



Effects of current density, bicarbonate and humic acid on electrochemical induced calcium phosphate precipitation

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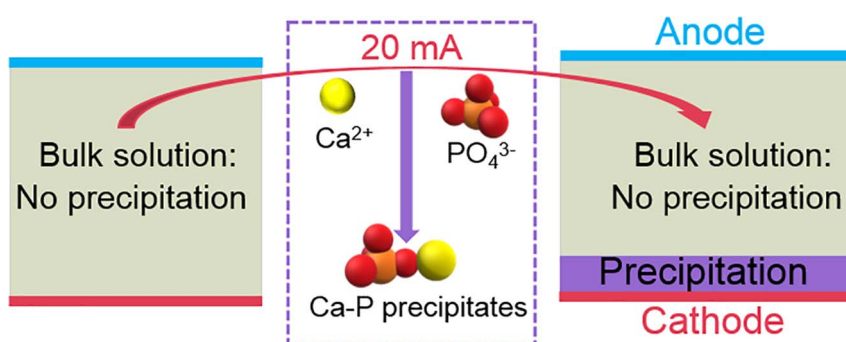
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HIGHLIGHTS

- Local high pH rather than bulk solution pH drives CaP precipitation.
- Humic acid coprecipitates with CaP and improves CaP precipitation.
- Bicarbonate at natural concentration promotes the removal of P.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphorus (P) removal and recovery from sewage as calcium phosphate (CaP) by chemical precipitation is a widely used method. To avoid the addition of chemicals to increase the pH of the bulk solution and the need for a further separation step in conventional chemical precipitation process, we developed an electrochemical method, which can locally increase the pH near a Ti cathode. The separation of product and liquid then happens simultaneously by accumulating CaP at the electrode surface. The current density plays a crucial role in this system. A current density of 19 A/m² results in the formation of crystalline CaP rather than amorphous CaP, but it does not enhance the removal of P in 24 h. Moreover, the current efficiency decreases with increasing current density. Furthermore, the increased H₂ production at high current density may push the precipitated CaP back to the bulk solution, resulting in its dissolution. In the presence of bicarbonate (1–5 mM) or humic acid (1–20 mg/L), the removal of P was higher. This is probably due to the inhibited CaP precipitation in the bulk solution which in turn leaves more Ca and P ions available for the local precipitation on the cathode. However, bicarbonate at high concentration (10 mM) dropped P removal from 52 to 25%. This is caused by competition of carbonate and phosphate with the free Ca²⁺ ions and also by buffering the produced hydroxide ions at the cathode. The study shows that P can be removed as CaP by electrochemical precipitation at low current densities at common concentrations of bicarbonate and humic acid.

1. Introduction

Phosphorus (P) plays an essential role in food production and may

become critical in supply with the rapidly growing world population [1–3]. As a finite resource, P rock is expected to be exhausted within the next few hundred years [1,2]. However, the discharge of P-containing

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streams even at low concentration may result in the eutrophication of surface water [4,5]. This results in harmful algal blooms (i.e., microcystin) and decreases the quality of water bodies for recreation [4,6]. To address future P scarcity and P discharge related environmental problems, it is therefore important to remove and recycle P in the waste streams.

The traditional ways for removing P include enhanced biological phosphorus removal [7,8], adsorption [9,10] and chemical precipitation [11]. Chemical precipitation, because of its easy operation and low cost finds wide application [11]. Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and calcium phosphate (CaP) based methods are widely suggested as efficient ways for removing and recovering P from waste streams [12–15]. The struvite process has the advantage of removing P and ammonium nitrogen ($\text{NH}_4\text{-N}$) simultaneously, whereas it is not effective when Mg and $\text{NH}_4\text{-N}$ to phosphate molar ratio deviate from the theoretical value ($\text{Mg}:\text{NH}_4\text{-N}:\text{PO}_4\text{-P} = 1:1:1$) [16,17]. In contrast, the CaP formation process is more adaptable to solution conditions and the associated CaP products are also more favorable for the existing fertilizer industry [14,16]. Previous studies indicate that CaP precipitation is dependent on Ca and P concentrations, presence or absence of seeds, co-existing ions and pH [15,18–20]. Therefore, P precipitation can be accomplished by increasing lattice ion concentrations including Ca and P ions and by increasing solution pH. Based on this, building waste and steel slag have been utilized as Ca sources for precipitating P [21–23]. In particular, the use of slag also increases the solution pH, in addition to provide Ca. Similarly, ions exchange membrane separated (bio)electrochemical cells have been developed for either enriching P and/or increasing solution pH, to improve phosphate separation and precipitation [24–28]. The function of membrane containing electrochemical system highly depends on the selectivity of membranes. While these processes are effective, the high costs and the fouling problems of membranes remain a challenge. Encouragingly, the early studies of Wang et al., [29] and Cusick and Logan [30] demonstrated the potential of electrochemical P recovery as struvite without using membranes. Recently, Yang et al. extended the use of membrane-free electrochemical cell for recovering P as CaP instead of struvite [31]. The principle of electrochemical precipitation (ECP) of CaP is that a local supersaturated environment for solid CaP phases can be created through water electrolysis in the vicinity of a cathode.

