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A three-step test of phosphate sorption efficiency of potential agricultural drainage filter materials

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ABSTRACT

Phosphorus (P) eutrophication of lakes and streams, coming from drained farmlands, is a serious problem in areas with intensive agriculture. Installation of P sorbing filters at drain outlets may be a solution. Efficient sorbents to be used for such filters must possess high P bonding affinity to retain ortho-phosphate (Pi) at low concentrations. In addition high P sorption capacity, fast bonding and low desorption is necessary. In this study five potential filter materials (Filtralite-P®, limestone, calcinated diatomaceous earth, shell-sand and iron-oxide based CFH) in four particle size intervals were investigated under field relevant P concentrations (0–161 μM) and retentions times of 0–24 min. Of the five materials examined, the results from P sorption and desorption studies clearly demonstrate that the iron based CFH is superior as a filter material compared to calcium based materials when tested against criteria for sorption affinity, capacity and stability. The finest CFH and Filtralite-P® fractions (0.05–0.5 mm) were best with P retention of ≥90% of Pi from an initial concentration of 161 μM corresponding to 14.5 mmol/kg sorbed within 24 min. They were further capable to retain ≥90% of Pi from an initially 16 μM solution within 1½ min. However, only the finest CFH fraction was also able to retain ≥90% of Pi sorbed from the 16 μM solution against 4 times desorption sequences with 6 mM KNO_3. Among the materials investigated, the finest CFH fraction is therefore the only suitable filter material, when very fast and strong bonding of high Pi concentrations is needed, e.g. in drains under P rich soils during extreme weather conditions.

1. Introduction

Soils in intensively farmed countries may be sources of phosphorus (P) due to decades of surplus application of P in organic and inorganic fertilisers (Heal et al., 2005; Delgado and Scalenghe, 2008; Buda et al., 2012). However, a P-enriched soil only becomes an environmental problem when connected to the aquatic environment by an effective transport pathway such as artificial drains (Heathwaite et al., 2003). Tile drains and ditches collect and direct the diffuse P contribution (loss) from fields to recipient waters and act as highways for both soluble and particulate P (Ulén et al., 2007). Despite substantial efforts over many years to reduce this transport, leaching of P from agricultural land to the aquatic environment is still a serious and costly problem in many parts of Europe and elsewhere (Delgado and Scalenghe, 2008; Ballantine and Tanner, 2010; Buda et al., 2012). Thus, to reach the goal of good water quality as stated in the EU Water Framework

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Directive (WFD) requires a substantial reduction of the diffuse P loss from farmland in many parts of Europe (Søndergaard et al., 2005; Kaasik et al., 2008).

While a range of P mitigation options have been tested for surface transport (Hoffmann et al., 2009), this is not the case for subsurface transport (Kröger et al., 2008). However, by installing a filter construction at the end of a drainage pipe, Penn et al. (2007) demonstrated an immediate reduction of drainage P leaching. This end-of-pipe approach could be carried out in connection with a small-scale constructed wetland (Reinhardt et al., 2005) or with flow-through filter structures in ditches (Penn et al., 2007). A great variety of different types of filters and filter materials for P retention have been described for retention of high P concentrations in wastewaters (Johansson Westholm, 2006; Penn et al., 2007; Cucarella and Renman, 2009; Vohla et al., 2011). However, it is questionable to directly transfer the experience obtained from these high P concentration studies to the low P concentrations in drainage water as the filter materials may behave differently at high and low solution concentrations (Agyei et al., 2002; Ádám et al., 2007). Therefore, the filter materials need to be tested at low P concentrations and short reaction times relevant for cleaning P contaminated drainage water.

