



Reliability analysis of nutrient removal from stormwater runoff with green sorption media under varying influent conditions



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HIGHLIGHTS

- Developed new technology to control nutrient leaching beneath stormwater infiltration basins, rapid infiltration basins, etc.
- Extended functional characterization of reaction kinetics of nutrient adsorption/absorption
- Utilized green sorption media to increase sorption capacity to reduce nutrient fate and transport impact

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ABSTRACT

To support nutrient removal, various stormwater treatment technologies have been developed via the use of green materials, such as sawdust, tire crumbs, sand, clay, sulfur, and limestone, as typical constituents of filter media mixes. These materials aid in the physiochemical sorption and precipitation of orthophosphates as well as in the biological transformation of ammonia, nitrates and nitrites. However, these processes are dependent upon influent conditions such as hydraulic residence time, influent orthophosphate concentrations, and other chemical species present in the inflow. This study aims to compare the physiochemical removal of orthophosphate by isotherm and column tests under differing influent conditions to realize the reliability of orthophosphate removal process with the aid of green sorption media. The green sorption media of interest in this study is composed of a 5:2:2:1 (by volume) mixture of cement sand, tire crumb, fine expanded clay, and limestone. Scenarios of manipulating the hydraulic residence time of the water from 18 min and 60 min, the influent dissolved phosphorus concentrations of $1.0 \text{ mg} \cdot \text{L}^{-1}$ and $0.5 \text{ mg} \cdot \text{L}^{-1}$, and influent water types of distilled and pond water, were all investigated in the column tests. Experimental data were compared with the outputs from the Thomas Model based on orthophosphate removal to shed light on the equilibrium condition versus kinetic situation. With ANOVA tests, significant differences were confirmed between the experimental data sets of the breakthrough curves in the column tests. SEM imaging analysis helps to deepen the understanding of pore structures and pore networks of meta-materials being used in the green sorption media. Life expectancy curves derived from the output of Thomas Model may be applicable for future system design of engineering processes.

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1. Introduction

Due to the impact of rapid urbanization, population growth and climate variability around the globe, understanding nutrient cycle problems in natural systems and the built environment has been deemed one of the fourteen grand challenges by the National Academy of Engineering in the United States (US) (NAE, 2008). High nutrient

concentrations, such as nitrogen and phosphorous, in freshwater bodies can pose a threat to human health and disrupt the structures and functions of natural ecosystems. For instance, phosphates, in the inorganic form, are preferred for plant uptake and excessive inputs may exceed the capacity of a water body, such as a lake or a stormwater wet pond, and result in eutrophication (Jeffrey, 1998). As a result, algal blooms can gradually cover the entire lake or pond surface, blocking sunlight penetration into the water column, leading to further ecological degradation (Li et al., 1972; Balls et al., 1989). To mitigate these consequences, the US Environmental Protection Agency (US EPA) has suggested critical loading levels for stormwater wet detention and retention ponds (EPA, 1986) and requires that all states implement guidelines to regulate pollutant mass loading of stormwater prior to its discharge into receiving water bodies under the Clean Water Act (CWA) (White and Boswell,

Abbreviations: HRT, hydraulic retention time; TMDL, total maximum daily load; BMP, best management practice; EPA, environmental protection agency; TP, total phosphorus; TSP, total soluble phosphorus; CWA, clean water act; BTC, break through curves.

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2006). These water quality standards are used as target concentrations to protect the public's health and welfare, enhance the quality of the water, and serve the purposes of the CWA.

To help meet these standards, best management practices (BMPs) are used in many stormwater management practices to mitigate high nutrient concentrations. A wide variety of sorption media have been effective at reducing nutrient levels for stormwater, including recycled material mixtures (Wanielista et al., 2008); mineral-based mixtures such as marble chips (Sengupta and Ergas, 2006) and oyster shells (Namasivayam et al., 2005), and organic materials such as leaf mulch (Ray et al., 2006), wood chips (Seelsaen et al., 2006) and alfalfa (Kim et al., 2000). Such media were selected for testing, which was composed of clay, sand, organic materials, or engineered compounds to remove more soluble reactive phosphorus (SRP) and total phosphorus (TP) (Wanielista et al., 2008; Xuan et al., 2009a; Chang et al., 2010). For instance, a new media mixture composed of cement sand, tire crumb, fine expanded clay, and limestone, was selected on the basis of its removal efficiencies, surface area, particle size, cost, and availability in Florida (Xuan et al., 2009b). Similar sorption media mixtures comprised of sand and tire crumb have been shown to be effective in the removal of nutrients in many environmental applications such as green roof installations (Wanielista and Hardin, 2006), constructed wetlands (Xuan et al., 2009a), on-site sewage treatment (Xuan et al., 2009b), and stormwater infiltration basins (O'Reilly et al., 2012). Materials in this media mixture used are capable of removing nutrients by physical, chemical, and biological means (Xuan et al., 2009b).

Chang et al. (2010) further presented extensive discussion of the spectrum of possible engineering applications of sorption media in natural systems and the built environment for the removal of nitrogen and phosphorus species. Previous research has explored the effects of pH and temperature on the reaction kinetics of nutrient removal rates of the sorption media in batch reactions (Hossain et al., 2010; Chang et al., 2010). This information in this paper aims to explore the phosphorus removal efficiencies with green sorption media under constant flow-through and estimate the life expectancy of the proposed media under varying influent conditions. Both findings will improve the understanding of the reliability of future engineering for stormwater treatment processes. The word "green" implies the use of recycled material such as tire crumb in the media mixes.

