

# Preparation of iron phosphate from sludge sourced from the electrocoagulation treatment of source-separated urine

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**Abstract** In order to prepare iron phosphate by waste sludge, we report a method for effective utilization of the sludge obtained from the electrocoagulation treatment of source-separated urine. The sludge was dissolved with hydrochloric acid and pretreated with H<sub>2</sub>O<sub>2</sub> and Na<sub>3</sub>PO<sub>4</sub>; finally, NaOH was added to precipitate iron phosphate from the solution. Thermal treatment of the precipitate at 750 °C in air yielded crystalline quartz-like anhydrous FePO<sub>4</sub>. The precipitate was characterized by a number of thermal techniques such as thermogravimetry/differential thermal analysis, scanning electron microscopy, and X-ray powder diffraction.

**Keywords** Iron phosphate · Sludge · Electrocoagulation · Source-separated urine

## Introduction

Approximately 50 % of the phosphate present in domestic wastewater originates from urine, with each individual producing around 1–1.5 L of urine per day

(Sundberg 1995; Jönsson et al. 1997). Source separation, collection, and treatment of urine have therefore attracted considerable attention over the past few years and regarded as a viable option for enhancing the removal of phosphate from wastewater treatment systems (Maurer et al. 2006). In most wastewater treatment systems, the removed phosphate was got into the sludge and could hardly be resource utilized. However, phosphorus-based compounds are utilized in a wide variety of applications, including agriculture, where they are one of the main components of a number of fertilizers. Currently, the main source of phosphorus for fertilizers is phosphate rock (Sengupta and Pandit 2011), which is a limited, non-renewable resource that is under threat of depletion (Van Vuuren et al. 2010). Hence, recovery of phosphorus from source-separated urine could help in meeting fertilizer demands while simultaneously reducing water pollution (Larsen et al. 2007). One attractive option that has been investigated in relation to phosphorus reuse as a fertilizer is the precipitation of struvite, a phosphate mineral with the formula NH<sub>4</sub>MgPO<sub>4</sub>·6H<sub>2</sub>O (Antonini et al. 2011; Etter et al. 2011). Besides struvite precipitation, phosphorus recovery from urine using hybrid anion exchange (Jeremy and Treavor 2013) and evaporation has also been investigated. Early results showed that these methods have the potential to be used in certain applications. However, there are a number of challenges relating to the recovery of phosphorus from source-separated urine on a larger scale. One of the main challenges is the storage and transport of a large amount of urine (Jenssen and Etnier 1996; Larsen and Gujer 1996), which increases resource utilization costs for the treatment, especially where the urine has been diluted with flush water.

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The use of electrocoagulation for the removal of pollutants from wastewater has recently attracted increasing attention, as it yields a number of advantages over other systems. These wide-ranging advantages include excellent effectivity, energy efficiency, safety, and cost efficiency. In addition, the process does not employ any additional reagents or microorganisms, also it is environmentally compatible, involves a quick and well-controlled reaction, and can be completely automated (Holt et al. 2005; Mollah et al. 2004). Studies on the removal of phosphorus from source-separated urine using electrocoagulation have been reported previously by Ikematsu et al. (2006) and Zheng et al. (2009), with their results demonstrating the high efficiency, stability, and convenience of the process. They reported that during the electrocoagulation process, phosphorus from the urine was condensed into a smaller volume of liquid, known as sludge. Transport and storage costs could therefore be reduced compared to those required for the high volumes of diluted urine.

The main components of the sludge produced from the electrochemical treatment of urine with iron electrodes were found to be the sparingly soluble  $\text{FePO}_4$ , and iron hydroxides. In this respect, iron phosphate was regarded almost as an “unavailable” fertilizer, and few reports could be found in relation to the use of such sludge. In addition, besides its potential use as a fertilizer, high-purity  $\text{FePO}_4$  could also be used as a raw material for the production of paint, food additives, catalysts, ceramic glazes, and cell materials (Scaccia et al. 2002, 2004). Therefore, if the preparation of pure  $\text{FePO}_4$  could be synthesized via electrocoagulation of a sludge obtained from the treatment of source-separated urine, not only the sludge could be utilized, but also an alternative route could be developed for the reduction of the phosphorus depletion crisis.

