



# Phosphate sorption by three potential filter materials as assessed by isothermal titration calorimetry



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## ARTICLE INFO

### Article history:

Received 8 October 2013

Received in revised form

11 April 2014

Accepted 16 April 2014

Available online 13 May 2014

### Keywords:

Calcium phosphates

CFH-12

Fe-oxides

Filtralite-P

Limestone

P sorbing reactions

## ABSTRACT

Phosphorus eutrophication of lakes and streams, coming from drained farmlands, is a serious problem in areas with intensive agriculture. Installation of phosphate (P) sorbing filters at drain outlets may be a solution. The aim of this study was to improve the understanding of reactions involved in P sorption by three commercial P sorbing materials, i.e. Ca/Mg oxide-based Filtralite-P, Fe oxide-based CFH-12 and Limestone in two particle sizes (2–1 mm and 1–0.5 mm), by means of isothermal titration calorimetry (ITC), sorption isotherms, sequential extractions and SEM-EDS. The results indicate that P retention by CFH is due to surface complexation by rapid formation of strong Fe–P bonds. In contrast, retention of P by Filtralite-P and Limestone strongly depends on pH and time and is interpreted due to formation of calcium phosphate precipitate(s). Consequently, CFH can unambiguously be recommended as P retention filter material in drain outlets, whereas the use of Filtralite-P and Limestone has certain (serious) limitations. Thus, Filtralite-P has high capacity to retain P but only at alkaline pH ( $\text{pH} \geq 10$ ) and P retention by Limestone requires long-time contact and a high ratio between sorbent and sorbate.

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## 1. Introduction

Surface and subsurface transport of phosphate (P) from fertilized agricultural fields to open waters may lead to eutrophication, reduced biodiversity and fish kills in lakes and streams (Ballantine and Tanner, 2010; Delgado and Scalenghe, 2008). To mitigate eutrophic waters is difficult (Sharpley et al., 2003) but reduction of agricultural P leaching by means of filter structures intercepting drains and ditches with P sorbing materials may be one way to improve the water quality (Ballantine and Tanner, 2010; Penn et al., 2007). Several materials have been proposed as P sorbing materials (PSMs) (Ballantine and Tanner, 2010; Cucarella and Renman, 2009; Vohla et al., 2011; Westholm, 2006) for use in landscape P filters (Penn et al., 2007; Reinhardt et al., 2005).

To handle the high water flow and relatively high P concentrations during peak flows found in farmland drains and ditches, PSMs must react fast and have a high affinity for P in order to effectively remove it. The P removal efficiency of most PSMs is typically related to pH and the presence of various Al, Ca and Fe compounds (Ballantine and Tanner, 2010; Cucarella and Renman, 2009; Vohla

et al., 2011; Westholm, 2006). Additionally, the particle size and hence specific surface area (SSA) of the sorbent particles increases reactivity and sorption capacity (Nair et al., 1984). Besides high P affinity and fast kinetics, PSM filters must also have good hydraulic conductivity to handle the high water flow seen in connection with rain-storms but at the same time also allow P-rich water to come into contact with the materials. Despite the abundance of literature on sorption to various PSMs such as Al and Fe oxides, limestone, shell-sand and various by-products from industry (Ballantine and Tanner, 2010; Cucarella and Renman, 2009; Vohla et al., 2011; Westholm, 2006), doubt still exists about detailed sorption reactions of these materials, and hence safe use and optimal management of these filters is not yet ensured.

Sorption isotherms are commonly used in P sorption studies of PSMs (Ballantine and Tanner, 2010; Klimeski et al., 2012; Westholm, 2006). Although useful for assessment of P sorption capacity and affinity, isotherms are not suited for determination of the precise sorption reactions (Veith and Sposito, 1977). Isothermal titration calorimetry (ITC) provides a sensitive and direct quantitative measure of heat of a reaction and can be used as a complementary technique for establishing P sorption reactions. For instance, Penn and Zhang (2010) found that  $\text{FeCl}_3$  titrated with  $\text{NaH}_2\text{PO}_4$  changed from exothermic to endothermic as the titration proceeded and interpreted this to a change of the P sorption