P in drainage water may consist of P in dissolved organic matter, particulate P and dissolved ortho-phosphate (Pi). The focus in this investigation will be on Pi, which denotes inorganic phosphate irrespective of the species ($H_2PO_4^-$, $HPO_4^{2-}$and/or PO_4^{3-}) In natural, unpolluted areas in Denmark, the Pi concentration in base flow drainage water is typically $\leq$1.6 μM but the concentration can be up to 42 μM in farmland drains (Andersen et al., 2006) and Penn et al. (2007) found more than four times this concentration in Maryland, US. The high water flow during rainstorms and fast frost-thaw transitions is critical because of high or very high P leaching during such peak flows (Grant et al., 1996; Johnes, 2007). To effectively remove the Pi during peak flows with high Pi concentrations, the filter material must react fast and possess high Pi sorption stability and capacity. Even though fast and substantial Pi sorption is mandatory for the practical use of the filter materials, it is also important with a stable bonding of sorbed Pi to ensure that Pi is not desorbed when the sorption condition changes, e.g. because of decreasing Pi concentration in the drainage water (Grant et al., 1996). This, however, is often overlooked in studies focussing on sorption capacity (Klimeski et al., 2012). The Pi removal efficiency of a filter material is closely related to the content of various Al, Ca, Fe and Mg (hydr)oxides and carbonates (Johansson Westholm, 2006; Ballantine and Tanner, 2010; Vohla et al., 2011). In addition to the elemental composition, the specific surface area (SSA) is important as sorption normally increases at increasing SSA. Although it is outside the scope of this study, high hydraulic conductivity of the filter material is also essential for use in high-flow drainage filters.

As a practical test of high Pi removal efficiency also under extreme conditions, we suggest the following three sorption/desorption criteria: (i) A capacity to retain $\geq$90% Pi from 161 μM solution within 24 min; (ii) A reactivity resulting in retention of $\geq$90% Pi from 16 μM solution within 1½ min; (iii) A stability resulting in dissolution of <10% of this retained Pi after four desorptions with artificial drainage water (6 mM KNO_3). A detailed discussion of these test criteria is given later in the paper. This concentration range is in line with the findings in natural drainage water as stated above and the contact time is based on field findings (Penn et al., 2007; Penn and McGrath, 2011).

Accordingly, the aim of the present investigation is to assess the sorption parameters of five manufactured filter materials (so-called Filtralite-P®, limestone, calcinated diatomaceous earth CDE, shell-sand and iron oxide based CFH). The assessment includes a characterization of the materials and a batch-mode testing of the Pi removal efficiency according to above-mentioned criteria of the materials in four particle sizes at low concentrations of Pi in artificial and natural drainage waters. To the best of our knowledge, this is the first study where various potential phosphorus filter materials are tested under the same field-relevant conditions, i.e. both at low to rather low Pi concentrations and very short to semi-short sorption (reaction) times. The materials chosen for this study have either been used or tested as wastewater filters or as an adsorbent/absorbent in other respects.

2. Materials and methods

2.1. *Filter materials*

Filtralite-P® is a Light Expanded Clay Aggregates (LECA)-resembling material calcinated at 1200 °C that was provided by Weber, Norway. The porous material contains granules of Ca/Mg oxides, which is the active sorbent. Limestone consists of a mixture of bryozo and coral chalk from the Danian formation at Faxe. The dried product was provided by Faxe Kalk A/S, Denmark. Calcinated diatomaceous earth (CDE) from the Fur formation calcinated at 750 °C was provided by Damolin A/S, Denmark. Shell-sand consisting of crushed sea shells was provided by DanShells Aps, Denmark. CFH-12 (CFH) consists of dried iron oxides, which was provided by Kemira Oyj, Finland.

2.2. *Filter material characterization*

Bulk samples of the five materials were analysed for pH, mineral composition, carbonate, oxalate- and citrate-bicarbonate-dithionite-extractable Al and Fe as well as total Al, Fe, Ca, Mg and Pi, while the specific surface area (SSA) was determined on all the particle size fractions. In addition, the total composition of the CFH and Filtralite-P® fractions was determined.

All analyses were carried out on ball-milled bulk materials. pH was measured potentiometrically in 0.01 M $CaCl_2$ using a solid:solution ratio of 1:2.5. The mineralogy of the materials was assessed by X-ray diffraction analysis on unoriented samples using a Siemens 5000 instrument equipped with Co-Kα radiation and a diffracted beam monochromator. Diffractograms were recorded from 10 to 90° 2θ using 0.03° 2θ steps and a step speed of 2 s. Diffraction peak positions were used to calculate d-values for mineral identification. The carbonate content was determined volumetrically by a calcimeter (Allison and Moodie, 1965). Oxalate-extractable aluminium (Al_{ox}) and iron (Fe_{ox}) were determined by