The aim of this study is to find a method to prepare iron phosphate by electrocoagulation sludge that produced during the phosphorus removal of source-separated urine with electrochemical technology, so that the sludge could be resource utilized rather than be abandoned as waste, and also the application of electrochemical method for the treatment of source-separated urine could be promoted if positive results could be found in this study.

## Materials and methods

### Electrocoagulation sludge

The electrocoagulation sludge was obtained from a laboratory study into the removal of phosphorus from source-separated urine by electrocoagulation using iron plates (Zheng et al. 2009). The sludge was filtered, then dried at 80 °C to give a sludge, which varied in color from earthy yellow to reddish-brown depending on the current density used (Zheng et al. 2009), and on the subsequent  $\text{FePO}_4$  to  $\text{Fe}(\text{OH})_3$  ratio which resulted. The color variation is due to  $\text{FePO}_4$  having a white color, and  $\text{Fe}(\text{OH})_3$  having a reddish-brown color.

### Preparation of $\text{FePO}_4$ from the sludge

$\text{FePO}_4$  was prepared according to a previously reported literature procedure (Scaccia et al. 2002, 2004). 10 g electrocoagulation sludge and 50 ml distilled water were placed into a 500-ml beaker, the sludge was dissolved by slowly adding of 10 M hydrochloric acid with magnetic stirring, altogether 55 ml hydrochloric acid was added while all the sludge was dissolved and the tested pH was under 1.0, and 30 ml 30 %  $\text{H}_2\text{O}_2$  added to oxidize both the organic materials and the  $\text{Fe}^{2+}$  species to give  $\text{Fe}^{3+}$  in solution. According to the study Ma et al. (1993, 1998), the optimum ratio of  $\text{PO}_4^{3-}$  to  $\text{Fe}^{3+}$  was no less than 5 for synthesis of  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , as the used materials to prepare  $\text{FePO}_4$  was the electrocoagulation sludge in this study, which obtained from a laboratory study into the removal of phosphorus from source-separated urine, and different amount of  $\text{FePO}_4$ ,  $\text{Fe}_3(\text{PO}_4)_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$  and other iron compounds could be existed in the sludge, while it was produced under different current density or with different urine solution, so the correct amount of Fe in the used sludge was not analyzed as it could hardly represent typical value of Fe content in certain sludge. During our study, it was found that while 0.1 M  $\text{Na}_3\text{PO}_4$  was slowly added to the solution to adjust the  $\text{Fe}^{3+}$  to  $\text{PO}_4^{3-}$  ratio, the solution color changed from yellow to colorless correspondingly, then the adjustment process was finished, and usually the added amount of  $\text{Na}_3\text{PO}_4$  was about 75–90 ml get white precipitate, for the synthesis of thermos analytical sample in this study, 78 ml  $\text{Na}_3\text{PO}_4$  was added. Finally, almost



150 ml 0.5 M NaOH was added slowly into the solution to increase the pH to 2.0 and yield the desired  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  as a white precipitate. The resulting precipitate was filtered and washed with distilled water, and dried in oven at 80 °C for 24 h in order to accelerate the drying process as reference mentioned (Scaccia et al. 2002, 2004), finally 13.6 g precipitate could be prepared. A portion of the precipitate was heated at 750 °C for 10 h to produce the anhydrate (Scaccia et al. 2002, 2004).

