the sand. Each tray had a drain that allowed the pot leachate to flow through the sand and drain to a sample bottle (Figure 1).

Pots were initially irrigated with deionized water. All subsequent irrigations included commercial fertilizer 15N-2.2P-12.5K (Peter Excel Cal-Mag; Everris NA, Marysville, OH) at three rates 150, 200, and 250 ppm nitrogen (N) for pansy, petunia, and chrysanthemum, respectively. The pots were fertigated as needed. Each species was grown until it reached a marketable size. Leachate volumes, nitrate,

Figure 1. Photo of Outside Pot sorption experimental setup.

ammonia, phosphate, sulfate, chloride, calcium, magnesium, iron, aluminum, and manganese concentrations were measured after each watering.

In-pot Sorption

P-saturated coated sand or plain sand was mixed with the standard potting mix at a ratio of 10, 20, 30, or 40%. A plain potting mix control was included for a total of nine treatments. Pansy, petunia, or chrysanthemum seedlings were transplanted in a 6" pot with five replications. Pots were initially irrigated with deionized water. At all subsequent irrigations, pots were fertigated with Hoaglands fertilizer solution made either with or without P. Pot leachate was collected from each pot and the leachate volume was determined. Phosphate concentrations were determined on the leachate at each fertigation. Electrical conductivity, pH, and chloride, sulfate, calcium, magnesium, and manganese concentrations were determined every two weeks.



Figure 2. Photo of in-pot sorption experimental setup

Research results and discussion:

Metals partitioning

The metals in AMD were primarily Fe (42%), Ca (26%), Al (20%), and Mg (8%). The percentage of these metals changes when the pH is adjusted during the precipitation process. Fe was still the predominant metal accounting for 63% while Al accounted for 31% of the mass. The metals partitioning between supernatant and precipitate was metal-specific. The metals Ca, Co, Mg, Mn, Ni, Sr, and Zn remained predominately in the supernatant while the metals Al, As, Cd, Cr, Cu, Fe, Pb, and Sb were predominately in the precipitate. Despite being major components of the AMD, Ca and Mg accounted for just 1.7 and 0.6% respectively of the precipitate mass. The majority of the As, Cr, Cu, Pb, and Sb precipitated; however, due to low concentrations in the raw water, they comprised just 3.6% of the mass of the precipitate. These results likely over estimate the percentage of metals precipitated as we used the highest concentrations reported in the literature. Additionally, there may have been interactions between metals that would not naturally occur as they would not be found together.

Leaching

The pots of coated sand were watered daily with tap water with samples being taken on days 1, 14, 28 and 42. Metal concentrations in the pot leachate were highest on the first day with most metals decreasing in concentration over time (Table 1). The metals with the highest concentrations were Ca and Mg with concentrations of 6,501 and 18 mg/L, respectively on day 1. These concentrations decreased rapidly over time with concentrations around or below tap water concentrations by day 42. Fe, the metal making up most of the coating had

concentrations of around 0.1 mg/L through the entire experiment. Concentrations of Al ranged from 0.7 to 1.0 mg/L. Concentrations of most of the other metals were less than 0.05 mg/L with Cd, Co, and Cu concentrations generally below detection. However, As concentrations ranged between 0.20 - 0.45 mg/L, Cr concentrations were initially 0.8 mg/L but dropped quickly and most troubling, initial Sr concentrations were 10 mg/L. These results indicate that AMD that contains heavy metals such as Al, Fe, Mn, and Co can be used to coat sand without concern as they are either not incorporated into the coating or they do not leach. However, AMD that contains Sr, Cr or As should not be used.