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process from adsorption to precipitation. ITC can be used for estimation of enthalpy for mineral–solution interactions in connection with traditional sorption measurements as the reaction proceeds (Appel et al., 2013; Kabengi et al., 2006; Penn and Warren, 2009; Penn and Zhang, 2010; Rhue et al., 2002). Briefly, ITC measures changes in heat emitted (exotherm) or absorbed (endotherm) along product formation when a solute is added stepwise to a solution or solid suspension. For each solute addition (injection), the heat  $q$  ( $\text{J s}^{-1}$ ) released or absorbed is given by Eq. (1):

$$q = V\Delta H\Delta[n_p] \quad (1)$$

Where  $\Delta[n_p]$  ( $\text{mol L}^{-1} \text{s}^{-1}$ ) is the change in product concentration,  $\Delta H$  is the enthalpy of the reaction ( $\text{J mol}^{-1}$  product), and  $V$  (L) is the volume of reaction mixture. Because  $q$  is directly proportional to the increase in mass of product formed at each injection, its magnitude will gradually decrease as the reaction approaches saturation (equilibrium) of the system. The time integrated heat  $Q$  (J) released or absorbed is directly proportional to the energy of interaction:

$$Q = V\Delta H \sum \Delta[n_p] \quad (2)$$

For a full introduction to this method see Steinberg (1981) and Freire et al. (1990). ITC is not a “stand alone” technique, as correct interpretation of the data requires additional knowledge of the system being studied (Penn and Zhang, 2010; Rhue et al., 2002). Furthermore, the calculated thermodynamic properties ( $q$  and  $Q$ ) can only be meaningfully interpreted for pure systems with one (or very few) reactions that can be identified.

In order to know which type of PSM to choose for landscape filters, it is central to understand the particular type of sorption reaction, e.g. whether it is a precipitation, surface complexation or ion exchange reaction. Thus, by means of ITC, sorption isotherms, sequential extractions and PSM characteristics, the objective of this study was to improve understanding of the reactions involved in P sorption by three potential commercial PSMs including  $\text{CaCO}_3$ -based Limestone, Ca/Mg oxide-based Filtralite-P and Fe oxide-based CFH-12 at two different particle sizes. These three materials were chosen based on a prior screening (Lyngsie et al., 2014).

## 2. Materials and methods

### 2.1. Materials

Limestone for this study consists of a mixture of bryozo and coral chalk from the Danian formation at Faxø in Denmark. The dried product was provided by Faxø Kalk A/S, Denmark. Filtralite-P produced by Weber, Norway is a Light Expanded Clay Aggregate (LECA)-resembling material calcinated at  $1200^\circ\text{C}$  consisting of granules of Ca/Mg oxides in a collapsed clay matrix. CFH-12 (CFH) produced by Kemira Oyj, Finland, consists of dried iron oxide. The particles of the three PSMs were separated by sieving into a 2–1 mm fraction and a 1–0.5 mm fraction.

### 2.2. Methods

All chemicals were of pro analysis or better quality and the water was double deionized (DI). All glass and plastic wares were acid-washed prior to use.

#### 2.2.1. PSM characteristics

The mineralogy of the materials was assessed by powder X-ray diffraction analysis (XRD) on unoriented specimens using a

Siemens D5000 instrument equipped with  $\text{Co-K}\alpha$  radiation and a diffracted beam monochromator. Diffractograms were recorded from  $5$  to  $80^\circ 2\theta$  using  $0.02^\circ 2\theta$  steps and a step speed of  $10 \text{ s}$ . Diffraction peak positions were used to calculate  $d$ -values for mineral identification.

