Chemosphere 83 (2011) 978–983

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Aluminum water treatment residuals as permeable reactive barrier sorbents to reduce phosphorus losses

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ARTICLE INFO

Article history:
Received 23 November 2010
Received in revised form 4 February 2011
Accepted 6 February 2011
Available online 4 March 2011

Keywords:
Permeable reactive barrier
Water treatment residual
Adsorption/desorption kinetics
Phosphorus

ABSTRACT

Two aluminum water treatment residuals (Al-WTRs) from water treatment plants in Manatee County, FL and Punta Gorda, FL were evaluated as potential permeable reactive barrier (PRB) media to reduce groundwater phosphorus (P) losses. Short-term (<24 h) P sorption kinetics and long-term P sorption capacity were determined using batch equilibration studies. Phosphorus desorption was characterized following P loadings of 10, 20, 30, 40 and >70 g kg^{-1}. Sorption and desorption studies were conducted on the <2.0 mm material and three size fractions within the <2.0 mm material. The effect of dissolved organic carbon (DOC) on P retention was determined by reacting Al-WTRs with P-spiked groundwater samples of varying initial DOC concentrations. Phosphorus sorption kinetics were rapid for all size fractions of both Al-WTRs (>98% P sorption effectiveness at shaking times $\geqslant$2 h). The effect of DOC was minimal at <150 mg DOC L^{-1}, but modest reductions (<22%) in P sorption effectiveness occurred at 587 mg DOC L^{-1}. The P sorption capacities of the Manatee and Punta Gorda Al-WTRs (<2.0 mm) are ~44 g kg^{-1} and >75 g kg^{-1}, respectively, and the lifespan of an Al-WTR PRB is likely many decades. Desorption was minimal (<2% of the P sorbed) for cumulative P loadings <40 g kg^{-1}, but increased (<9% of the P sorbed) at cumulative P loads >70 g kg^{-1}. The <2.0 mm Manatee and Punta Gorda Al-WTRs are regarded as ideal PRB media for P remediation.

1. Introduction

Over the last three decades, Lake Okeechobee, FL has experienced accelerated eutrophication due to excessive phosphorus (P) inputs from agricultural activities that dominate land use in the watershed (Hiscock et al., 2003). Ditch networks are used throughout the basin for drainage and irrigation purposes, and the network has effectively modified the hydrologic regime of extensive areas of the Lake Okeechobee Basin (LOB). The ditch system serves as a rapid conduit for transport of P to Lake Okeechobee. Intensive P management strategies are necessary to reduce P loadings sufficiently to meet the ecological restoration target, and interception and treatment of P entering the drainage ditch water is suggested here as an appropriate management strategy.

Permeable reactive barriers (PRBs) are a proven technique for groundwater remediation, with many years of operation continually meeting the design goals at most sites (e.g. Puls et al., 1999; Blowes et al., 2000; Henderson and Demond, 2007), but the success of the technology depends on the selection of a viable reactive medium. The primary criterion for selecting a medium is reactivity with the target contaminant. Sorption reactions are emphasized as appropriate mechanisms for P removal in the LOB; thus, PRB media should possess the ability to irreversibly bind P for a long time (high sorption capacity and long-term stability). Further, contact time between PRB media and P-laden groundwater is likely limited during high rainfall events due to rapid lateral groundwater movement, and rapid (<24 h) P retention kinetics of PRB media are likely critical to reducing P export from the landscape. A PRB medium should also have physicochemical and hydraulic properties that mimic the native soil to minimize deleterious effects to the native hydrology and vegetation, and be regionally available in sufficient and economically feasible quantities (Day et al., 1999).

