



Interaction of calcium, phosphorus and natural organic matter in electrochemical recovery of phosphate

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ABSTRACT

To address the issues of eutrophication and the potential risk of phosphorus (P) shortage, it is essential to remove and recover P from P-containing streams to close this nutrient cycle. Electrochemical induced calcium phosphate (CaP) precipitation was shown to be an efficient method for P recovery. However, the influence of natural organic matter (NOM) is not known for this treatment. In this paper, the behavior of NOM and its effect on CaP precipitation was studied. In contrast to studies where NOM hindered CaP precipitation, results show that the interaction of NOM with CaP improves the removal of P, independent of the types of NOM. The P removal at the average increased from $43.8 \pm 4.9\%$ to $58.5 \pm 1.2\%$ in the presence of 1.0 mg L^{-1} NOM. Based on the yellow color of the CaP product, NOM is co-precipitated. The bulk solution pH with and without buffers has totally different effects on the precipitation process. Without buffer, CaP precipitates on the cathode surface in a wide pH range (pH 4.0–10.0). However, the precipitation process is completely inhibited when the bulk solution is buffered at pH 4.0 and 6.0. This is probably due to neutralization of OH^- by the buffers. Regardless of the presence or absence of NOM and solution pH, the recovered products are mainly amorphous CaP unless the electrolysis time was increased to seven days with 4.0 A m^{-2} , in which crystalline CaP formed. These findings advance our understanding on the interaction of Ca, P and NOM species for the application of electrochemical method for P recovery from real wastewater.

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1. Introduction

Phosphorus (P) plays an essential role for all living organisms (Desmidt et al., 2014). P fertilizers are also needed to secure food production. However, the diminishing reserves of P rock are not adapted to the growing demand of P (Elser and Bennett, 2011; Reijnders, 2014). Indeed, on the one hand, P can be a scarce resource in the future, on the other hand, plenty of P containing waste streams are discharged to water bodies, resulting in an environmental catastrophe, namely eutrophication (Elser and Bennett, 2011). However, if we can recover the lost P and re-use it as a constituent in fertilizer, this can reduce the risk of P shortage and alleviate eutrophication problems (Mayer et al., 2016).

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Various methods including enhanced biological phosphorus removal (Tervahauta et al., 2014; Cunha et al., 2018b), adsorption (Kumar et al., 2017) and chemical precipitation have been applied to remove P from waste streams. Among them, the most common way is chemical precipitation because of its easy operation and efficiency (Ye et al., 2017). For the sake of re-use, the chemical precipitation method has shifted from using Fe and Al salts, which produce hardly bio-reusable P salts, to struvite (MgNH_4PO_4) and calcium phosphate (CaP), which can be used as a slow release fertilizer or as raw materials for the fertilizer industry, respectively (Tervahauta et al., 2014; Hao et al., 2013; Hug and Udert, 2013). Previous studies indicate that the concentrations of the associated lattice ions and pH affect the removal performance of P since these variables determine the driving force for the precipitation of a species in chemical precipitation process (Song et al., 2002; Shih et al., 2017). On the basis of this, a variety of Mg or Ca sources, such as natural brucite (Hovelmann and Putnis, 2016), building waste (Yang et al., 2016) and steel slag (Barca et al., 2012) had been

applied to achieve efficient and cost effective P removal. The advantage of these Mg or Ca sources is that they not only provide Mg^{2+} or Ca^{2+} but also able to increase solution pH. Particularly, the membrane containing electrochemical system, which can enrich phosphate concentration and increase solution pH simultaneously, receives a lot of attention (Zhang et al., 2013; Kappel et al., 2013; Xie et al., 2014; Qiu et al., 2015). However, the associated fouling issues of membranes remain a challenge. The inspiring point, however, is that several studies showed the possibility of a membrane free system for P removal and recovery (Wang et al., 2010; Cusick and Logan, 2012).

Lei et al. (2017) recently reported an efficient membrane free system which induces CaP precipitation at the cathode surface over a wide pH range. It was proposed that the production of hydroxide ions on the surface of the titanium cathode through water electrolysis is responsible for P precipitation. In the tests described in Lei et al. (2017), calcium nitrate and sodium phosphate in a background matrix of sodium sulfate in MilliQ (18.2 M Ω cm) water was used. Further assessment of the applicability of the membrane-free system requires adding other components that could be naturally present and that may interfere with the precipitation of CaP. Previous non-electrochemical studies have shown that both Mg^{2+} and carbonate inhibit CaP precipitation by replacing lattice Ca and decreasing free Ca by complexation, respectively (Cao and Harris, 2007; Hermassi et al., 2016; Cunha et al., 2018a). In particular, it was reported that natural organic matter (NOM) inhibits the precipitation of CaP by decreasing free aqueous Ca ions and blocking nucleation sites (Song et al., 2006; Cao et al., 2007; Sindelar et al., 2015). NOM is a complex matrix of heterogeneous mixture of organic compounds (Matilainen et al., 2010) and coexists with Ca and P in every aquatic and soil system (Sindelar et al., 2015). The complex structure and functional groups of NOM allows ion exchange and complexation (Hahn et al., 2017), and thereby may interact with lattice ions and thence influence CaP precipitation. However, the interaction of NOM on CaP precipitation in electrochemical systems, to our knowledge, has not been studied, nor the effect of NOM from different sources (or the combined effect of NOM) and solution pH on CaP precipitation. Electrochemical induced CaP precipitation depends on the local chemical environment near the cathode surface. It is also known from literature that though NOM in general shows inhibiting effects on CaP precipitation in conventional chemical precipitation process, the negative role can be overcome by increasing solution pH (Song et al., 2006; Sindelar et al., 2015). Since the electrochemical system can create a high local pH by OH^- production at the vicinity of the cathode, the negative effects of NOM may be eliminated in this system.

