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Short communication

Formation of pure struvite at neutral pH by electrochemical deposition

C.-C. Wang[a,b], X.-D. Hao[b,*], G.-S. Guo[a,**], M.C.M. van Loosdrecht[c]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China*
[b] *The R & D Centre of Sustainable Environmental Biotechnology, Beijing University of Civil Engineering and Architecture, 1 Zhanlanguan Road, Beijing 100044, PR China*
[c] *Department of Biochemical Engineering, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands*

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ABSTRACT

Previously we showed that pure struvite could be recovered from wastewater at neutral pH. This omits the need for adding alkalinity to the process. However, at a neutral pH value the reaction is relatively slow making it practically not a good system from an engineering point of view. In this study, electrochemical deposition was evaluated as a means to improve the formation of pure struvite at a neutral pH value. An electrolytic cell with an inert Pt (or graphite) anode and a nickel cathode was set up for the experiment. The generation of OH^- via electrochemical reduction of dissolved oxygen slightly increased the interfacial pH near the cathode, resulting in rapid formation of the precipitates. The structure, morphology, composition and thermal properties of the harvested precipitate were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), microscopic analysis, infrared (IR) spectra, energy-dispersive spectrometry (EDS), element analysis (EA) and thermo-gravimetric analysis (TGA). All the analyses support formation of pure struvite in the precipitate.

1. Introduction

Eutrophication in surface waters associated with the realization that phosphorus is likely the most limiting element on earth has recently promoted extensive studies on recovering phosphorus from wastewater. Crystallization of struvite (magnesium ammonium phosphate – MAP: $NH_4MgPO_4{\cdot}6H_2O$) represents an interesting technique to recover phosphorus from wastewater [1–7] or urine [8,9] or manure [10,11]. Struvite is a premium grade slow releasing fertilizer and could be directly used for horticulture and agriculture, such as potato production, and even used for fish farming, like trout and salmon population conservation [12]. The recovered product, struvite, is easy to handle and free of traditional sludge-handling problems.

For the above reasons, struvite from phosphate-rich wastewater (anaerobic supernatant/urine and/or animal wastes) has become one of the most interesting products among recovered phosphate-based precipitates. Some processes recovering struvite have been theoretically and experimentally investigated by chemists, biochemists and civil engineers [8,9,13–15].

Precipitation of struvite is controlled by factors as the concentrations of Mg^{2+}, NH_4^+ and $H_nPO_4^{3-n}$ as well as ionic strength, pH and temperature. Among them, pH is generally considered to be a key factor controlling formation of struvite; the optimal range of pH as reported is 8.0–11.0 [13,16–20]; most of speakers at the 4th international conference on nutrient recovery from wastewater streams (Vancouver, Canada on May 10–13, 2009) declared that they recovered 'struvite' from wastewater/wastes certainly at high pH values. High pH values have the disadvantage that they require addition of alkalinity and a potential co-precipitation of carbonates. For use as fertilizer a pure struvite mineral would be optimal, also a pure struvite mineral would require less transport costs and energy per unit of P recovered. A recent experimental study of ours revealed that alkaline pH could not result in formation of pure struvite and that even no struvite existed at pH > 10.0 in the recovered phosphate-based precipitates [21], which was caused by the existence of Ca^{2+} in solution [16,17,21].

Our study identified that the optimal pH for the formation of pure struvite fell in the range of 7.0–7.5 [21], however the precipitation rate of struvite was quite low. This means that engineering of a natural struvite precipitation process is difficult at a neutral pH value.

It is really necessary to explore an efficient method for speeding up formation of pure struvite near the neutral pH. Electrochemical deposition was earlier reported as an efficient method to trap calcium carbonate ($CaCO_3$) for softening hard water [22]. Clearly, Moussa et al. [23] also used this method to deposit pure struvite on electrode surface from an aqueous solution containing phosphate, ammonium and magnesium ions, in which the experimental cell was a three-electrode system consisting of gold grid and

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* Corresponding author. Tel.: +86 10 8060 452; fax: +86 10 6832 2128.
** Corresponding author. Tel.: +86 10 6443 4808.