Water treatment residuals are attractive PRB medium for use in environmental P remediation because the residual components (particularly the metal hydroxides/oxides) in the WTRs are reactive. Aluminum-WTRs (Al-WTRs) are residuals from the use of alum [$Al_2(SO_4)_3 \cdot 14H_2O$] during the drinking water purification process. The residual product consists primarily of sediment, amorphous Al hydroxides/oxides, activated carbon, and polymers

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Abbreviations: Al-WTR, aluminum–water treatment residual; Alox, oxalate-extractable aluminum; DOC, dissolved organic carbon; LOB, Lake Okeechobee basin; P, phosphorus; PRB, permeable reactive barrier; PSI, phosphorus saturation index; PSE, phosphorus sorption effectiveness; S_{max}, maximum P sorption capacity.

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doi:10.1016/j.chemosphere.2011.02.014

removed from water during the treatment of source waters. These residuals are attractive for use in environmental P management because the Al oxide/hydroxide components of Al-WTRs can irreversibly bind large amounts of P (Makris et al., 2004, 2005). Reported Al-WTR maximum P sorption capacity (S_{max}) values range from 0.7 to 175 g kg^{-1} (Dayton et al., 2003; Novak and Watts, 2004; Makris et al., 2005; Babatunde et al., 2009). The variability in S_{max} values is primarily attributed to differences in the amount of amorphous (oxalate extractable) Al present in the WTR (Gallimore et al., 1999; Elliott et al., 2002), and differences in specific surface area (microporosity; Makris et al., 2005). Differences in these properties are, in turn, attributed to source water chemistry, alum loading rates used during water treatment, and processing (drying) of the residual. Aluminum-WTR P sorption kinetics are biphasic, with rapid initial sorption (~24 h; Makris et al., 2004), followed by a slower second phase that continues for weeks (Makris et al., 2005). Novak and Watts (2005) showed that P sorption kinetics were inversely related to Al-WTR particle size, and that particle size strongly influenced Al-WTR S_{max} and P sorption kinetics. Aluminum-WTRs are not influenced by redox conditions (O'Connor et al., 2005), and Al-WTR retained P is stable within the pH range (pH 4–7) common to most soils of agricultural importance (Agyin-Birikorang and O'Connor, 2007). Aluminum-WTRs are useful for controlling P mobility in most soils (Elliott et al., 2002; O'Connor et al., 2005; Agyin-Birikorang et al., 2007) and warrant further investigation as a viable PRB media.

Many of the high-P containing soils in the LOB are impacted from legacy applications of manures (Nair and Graetz, 2002), and groundwater at these sites can contain appreciable quantities of dissolved organic carbon (DOC). Lane (2002) reported a 20% reduction in Al-WTR P sorption capacity when solution DOC concentrations were increased from 0 to ~87 mg L^{-1}, suggesting that the effectiveness of an Al-WTR PRB could be reduced given the groundwater DOC concentrations expected at manure impacted sites. Further, the stability of P sorbed in the presence of high DOC is unknown.

We surveyed water treatment facilities in Florida, and the operators of the water treatment facilities in Bradenton (Manatee County Water Treatment Plant) and Punta Gorda (City of Punta Gorda Water Plant) reported considerable quantities of Al-WTR production (37 650 and 240 Mg yr^{-1}, respectively) of sufficient solids content (reported as 50–90%). Both these facilities were within a financially feasible transportation distance and thus warranted further investigation as potential PRB media. The objectives of the study were to (i) determine the physiochemical and hydraulic characteristics of the Manatee and Punta Gorda Al-WTRs, (ii) evaluate the rapid (<24 h) P sorption kinetics of various size fractions of candidate Al-WTRs, (iii) determine the effect of DOC on Al-WTR sorption effectiveness (iv) determine the maximum P sorption capacity (S_{max}) and P desorption characteristics (bulk material and various particle size fractions) of candidate Al-WTRs, and (v) integrate these findings to estimate the "life-span" (time before S_{max} is exceeded) of an Al-WTR PRB under various field scenarios.