### Analysis methods and instruments

The micromorphology of the precipitates and the calcined products was studied by scanning electron microscopy (SEM) (Hitachi, S-2150, Japan). The precipitates and calcined products were characterized by X-ray powder diffraction (XRD) (Rigaku, D/max-2200/PC, Japan) using  $\text{CuK}\alpha$  radiation. The dehydration pattern of  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  was studied by differential thermal analysis (DTA, DTA1600, USA) and thermal gravimetric analysis (TGA or TG, TGA2050, USA). A 10 mg sample was heated over 25–800 °C at a rate of 10 °C  $\text{min}^{-1}$ , with a flow rate of 100  $\text{mL min}^{-1}$  of air.  $\alpha\text{-Al}_2\text{O}_3$  was used as the reference material, and samples were run in open platinum pans.

## Results and discussion

### Scanning electron microscopy (SEM)

SEM images of the prepared  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{FePO}_4$  samples are shown in Fig. 1 below.

As can be seen in Fig. 1a, the particle size of the prepared  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  was generally smaller than 5  $\mu\text{m}$ , while

the particle size of the anhydrous  $\text{FePO}_4$  was larger, with the majority of fragments exceeding 5  $\mu\text{m}$ . This observation is likely to be due to the dehydration process used to form  $\text{FePO}_4$ . During the heating of  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  at 750 °C, water was lost from the crystals, and the  $\text{FePO}_4$  granules could cluster together to form the larger particles, which can be seen in Fig. 1b.

### X-ray diffraction (XRD)

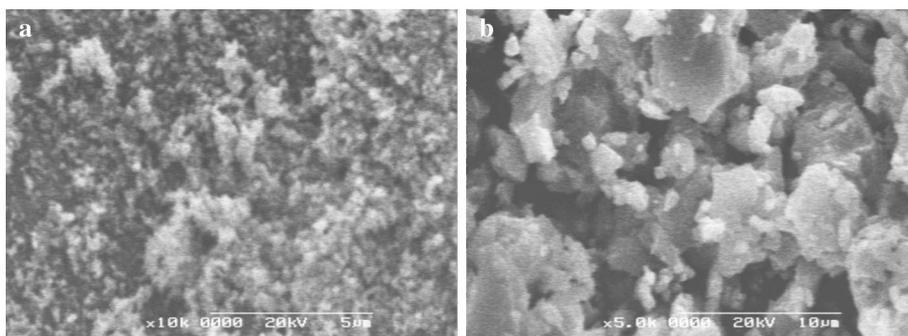
The XRD patterns obtained for  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{FePO}_4$  are shown in Fig. 2.

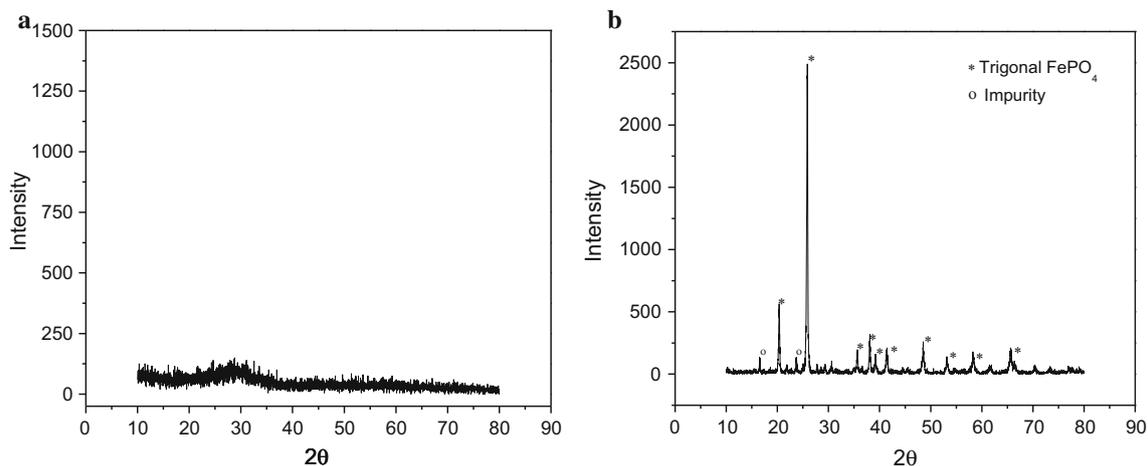
As shown in Fig. 2a, a poorly resolved pattern was observed for  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , while the XRD pattern of the precipitate calcined at 750 °C/10 h in air clearly demonstrated the presence of a crystalline sample. The major reflections in Fig. 2b can be attributed to a trigonal quartz-like structure for anhydrous  $\text{FePO}_4$  (Scaccia et al. 2002, 2004), whereas other minor reflections around 20.4, 25.9, 35.7, 38.1, 38.2, 39.2, 41.5, 48.5, 53.2, 58.4, and 65.8° were indicative of the formation of  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$  secondary phase, or anhydrous iron phosphate (Scaccia et al. 2002, 2004). By the XRD analysis, conclusion could be made that  $\text{FePO}_4$  could be synthesized with electrocoagulation sludge by the method used in this study, though there were some impurity materials in the precipitate, but the major content was definitely  $\text{FePO}_4$ .