The sorption media act as a sorbent for each chemical species, reacting physically and chemically with those sorbents until equilibrium is reached and the media is saturated through the processes of attachment and adsorption. Adsorption–desorption processes mostly determine the concentrations of inorganic-P in solution over a short period of time which are followed by the influences of solid-state diffusion, precipitation–dissolution, and immobilization mineralization over longer periods (Murrman and Peech, 1969). Attachment and adsorption may be achieved by the chemical and physical forces of surface interactions, London-van der Waals, surface hydration of ions, steric interactions of adsorbed macromolecules, the interaction of hydrophobic surfaces, and ionic or covalent bonding (Tobiason and O'Melia, 1988; Benjamin, 2002). Phosphorus begins adsorbing to surfaces until all the sites are filled and then diffuses into the particle via adsorption (Reddy et al., 1999). Due to these processes, sorption is temporally dependent (Barrow, 1978). For many wetland treatment systems, phosphorus removal increases with increasing hydraulic retention time (HRT) (Tang et al., 2008), although for an active slag filter, phosphorus removals declined logarithmically with respect to retention time (Shilton et al., 2013). For materials such as quartz sand, anthracite, and shale, it was found that adsorption occurred within short contact times (less than 2 h) and after which adsorption remained constant (Jiang et al., 2014).

The contaminants are absorbed at a rate dependent on diffusion processes within the biofilm, which are determined by its water-binding capacity and mobility (Singh and Walker, 2006). Compounds present within pond water and sediments, such as iron, calcium, aluminum, and

magnesium, may aid adsorption to allow a much greater orthophosphate removal rate due to phosphorus precipitation (Sample et al., 1980).

2. Science questions, hypotheses, and study objectives

The phosphate concentration in solution is also a function of diffusion rate regulating the surface reactions of green sorption media, which is affected by the properties and concentrations of ions in question. Barber (1980) found that the diffusion of phosphate ions is much lower in soil than in free water, where the lower the nutrient diffusion coefficient, the greater the reduction in concentration at the surface. Therefore, the ions found in pond water are thought to regulate and facilitate diffusion of phosphorus into sorption media. These ions found suspended in the water column also function to precipitate the phosphate, which may be either reactively filtered or inertly filtered as particle bound pollutants via sedimentation, straining, and deep filtration (Crittenden et al., 2005). Phosphate precipitation is usually promoted as Fe and Al phosphates form in acid soils and as Ca and Mg phosphates occur in alkaline and calcareous soils (Sample et al., 1980). The fractionation of inorganic P can be into three distinct classes of compounds, explicitly phosphates of Fe, Al, and Ca, some of which may not include all of them within the coatings of Fe oxides and hydrated oxides. The calcium carbonate limestone in the green sorption media mixture also contributes to the precipitation of phosphate due to the presence of Ca.

The removal of nitrogen species may be removed by the media physiochemically or biologically. These biological processes may be defined by several key chemical reactions which ammonia is oxidized to nitrite and nitrate (Sawyer et al., 2003). Denitrification then proceeds to reduce nitrate to nitric oxide or nitrogen gas with the use of a carbon source as an electron donor (Sawyer et al., 2003). However, these uptake quantities vary depending upon the solids retention time (SRT) and environmental conditions, as Hossain et al. (2010) showed with the nutrient media.

Science questions in this study include: 1) What is the orthophosphate (PO_4^{3-}) ion sorption capacity of the media with a varying input orthophosphate solution using distilled water and how is the capacity impacted by changing hydraulic retention time (HRT) and orthophosphate influent concentrations? 2) Does the adsorption capacity vary when using spiked pond water? 3) Is nutrient removal enhanced within a column via using spiked pond water due to the presence of more ions? 4) How do these orthophosphate removal efficiencies differ when the media column is saturated under no-flow conditions? 5) How do the surface characteristics of the green sorption media assist in nutrient removal? and 6) How can these values derived from the column experiments determine the life expectancy of the sorption media?

With these science questions, it is hypothesized that chemophysical orthophosphate removal will be evidenced by the inclusion of the pond water due to the presence of increased ions and cations, primarily calcium (Hypothesis 1 hereafter). The Thomas Model addresses an equation frequently used to estimate the adsorption capacity of a medium. There is a discrepancy between predicted curves of the Thomas Model and observed curves based on the column study due to the complicated ion effects in the pond water (Hypothesis 2 hereafter). When the media column is saturated under no-flow conditions, it is hypothesized that orthophosphate removal efficiency is due to higher HRT (Hypothesis 3 hereafter). When the columns receive varying influent concentrations or undergo different HRTs with distilled water, it is hypothesized that the adsorption patterns associated with breakthrough curves would be significantly different throughout the whole testing time frame (Hypothesis 4 hereafter). It is also hypothesized the morphological structure of expanded clay and tire crumb in green sorption media assists in orthophosphate removal due to microstructure (Hypothesis 5 hereafter). The objectives of this study are thus to: 1.) conduct phosphorus adsorption isotherm tests to estimate the mass orthophosphate removed per gram media in the absorbent

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