The objective of this study is to elucidate the influence of NOM on CaP precipitation in the electrochemical system. Specifically, we studied the effects of NOM from different sources at different pH conditions. We also investigated the effect of electrolysis time on the electrochemical interaction of Ca, P and NOM and the associated impact on chemical and physical properties of precipitates.

2. Materials and methods

2.1. Materials

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) was bought from Merck (Germany). Disodium phosphate (Na_2HPO_4), sodium sulfate anhydrous (Na_2SO_4), phthalate (pH 4 buffer), citrate (pH 6 buffer) and borate (pH 10 buffer) were obtained from VWR (Leuven, Belgium). Electrodes were provided by MAGNETO Special Anodes BV (Schiedam, The Netherlands). Three types of NOM were purchased from the IHSS (International Humic Substances Society) as dry solid extracts: Suwannee River NOM (2R101N, NOM₁), Nordic

Lake NOM (1R108N, NOM₂) and Pony Lake NOM (1R109F, NOM₃). No further purification is performed on these NOMs. All solutions were prepared in MilliQ water (18.2 M Ω cm).

2.2. Setup

As shown in Fig. 1, the electrochemical cell consists of a working electrode (cathode), a counter electrode (anode) and an Ag/AgCl reference electrode. The constant current condition was provided by a potentiostat (VERTEX, IVIUM Technologies, The Netherlands). The cathode is a pure Ti disc (\varnothing 8.0 cm, thickness 0.1 cm, grade A) and is perpendicularly welded to a 12-cm long rod (\varnothing 0.3 cm). The anode has the same design as the cathode and was coated with 10 g/m² Ru-Ir. The total solution in the electrochemical cell (800 mL) is circulated with a pump at a flow rate of 70 mL/min.

2.3. Batch experiments

For preparation of the test solutions we used stock solutions of Ca^{2+} (0.4 M) and $P-PO_4$ (0.24 M) to obtain final concentrations of 1.0 mM total Ca and 0.6 mM P. In this paper, we used the term "P" to represent all soluble phosphorus species in the bulk solution. In all batch tests, we added 50 mM Na_2SO_4 to maintain the electrolyte conductivity. We first chose NOM₁ as the typical reference NOM and investigated its effect on CaP precipitation in the range of 1.0–10.0 mg L⁻¹ and subsequently studied the effects of NOM sources. We also examined the effects of pH in buffered and unbuffered solutions on P recovery. We performed all the electrochemical experiments at a constant current density (4.0 A m⁻²) for 24 h at room temperature. All the tests were at least done in duplicate. The data is shown as mean plus standard deviation. Solids on the cathode surface were collected and dried at room temperature. It should be noted that the solid precipitates were not washed with MilliQ (18.2 M Ω cm) water in preventing of potential dissolution or recrystallization of precipitates.

2.4. Analysis

The soluble Ca and P concentrations were analysed by ICP-AES. NOMs were characterized with Liquid Chromatography-Organic Carbon Detection (LC-OCD) (Model 8, DOC-LABOR, Karlsruhe, Germany). Detail information about the analysis of LC-OCD can be found in a previous publication (Semitsoglou-Tsiapou et al., 2016). Prior to the analysis, the samples were filtered with a 0.45 μ m filter.

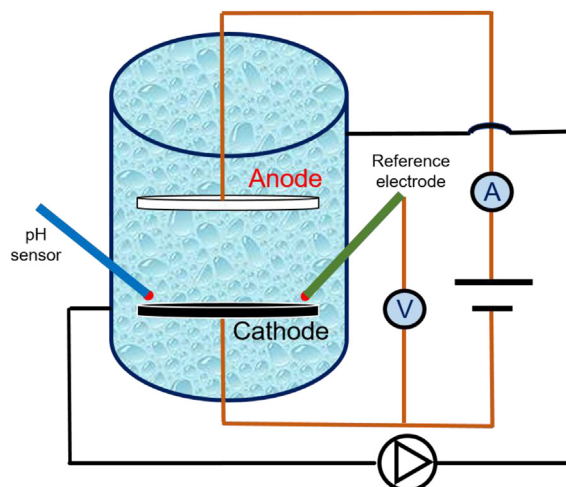


Fig. 1. Schematic diagram of the setup.

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