E-mail addresses: xdhao@hotmail.com (X.-D. Hao), guogs@mail.buct.edu.cn (G.-S. Guo).

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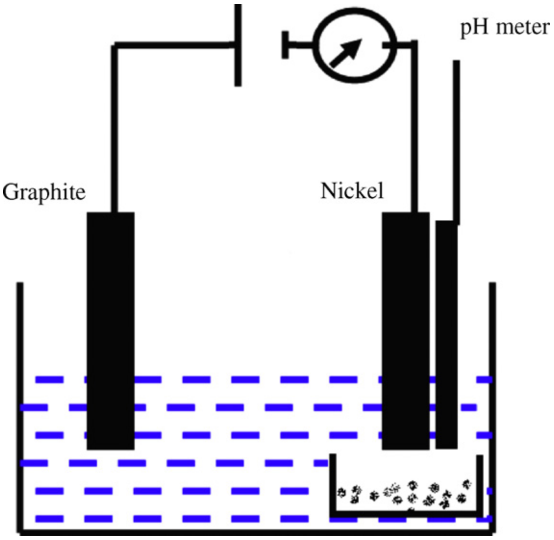

Fig. 1. Schematic drawing of experimental electrochemical deposition setup.

nickel rod as the working electrodes respectively and the saturated $Hg/HgSO_4$ reference electrode (SSE). Inspired by this successful performance, we decided to investigate whether electrochemical deposition could be applied to trap and recover struvite with a high purity near the neutral pH from synthetic wastewater and/or real wastewater with cheaper electrodes.

With this article, a lab-scale experiment was set up to demonstrate the proposed potential of recovering pure struvite near a neutral pH value with electrochemical deposition, in which a two-electrode system was employed. After phosphate-based precipitates were recovered, their structure, morphology, composition and thermal properties were analyzed respectively by X-ray diffraction (XRD), high-resolution color digital camera, infrared (IR) spectra, element analysis by acid dissolution method [21] and thermo-gravimetric analysis (TGA). These analyses indicate that pure struvite was completely possible to be recovered around the neutral pH. Besides the purity of the harvested precipitates, we paid more attention to the phosphate removal efficiency from the treated solutions. The experimental results demonstrated that electrochemical deposition is indeed an alternative potential method to trap and recover struvite from phosphate-rich wastewater.

2. Materials and methods

2.1. Materials

Analytical grade chemicals ($NH_4H_2PO_4{\cdot}2H_2O$, $MgSO_4{\cdot}7H_2O$, and NaOH) were used as received without further purification. The crystal structure was identified by X-ray diffraction (Rigaku D/max IIIA). The microscopic image was analyzed scanning electron microscopy (Hitachi: TM-1000). IR spectra were recorded on a PerkinElmer FT-IR Spectrum spectrophotomer in the region of 400–4000 cm^{-1} using KBr pellets. TGA was performed from 30 to 800 °C in a N_2 stream at a flow rate of 10 °C min^{-1} on a ZRY-1P TGA system using α-Al_2O_3 as reference material. The Semi-quantitative element analysis was performed on electronic probe micro-analyzer (JXA-8100+INCA EDS).

2.2. Setups of electrochemical deposition

The setup (I) of electrochemical deposition is shown in Fig. 1. It is actually an electrolytic cell (300.0 ml) composed of an inert platinum sheet (12.0 cm × 2.0 cm × 0.1 cm) as anode and a nickel sheet (12.0 cm × 2.0 cm × 0.1 cm) as counter electrode, in which the electrode space is 2.0 cm. A pH meter (Mettler Toledo) was installed near the cathode to measure the pH value close to the interphase. The exerted potential was at 3–12 V (DC). The inert platinum sheet can be replaced by cheaper electrodes as anode, like Ru–Ir–Ti alloy nets (12 cm × 2 cm × 0.1 cm) or low porosity graphite rode (Φ0.5 cm × 12.0 cm).