While the concept was proven recently, the presence of co-existing ions in municipal wastewater needs to be investigated in order to further develop an effective ECP system for P recovery as CaP. Previous studies suggest that CaP precipitation from solution is inhibited by Ca chelators including carbonate and natural organic matter by blocking active sites and decreasing free Ca^{2+} [20,32–35]. However, these studies were done in bulk solution. None of these studies were done in an electrochemical system where a local high pH at the cathode is established.

Therefore, the objective of this work was to investigate the performance of the ECP system in the presence of common water matrices. Bicarbonate and humic acid are typical representatives of inorganic and organic contents in both natural and engineered systems. In addition, as Ca chelators, they may affect the precipitation behavior of CaP. Therefore, for the first time, we explored their effects on CaP precipitation in the ECP system with different current densities. Also, given the different Ca/P molar ratio in different types of wastewater, the effect of Ca/P molar ratio on CaP precipitation was also addressed. These results may advance our understanding of the ECP process and provide insights for optimizing P removal and recovery in the ECP system.

2. Methods and materials

2.1. Materials

Na_2HPO_4 , Na_2SO_4 , NaHCO_3 were purchased from VWR (Leuven, Belgium). $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was purchased from Merck. Humic acid (HA)

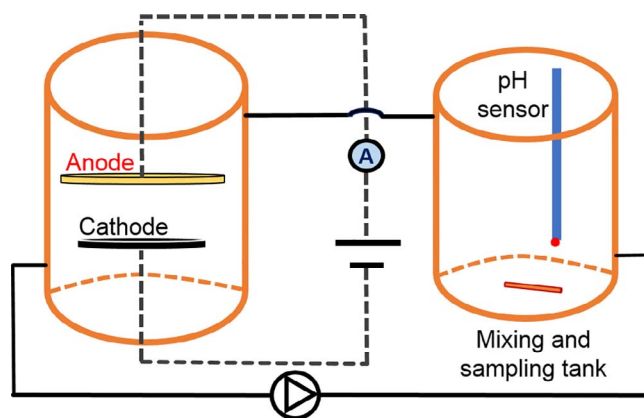


Fig. 1. Schematic view of the electrochemical phosphorus recovery setup.

was obtained from ACROS ORGANICS. Commercial hydroxyapatite (HAP) used for XRD measurement was bought from Sigma-Aldrich. Solutions were prepared with MilliQ water. The electrodes were provided by MAGNETO Special Anodes BV (Schiedam, The Netherlands).

2.2. Electrolysis setup

As shown in Fig. 1, the electrochemical setup consists of a working cell where CaP precipitation took place and a sampling tank. Each cell contained 500 mL solution and the solutions in the cell and the tank were circulated at a flow rate of 100 mL/min. In the working cell, the anode (Pt coated Ti mesh, \varnothing 10 cm) and the cathode (Ti plate, \varnothing 8.2 cm) were placed on top and bottom part of the cell respectively, each with a perpendicular connected 12 cm long Ti rod (\varnothing 0.3 cm). The distance between the electrodes was 2.7 cm. The pH was monitored by a weekly calibrated pH electrode (Endress Hauser, Germany) and logged by a computer program (Liquisys M CPM 253, Endress + Hauser, Naarden, The Netherlands).

2.3. Electrolysis experiments

Initial 1000 mL solutions containing predetermined concentrations of Ca^{2+} and $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ were prepared by mixing suitable volume stock solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and Na_2HPO_4 and were distributed equally to the working and sampling cells. The concentration of Ca and P varies in wastewater and changes with the sampling location in wastewater treatment plants (WWTPs). Therefore, we performed ECP experiments where the P (as phosphate species) concentration varied from 0.2 to 1.5 mM and the Ca concentration ranged from 0.5 to 2.5 mM. We performed all experiments at 3.8 A/m^2 unless the effect of current density was studied. We added 50 mM Na_2SO_4 to maintain the conductivity of tested solutions. As it was already concluded that the local high pH at the cathode drives P precipitation in this system [31], the initial solution pH was not adjusted, but a pH established (8.2 ± 0.2) by all added reagents. To study the effects of bicarbonate and HA, bicarbonate was added as sodium bicarbonate powder and HA was added from its stock solution (500 mg/L). The stock solution was prepared by dissolving commercial HA powder in MilliQ water for over 24 h and purified at alkaline (pH 11.0) and neutral conditions combined with filtering (100 μm filter). The actual concentration of HA used in this study was below the designed value because of the filtration of some undissolved parts of the commercial HA. All experiments were repeated, and the data was present as the average plus the standard deviation.

2.4. CaP collection

For all conditions that we tested, we did not observe CaP

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