Metal	LEACHATE								Tap Water	Drinking Water Std.
	Day 1		Day 3		Day 28		Day 42			
	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.		
Al	0.97	0.05	0.54	0.03	0.77	0.05	0.68	0.02	0.32	0.20
As	0.45	0.02	0.25	0.01	0.20	0.04	0.43	0.02	<0.009	0.01
Ca	6,501	486	576	11	77	27	29	1	43.62	
Cd	BDL		BDL	BDL	0.01	0.00	BDL		<0.004	0.005
Co	BDL		BDL	BDL	<0.002	BDL	BDL		<0.002	
Cr	0.80	0.06	0.02	0.00	0.02	0.01	BDL		<0.009	0.1
Cu	BDL		BDL	BDL	0.04	0.01	BDL		0.02	1.3
Fe	0.32	0.06	0.302*		0.07	0.02	0.10	0.06	<0.002	0.30
Mg	17.8	0.7	10.1	0.6	7.1	0.4	9.7	0.4	8.4	
Mn	0.01	0.00	BDL	BDL	0.03	0.01	BDL		<0.005	0.05
Ni	0.01		BDL	BDL	0.04	0.01	BDL		<0.030	
Pb	0.02	0.00	BDL	BDL	0.05	0.02	BDL		<0.008	0.015
Sb	0.03	0.01	0.03	0.01	0.07	0.01	0.02	0.00	<0.015	0.01
Se	0.09*		<0.019	BDL	0.09	0.06	BDL		<0.019	0.06
Sr	10.35	0.11	0.58	0.01	0.10	0.02	0.07	0.00	0.52	
Zn	0.01	0.00	0.90**		0.02	0.01	0.04	0.04	0.01	5.00

BDL - Below Detection Limit, *reported value is from the one sample in five that was above the detection limit

A second leaching experiment was done where pot leachate was collected daily to examine how leachate varied over shorter time periods. We used the remaining spiked coated sand (2 pots) and regular coated sand (3 pots) and measured pH, and sulfate, Fe, Al, Ca, Mg, and Mn concentrations.

The pH of the leachate varied between 7.5 and 8.8 with a mean of 8.2. The pH of tap water ranged between 7.5 to 8.0. Initial sulfate concentrations were between 434 to 494 mg/L and then increased to a maximum of 2443 mg/L on day 5. The concentrations decreased such that by day 18 the sulfate concentrations were 170 to 300 mg/L. Sulfate concentrations continued to decrease but at a slower rate and were 70 mg/L at the end of the 30 day experiment. Tap water concentrations ranged between 55-75 mg/L.

Initial calcium and magnesium concentrations were extremely high on the first day, 8899 and 534 mg/L, respectively. Calcium concentrations decreased to around 100 on the next 3 days before increasing again to a high of 610 mg/L on day 8 after which concentrations decreased slowly to 116 mg/L by day 20. Concentrations at the end of the experiment were comparable to tap water at 30 mg/L. Magnesium concentrations followed the same pattern with concentrations around 30 mg/L on days 2 through 5 increasing to 40 on day 8 and they decreasing to 19 by day 11. Concentrations decreased to 7.3 by day 22 and then increased to 12 at day 30.

Fe, Al, and Mn were all at low concentrations. Initial iron concentrations were 0.57 mg/L but dropped to 0.35 mg/L by day 3 and further decreased to 0.10 mg/L by day 10. From day 20 to day 30 concentrations were 0.03 to 0.05 mg/L. Aluminum concentrations varied between 0.23 to 1.1 mg/L with no apparent pattern. Initial manganese concentrations were 0.24 but dropped to 0.03 mg/L on day 2 and remained less than 0.06 for the remainder of the experiment with an average concentration of 0.02 mg/L

The leaching experiments demonstrated that the coated sand needs to be rinsed before use to remove sulfate, calcium and magnesium which leach at high concentrations. The rinsing will also remove heavy metals that are loosely bound. The pH of the leachate was generally stable. The experiments confirmed previous experiments where the major metals in AMD (Fe, Al, and Mn) were retained within the coating with insignificant losses to the leachate. A washing protocol for the coated sand has been developed to avoid the initial flush of metals when the coated sand is used. Leaching analysis will be done on washed coated sand that was spiked with heavy metals to ascertain efficacy of the procedure in removing those metals. Additionally, SEM will be done on both washed coated sand and washed coated sand spiked with heavy metals to evaluate the presence of metals within the coating.