2.3. Preparation of electrolyte

I: 1.5 mmol $NH_4H_2PO_4{\cdot}2H_2O$ was dissolved in 0.15-L ultra pure water; II: 1.5 mmol $MgSO_4{\cdot}7H_2O$ was dissolved in 0.15-L ultra pure water. The equal volume of above-stated solutions I and II was mixed together, and then moved into the setup, in which the concentrations of the three main ions (Mg^{2+}, $NH_4{}^+$ and $H_nPO_4{}^{3-n}$) were in the ranges of normal values found in waste streams such as the supernatant from anaerobic digesters. The pH value was adjusted to the desired point (7.0–7.5) by adding the NaOH solution of 1 mol L^{-1}.

2.4. Formation of the phosphate-based precipitates

As soon as electricity was applied on the system, some gas bubbles were released both from anode and cathode. At the same time, the pH value in solution near the cathode increased slowly (7.0–7.5), and the precipitates appeared and layered on the electrodes. The precipitates obtained from different cathodes such as Pt sheet, Ru–Ir–Ti alloy nets and low porosity graphite rode were similar. Only the struvite precipitates harvested on Pt sheet under 3 V were chose to be identified by X-ray diffraction, scanning electron microscopy (SEM), IR spectra, and TGA. The content of struvite in the precipitate was analyzed according to the ammonium ($NH_4{}^+$) content by acid dissolution method [21].

3. Results and discussion

3.1. Formation of the struvite precipitates by electrochemical deposition

In principle, formation of struvite should be characterized by the simultaneous presences of Mg^{2+}, $NH_4{}^+$ and $H_nPO_4{}^{3-n}$ in the precipitates, as expressed by Eq. (1). Obviously, pH is a key factor controlling formation of struvite.

$$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + (n+1)H^+ \quad (1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \quad (3)$$

When the experiment started, the generation of OH^- increased the interfacial pH (up to 7.5) near the cathode [24], as illustrated by Eqs. (2) and (3), which was subjected to the diffusion rate of oxygen towards the cathode and the consumption rate of OH^- by the chemical reactions forming the precipitates. Along with the increase of OH^- concentration near the cathode, Mg^{2+}, $NH_4{}^+$ and $H_nPO_4{}^{3-n}$ ions may react with each other to initiate the nucleation and growth of struvite, then more struvite precipitates were formed and layered on the cathode electrodes or settled down to the organic glass receiver.

3.2. XRD and image analyses of the harvested precipitates

The morphology of the precipitated crystals was characterized by XRD and microscopic analysis. As a reference, purchased pure struvite (Alfa-Aesar, US) was used to compare the XRD patterns between the purchased struvite and harvested precipitate. The XRD patterns of these samples are shown in Fig. 2, in which also a stan-

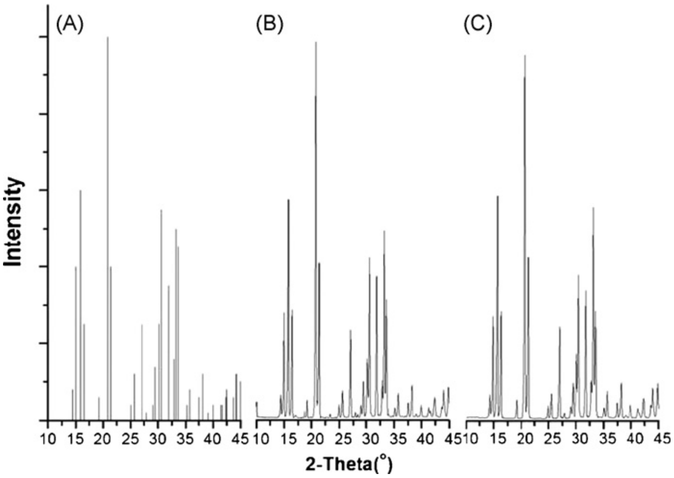

Fig. 2. XRD patterns of the purchased pure struvite and the harvested precipitates on Pt sheet (A: standard pattern PDF#15-0762; B: purchased struvite (labelled purity: 99.0%); C: harvested precipitates).

dard XRD pattern from the data base (PDF#15-0762) for powder diffraction pattern for struvite is also included (A).