pH of the PSMs was measured potentiometrically in  $0.01 \text{ M CaCl}_2$  solution using a material:solution ratio of 1:2.5. Total contents of Al, Fe, Ca and Mg ( $\text{Al}_{\text{Total}}$ ,  $\text{Fe}_{\text{Total}}$ ,  $\text{Ca}_{\text{Total}}$ ,  $\text{Mg}_{\text{Total}}$ ) were determined after dissolution of the materials in a mixture of concentrated nitric acid, hydrogen peroxide, hydrochloric acid and hydrofluoric acid (EPA 3052) and were measured by inductive coupled plasma mass spectroscopy (ICP-MS) on an Agilent 7500C instrument. Oxalate-extractable iron ( $\text{Fe}_{\text{Ox}}$ ) was determined by extraction with  $0.2 \text{ M}$  ammonium oxalate for  $2 \text{ h}$  at pH 3 in the dark (Schwertmann, 1964) with quantification of Fe by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Spectro Cirrus CCD instrument. Reactive Ca and Mg in Filtralite-P and Limestone were determined by titration of  $0.25 \text{ g}$  PSM suspended in  $7.5 \text{ mL}$  water with  $0.005 \text{ M HNO}_3$  while stirring to the same final pH as after the 25 titrations with  $0.01 \text{ M NaH}_2\text{PO}_4$  described below. The suspension was filtered using a  $0.22 \mu\text{m}$  Millipore filter and the Mg and Ca concentrations were determined in the clear filtrate by atomic absorption spectroscopy (AAS) using a Perkin Elmer 3300 instrument. Total inorganic P ( $\text{P}_{\text{Total}}$ ) was determined by extraction with  $6 \text{ M H}_2\text{SO}_4$  for  $10 \text{ min}$  at  $70^\circ\text{C}$  (Mehta et al., 1954). Plant available phosphorus ( $\text{P}_{\text{Olsen}}$ ) was determined through 3 combined sequential extractions with  $0.5 \text{ M NaHCO}_3$  adjusted to pH 8.5 (Olsen and Sommers, 1982). The concentration of P in the extracts was determined by the molybdenum-blue method (Murphy and Riley, 1962). All analyses were carried out in triplicates. The specific surface area (SSA) of the different fractions was determined by applying the BET equation to  $\text{N}_2$  adsorption data obtained by means of a Micromeritic Gemini VII 2390a instrument (Brunauer et al., 1938) after the sample has been outgassed for  $12 \text{ h}$  at room temperature. The reported SSAs are the average of five separate measurements.

#### 2.2.2. Isothermal titration calorimetry

All ITC experiments were conducted on a CSC 4200 Isothermal Titration Calorimeter (CSC Inc., Lindon, UT) at  $25^\circ\text{C}$ . The ITC has a sensitivity of  $0.418 \mu\text{J}$  detectable heat effect and a “noise level” of  $\pm 0.0418 \mu\text{J s}^{-1}$  (deconvoluted signal). The ITC investigations were carried in two ways, i.e. as single-point and as multiple-point titrations. For single-point P sorption titrations,  $100 \text{ mg}$  of the material was placed in a  $1.3 \text{ mL}$  reaction vessel and suspended in  $750 \mu\text{L}$  of DI water,  $250 \mu\text{L}$   $0.01 \text{ M NaH}_2\text{PO}_4$  was added in one injection and the heat production monitored for the following  $5 \text{ h}$ . For the multiple-point P sorption titrations,  $25 \text{ mg}$  of the material was placed in the reaction vessel and suspended in  $750 \mu\text{L}$  of water. Under continuous stirring, the suspension was titrated with  $0.01 \text{ M NaH}_2\text{PO}_4$  by adding a total of  $250 \mu\text{L}$  in 25 increments of  $10 \mu\text{L}$  with  $5 \text{ min}$  between each injection. In order to compensate for heat of dilution, a blank was run where P solution was stepwise added in the same manner to water as to the PSM suspension. In addition, the heat of neutralization of Filtralite-P was determined by titration of  $25 \text{ mg}$  Filtralite-P in  $750 \mu\text{L}$  of water with  $0.005 \text{ M HNO}_3$  to pH 7.4, which was the final pH after titration with  $0.01 \text{ M NaH}_2\text{PO}_4$ . All ITC experiments were run as duplicates.

#### 2.2.3. P sorption isotherms

Supplementary batch sorption isotherms were conducted in the same manner and at the same solid:solution ratio as the corresponding ITC titration, but scaled up 10 times. Accordingly,  $0.25 \text{ g}$  of PSM was suspended in  $7.5 \text{ mL}$  water and stepwise added  $0.1 \text{ mL}$  of  $0.01 \text{ M NaH}_2\text{PO}_4$  with  $5 \text{ min}$  between each addition. Only the first 8

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