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Comparison of Phosphorus Sorption by Light-Weight Aggregates Produced in the United States*1

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ABSTRACT

In this study, phosphorus (P) sorption of thirteen light-weight aggregates (LWAs) from USA was compared during batch equilibrium experiments in order to identify those materials which had the highest P sorption capacity for further study. Seven different levels of sorption activity were observed, which were broadly grouped into three categories—high performing, middle performing, and low performing aggregates. Chemical analysis of Ca, Al, Fe, and Mg was used to describe the differences between LWAs. There was a significant correlation between cation (especially Al, Ca, Fe, and Mg) content and P sorbed. Langmuir isotherms were used to describe P sorption maximum and binding affinity for four of the top five performing LWAs, Universal, Stalite "D", Stalite "Mix", and TXI. The fifth aggregate, Lehigh, exhibited more complex sorption, and was better described by the Freundlich isotherm. Universal had a mean P sorption at the highest concentration of 824 mg kg^{-1}, well above its calculated sorption maximum (702 mg kg^{-1}), and also had the highest binding affinity (1.1 L mg^{-1}). This experiment suggests that the top performing LWA (Universal) may perform poorly in column and field studies due to observed precipitates, which could degrade constructed wetland performance. Other LWAs may exhibit superior field performance due to their high calculated sorption maxima. In general, these results highlight the importance of batch experiments as a first step in identifying materials suitable for column and field experiments.

Key Words: binding affinity, constructed wetlands, equilibrium P concentration, media, P sorption capacity

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Water pollution, a significant and growing problem, results from excessive amounts of nutrients entering U.S. waterways. One of the most serious impacts of excessive nutrient load is the 20 000 km^2 "dead-zone", extending from the mouth of the Mississippi River into the Gulf of Mexico (Donner and Kuchharik, 2008). Because phosphorus (P) is typically a limiting nutrient in natural freshwater systems, excessive amounts of P result in eutrophication in these systems. Eutrophication damages waterways by lowering the dissolved oxygen content, causing fish kills, increasing sedimentation, and significantly altering the ecology of the water bodies and waterways. These alterations lead to the impairment of both the economic and recreational uses of the waterway (USEPA, 2000a). The Environmental Protection Agency's National Water Quality Inventory report (1996) identified excessive nutrients as the leading cause of impairment in lakes and the second leading cause of impairment in rivers (USEPA, 2000b). The threat posed by nutrients to the nation's lakes and rivers is not a simple problem to solve. Nutrient pollution occurs from both point and non-point sources. Fertilizer is a major source of P pollution. Much of the world's food supply, and consequently economic health, depends on the use of fertilizers to produce the food we need. Increases in corn production to meet ethanol demand could increase P loading to watersheds by 25% (Simpson *et al.*, 2008), thus further degrading already stressed watersheds in the United States.

One recommended management practice for controlling nutrient pollution is to design constructed wetlands (CWs, USEPA, 2005). Constructed wetlands are used in a wide array of wastewater treatment applications from acid mine drainage to helping achieve tertiary treatment of municipal wastewater (USEPA, 2005). CWs are useful in small- to medium-scale wastewater situations where conventional tertiary control of wastewater is not economically feasible. However, the use of CWs to remove P is limited by the media

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used in CWs. Horizontal subsurface-flow CWs are typically constructed 70–80 cm deep, with some type of liner material and dikes high enough to provide a measure of “free board” for rain events as well as to prevent surface water from entering during storm and associated run-off events. Wastewater is channeled through a vegetated soil matrix providing more water to soil contact and greater P adsorption. Subsurface-flow wetlands require a substrate material with a sufficiently high hydraulic conductivity to avoid short-circuiting. Typically, sands or gravels have been used as media in CWs, but these materials have poor P sorption performance. What is needed is a substrate material that possesses both excellent hydraulic conductivity and P adsorption capacity. One such promising class of materials is expanded clay, shale, or slate aggregate, also known as light-weight aggregate (LWA).

LWAs have been used in structural concrete and masonry applications for the last 80 years and their use has expanded into geotechnical applications as light-weight fill (Holm and Valsangkar, 1993). Their unique properties make them an interesting class of material for constructed wetland applications. LWAs are produced from clay, slate, or shale aggregate by heating over 1 150 °C in rotary kilns. This intense heating causes the material to expand and become pliable as mineral oxides off-gas. These gases form a multitude of individual bubbles which expand and bloat the material to 1.5–2 times its original size. The expanded material is very durable, with a cellular structure consisting of non-interconnected pores (Holm and Valsangkar, 1993). This cellular structure means that LWAs typically have low specific gravities (1.25–1.40, oven dried) and are more permeable than conventional fill material for CWs.

The ability of submerged LWAs to adsorb water over time indicates LWAs might possess more sites for sorption than conventional fill materials for CWs. However, some LWAs have shown significant P sorption capacity (Zhu *et al.*, 1997) while others were shown to be chemically inert (Johansson, 1997). Zhu *et al.* (1997) compared various LWAs that were mostly European LWAs but included one USA product. They found that the USA produced LWA (Utelite®) surpassed all other LWAs in P adsorption performance. Utelite® sorbed more P, by an order of magnitude, than an iron-rich sand aggregate.

Finally, there is a more practical advantage to using LWAs in constructed wetland applications. LWAs provide more volume per unit weight than typical sand or gravel aggregate, which would lower transportation and construction cost for CWs. Additionally, LWAs provide a significantly greater surface area for P sorption and microbial growth when compared to the same amount of sand/gravel aggregate without decreasing the porosity of the medium. This is important because P control is achieved predominantly through sorption processes. It is anticipated that at some point a constructed treatment wetland’s ability to sorb P will become compromised. Possible solutions are to replace the wetland, essentially rebuild it, or add pre- and/or post-filters comprised of LWA. Additionally, the reduced costs of LWAs may allow operators to install pre- and post-treatment LWA filters to existing constructed wetland systems depending on site conditions and land availability.

A comparison of 13 USA produced LWAs would help identify potential LWAs for further study and eventually increase the use of LWAs in constructed wetland applications in USA. Comparing the 13 LWAs also helps identify patterns based on geologic formation. It is important to evaluate LWAs resulting from different geologic formations, since chemical composition is critical to P sorption capabilities. Comparing USA produced LWAs would assist wetland designers in choosing more appropriate materials for their projects. Although laboratory isotherm experiments do not exactly replicate conditions in the field, they provide a means to quantitatively evaluate the P sorption capacity of a substrate. Substrates with low P sorption capacities will typically perform worse in field experiments than substrates with high P sorption capacities (Mann and Bavor, 1993).

This study was conducted to compare the performance of various USA produced LWAs to sorb P during batch equilibrium experiments. This study is believed to be the first comparison study of USA produced LWAs and is modeled after a study by Zhu *et al.* (1997) comparing several LWAs and natural sands in Norway. The specific objectives for this study were: i) to determine sorption maxima and sorption constants which would provide information about the binding affinity of the aggregate for P; ii) to determine equilibrium P concentration at zero net P sorption (EPC_0); and iii) to compare materials using chemical composition, sorption maxima, binding affinity, and EPC_0.

MATERIALS AND METHODS

Light-weight aggregates

Seven companies provided 13 LWAs with three companies providing more than one product. Universal Aggregates, W. Mifflin, PA, USA provided a coal furnace by-product (Universal) that is composed of