As shown in Fig. 2, no clear differences on both position and intensity of the peaks can be observed by comparing the XRD patterns from the pure struvite and the harvested precipitate. The harvested precipitates crystals are shown in Fig. 3, which are small transparent sticks (0.5–2 mm). Based on these observations, the harvested electrochemical precipitate and the pure struvite are very much alike.

3.3. Infrared spectra of the harvested precipitates

Identifying the harvested precipitate as a pure struvite could was further confirmed by infrared spectra. The assignments of the peaks for the harvested precipitates match well with the reported values for pure struvite (Table 1).

3.4. Thermo-gravimetric analysis (TGA) of the harvested precipitates

The theoretical mass loss for the struvite formula ($MgNH_4PO_4{\cdot}6H_2O$) upon heating is 51.42%, which is composed of mass losses as water (contributing 44.08%) and as ammonium (contributing 7.34%). As shown in Fig. 4, the thermal decomposition was occurring at a temperature of 111.4 °C, while the observed weight loss of 52.49% matches well with the theoretical and the reported values (at 51.42%) [26].

Table 1
Comparison of Infrared spectra between the harvested precipitate and the pure struvite.

Bonds/vibrations	Reported value [25] (cm^{-1})	Observed value (cm^{-1})
NH_4^+ ν_4 asym bending	1430	1435.24
$\nu_3(PO)_4^{3-}$ antisym str	1010	1007.05
$\nu_4(PO)_4^{3-}$ P–O bend	570	571.49
$\nu_2(PO)_4^{3-}$	450	462.07

3.5. Semi-quantitative element analysis of the harvested precipitates

The results of the elemental analyses performed by energy-dispersive spectrometry (EDS) are illustrated in Fig. 5. As shown in Fig. 5, the EDS result of the precipitates (A) matches very well with the standard struvite pattern (B). According to the EDS analysis, the phosphorus atomic concentration is equal to the magnesium concentration. Regretfully, the EDS technology is not able to exactly measure the content of nitrogen.

3.6. Element analyses and calculating the content of struvite in the precipitates

A dissolution method developed by Hao [21] was used for the element analyses of the harvested precipitate on the Pt sheet. The elemental analyses indicated the measured molar concentrations for the purchased struvite were $c(NH_4^+\text{-}N) = 0.6456$ mM, $c(TP) = 0.6464$ mM and $c(Mg^{2+}) = 0.6532$ mM respectively. These measured molar concentrations are very close to the calculated molar ones at 0.6520 mM for each element (N/P/Mg) based on the struvite formula ($MgNH_4PO_4{\cdot}6H_2O$). With this method, the concentrations of NH_4^+-N, TP and Mg in the harvested precipitate were at 0.6329 mM, 0.6401 mM and 0.6530 mM respectively. 1 mol of NH_4^+-N could be equivalent to 1 mol of pure struvite. Therefore, the content of struvite in the precipitate can be calculated at 97.1%, which means that the harvested precipitates contain the very high content of pure struvite. The phosphate removal rate in the original solution was also analyzed; the results reveal that up to 94.5–96.1%

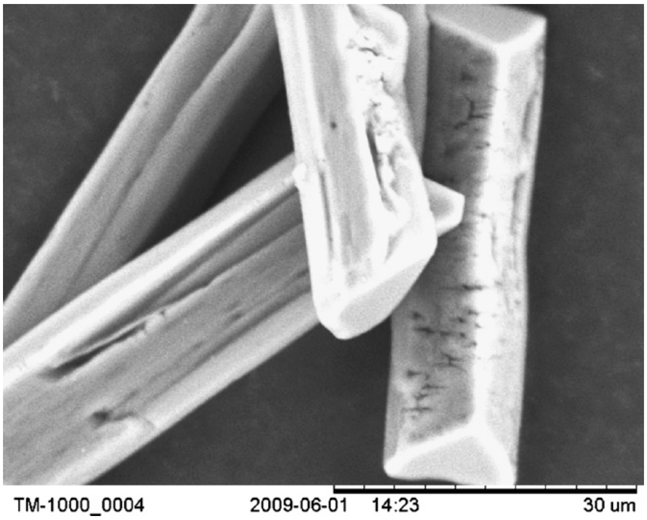

Fig. 3. SEM image of the harvested precipitates on Pt sheet.