2. Materials and methods

2.1. Physiochemical and hydraulic properties

A ~15 kg sample of the Punta Gorda Al-WTR was shipped directly from the City of Punta Gorda Water Treatment Facility to our research group in August, 2009. About 30 kg of Manatee Al-WTR archived from a previous study (Agyin-Birikorang and O'Connor, 2007) was also utilized. The Al-WTRs were sieved (<2.0 mm) and thoroughly mixed to create homogeneous sub-samples. Physicochemical and hydraulic properties (particle size distribution, organic matter content, pH, EC, oxalate-extractable P, Fe, and Al, hydraulic conductivity, bulk density, and porosity) of the Al-WTRs were determined in triplicates using standard methods, as described in the Supporting information section.

2.2. Short-term phosphorus sorption kinetics

Short-term (<24 h) P sorption kinetics were determined on four size fractions of the Manatee and Punta Gorda Al-WTRs: bulk sample (<2 mm; termed "sieved"), very coarse sand, coarse sand, and medium sand (0.25–2.0 mm; collectively termed "coarse sand"), fine and very fine sand (0.045–0.25; collectively termed "fine sand"), and silt and clay (<0.045 mm). Particle size distribution was determined using standard laboratory methods for sand-size dry fractionation (NRCS, 2004) with no chemical pretreatment.

A batch equilibration study was conducted as described in Supporting information. Samples were reacted with 5 mg P L^{-1} solution (1:20 soil:solution ratio; 50 mg kg^{-1} maximum P load) on a platform shaker for 0.5, 1, 2, 4, 8, 16, and 24 h. Each treatment (Al-WTR × 5 mg P L^{-1} concentration) was conducted in triplicate. Equilibrium P concentrations were determined colorimetrically (Murphy and Riley, 1962), and the amount of P sorbed calculated as the difference between the initial P load (adjusted to account for residual P contribution) and the equilibrium solution P mass. Phosphorus sorption effectiveness (PSE) was determined by dividing the mass of P sorbed by the mass of P added, and expressed as a percent.

Time series analyses were conducted using the PROC TSCSREG procedure of the SAS software (SAS Institute, 2009) to compare P sorption at each shaking time. The system was considered to be in equilibrium when no significant differences in P sorption occurred among the subsequent shaking times. Differences in PSE among Al-WTR size fractions were statistically analyzed for each shaking time to determine the effect of size fraction on P sorption kinetics. Means were tested for separation using Tukey's mean separation procedure at a significance (α) level of 0.05. All data conformed to the normal distribution and constant variance assumptions of analysis of variance.

2.3. Al-WTR P retention in the presence of DOC

Four shallow groundwater samples (<1 m below the ground surface) were collected from a ~14 ha manure impacted pasture in the LOB. Samples were filtered (0.45 μm), acidified (pH < 2.0), and analyzed for DOC (Shimadzu TOC 5050; EPA 415.1, WBL-AN-011). The samples possessed DOC concentrations of 25.5, 59.5, 148, and 617 mg L^{-1}. The groundwater containing 617 mg L^{-1} was diluted 2-fold and 4-fold to provide additional DOC concentrations of 308 and 154 mg L^{-1}, respectively. Each of the groundwater samples was spiked using a 1000 mg L^{-1} P standard to mask differences in P concentrations and obtain a uniform P concentration of 50 ± 0.6 mg L^{-1} (mean ± standard error). The final DOC concentration of each sample was adjusted to account for the dilution (<5% of the total sample volume) associated with the P addition. Spiked (50 mg P L^{-1}) 0.01 M KCl (negligible DOC) was used as the control matrix.

A batch equilibration study (1:20 solid:solution ratio; 1 g kg^{-1} P load) was conducted according to the method described in Supporting information. Each treatment (Al-WTR × DOC concentration) was conducted in triplicate. Cumulative P loadings differed slightly (<0.24 g P kg^{-1}) among treatments, so the effect of DOC concentrations on P sorption was determined by comparing PSE differences among treatments.

Three 24 h, 1 g kg^{-1} P loading events were conducted in succession. The equilibrium solution was removed from the centrifuge tubes following the final P loading event, replaced with zero-P