P sorption

Outside Pot Sorption

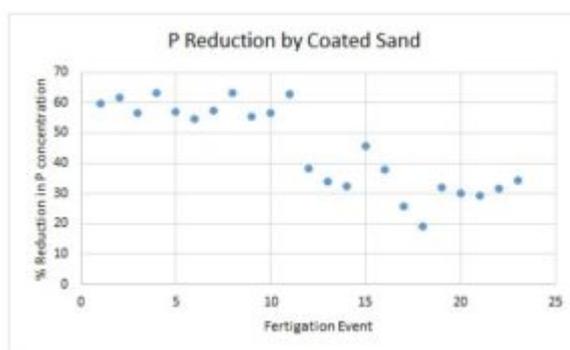


Figure 3. Reduction in P concentration at each fertigation.

Coated sand was effective at sequestering substantial amounts of phosphorous. Pansy, receiving the lowest fertilizer concentration, had 56% of the P removed, while petunia, receiving a medium fertilizer concentration, and chrysanthemum receiving the highest concentration of fertilizer, removed 51% and 41% of the P, respectively. Through the first eleven fertigations, the coated sand removed 59% of the P, while, it removed 33% of the P in the remaining twelve fertigations (Figure 3).

There does not appear to be any sorption of either nitrate or ammonium by the coated sand (data not shown). Conversely, 80% of the manganese in the leachate was removed by the coated sand. Initial calcium and magnesium concentrations were five and two times higher in the coated sand samples, respectively. Over the course of the experiment, calcium and magnesium concentrations gradually decreased. Iron and aluminum concentrations were comparable between the plain and coated sand indicating that the AMD coating was not breaking down and releasing either iron or aluminum. Data analysis is ongoing.

In-pot Sorption (currently in progress)

The higher the proportion of coated sand in the potting media the greater the amount of P sorbed. In the initial fertigation, in pots with 10% coated sand and receiving fertilizer with P, 35 to 38% of the P was sorbed, and increased to 86 to 91% in pots with 40% coated sand. P sorption is decreasing slightly with each subsequent fertigation. In pots receiving fertilizer without P, the P in the potting media itself is mostly retained within the pot. In pots with 10% coated sand, only 2 to 6% of the P was present in the leachate. Pots with higher proportions of coated

sand retained more P. The P supplied by the potting mix and present in the leachate is decreasing with each fertigation.

Participation Summary

Education & Outreach Activities and Participation Summary

PARTICIPATION SUMMARY:

Outreach description:

In February of 2020, we attended the West Virginia University Small Farms Conference and surveyed consumer perception of iron-coated sand. We had 48 respondents. Of those respondents, nearly half were crop producers: farmers (33%), high tunnel (8%), and greenhouse (4%) producers. Home gardeners consisted of about one-third (31%), while 23% of respondents identified themselves as other. The majority of the respondents, 81%, felt that controlling phosphorus runoff is important. Also, 60% of the respondents indicated they were likely to use the iron-coated sand. When the respondents were asked how likely they were to purchase plants grown in coated sand, 77% indicated they were likely to purchase these plants. A small group (8%) of respondents would like to see an alternative source of iron for coating the AMD. In general, most of the respondents supported using the AMD iron-coated sand in the agricultural industry.

Additional Information on Why Participants Chose Their Answers:

- Of the 77% that indicated they were likely to purchase plants grown in coated sand, 25% cited environmental concerns as their primary reason (the most common reason), 22.2% cited crop quality as their primary reason, and 16.6% cited being open to trying something new as their primary reason.
- Of the 33% that were not likely to purchase plants grown in coated sand, 83% of those respondents said their primary reason was that they did not purchase plants (they grew from seed or cuttings). The remaining 17% said they needed more information before considering purchasing.
 - This indicates that no one was directly opposed to the iron-coated sand.
- Of those 8% that wanted an alternative source, half said they needed more information on AMD before accepting it as a source.
- When asked if they would use iron-coated sand in their current operation, 26.7% were neutral towards the idea, and 2/3rds of those people cited needing more information on effects or costs as their primary reason.
 - This indicates that education and research could influence more people to use the sand.

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