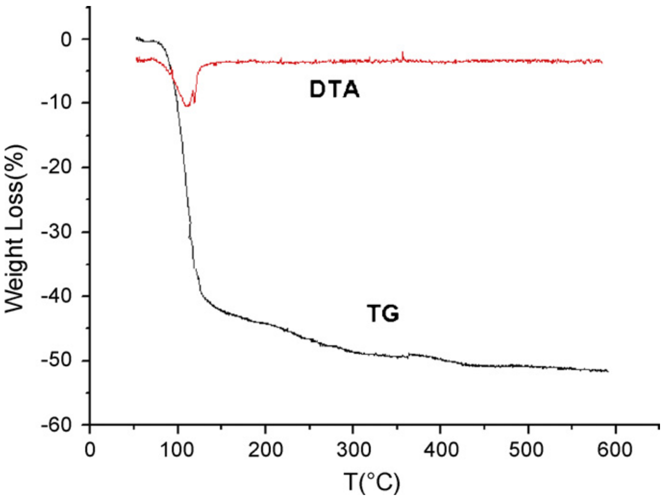

Fig. 4. TGA and DTA patterns of the harvested precipitates on Pt sheet.

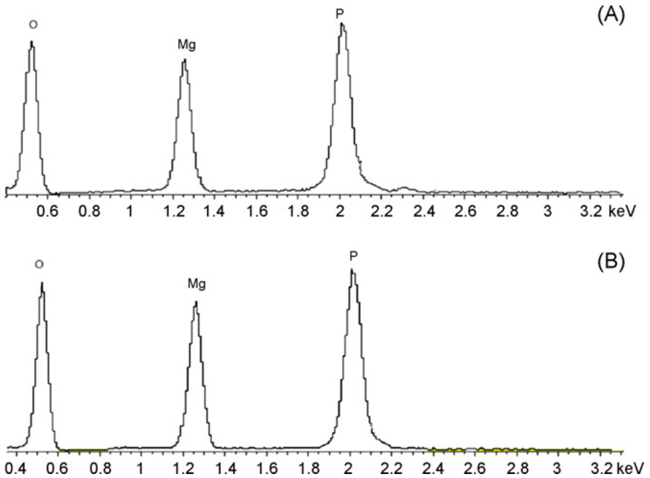

Fig. 5. Energy-dispersive spectrometry analyses of the harvested precipitates on Pt sheet (A) and the purchased struvite from Alfa-Aesar (B).

of the phosphate removal rate was achieved, which reveal that electrochemical deposition can satisfy both high purity of struvite and high removal rate of phosphate.

In order to test the impact of foreign ions like calcium ion, under the complete same conditions as described above, another series of experiments were performed with tap water as a solvent instead of pure water. The tap water in Beijing mainly consists of ground water, with a high mineral content: $c(Ca^{2+}) = 2.17$ mM and $c(Mg^{2+}) = 1.34$ mM. The preliminary experimental results reveal that calcium ion in the tap water had a negative impact on formation of struvite, as described in the traditional chemical precipitation of struvite [21], which can also be confirmed by XRD, SEM, and element analysis. Moreover, the existence of calcium ion also decreased the phosphate removal efficiency from the solution to 50%-60%. Further research will be conducted to explain the impact of foreign ions (including calcium ion) and other factors (like temperature) on formation of struvite and the phosphate removal efficiency from tested solutions.

4. Conclusions

All the results and analyses have demonstrated the feasibility of electrochemical deposition for recovering pure struvite from waste streams at a neutral pH value, which could be easily realized at a lower voltage (DC: 3–12 V). Furthermore, this method could realize both the high phosphate removal efficiency in solution and the highly pure content of struvite in the recovered precipitate. This would make engineering recovering pure struvite at the neutral pH value possible. Further large-scale experiments have to be followed to ascertain key controlling factors affecting formation of struvite, and to develop some new setups with cheaper and stable anodes and cathodes.

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