### Thermogravimetry, derivative thermogravimetry, and differential thermal analysis (TG/DTG/DTA)

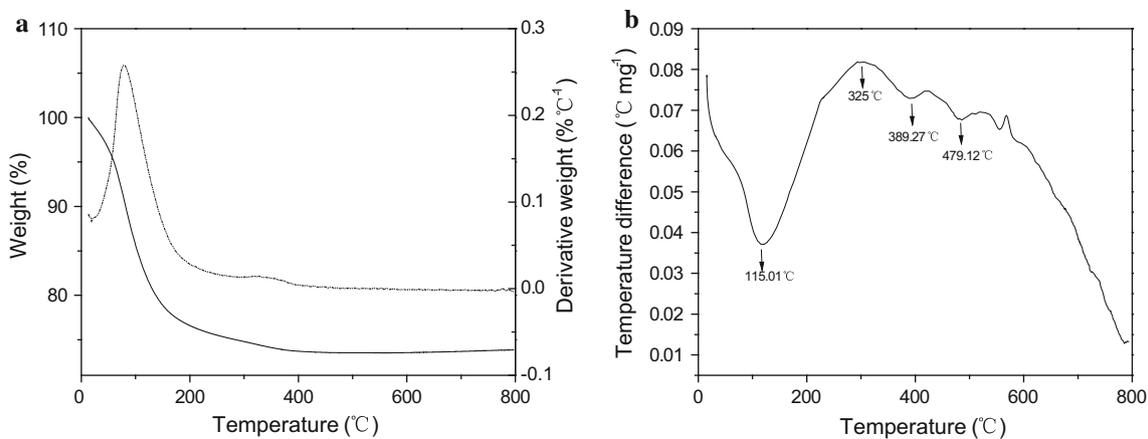
It was important to carry out a number of different types of thermal analysis in order to give a full picture of the behavior

**Fig. 1** SEM images of the prepared  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  (a) and  $\text{FePO}_4$  (b)





**Fig. 2** XRD pattern of the precipitated iron phosphate ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ) (a) and calcined iron phosphate ( $\text{FePO}_4$ ) (b)



**Fig. 3** TG (solid line) and DTG (dashed line) curves of the precipitated iron phosphate ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ) (a) and DTA curve of the precipitated iron phosphate ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ) (b)

of the sample upon heating. The TG/DTG/DTA curves of the precipitated iron phosphate (hydrate) are shown in Fig. 3.

As can be seen in Fig. 3a, the TG curve shows a weight loss between ambient temperature and 235.37  $^\circ\text{C}$  (corresponding to a DTG peak at 78.89  $^\circ\text{C}$ ), the weight loss can be assigned to the elimination of crystallization water, because organic material existed in urine was soluble and only a few parts of organic material could be co-precipitated into the electrocoagulation sludge (Ikematsu et al. 2006), also  $\text{H}_2\text{O}_2$  was added into the solution during the synthesis process to remove the possible organic material in the as  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  precipitation, so the weight change in TG curve was mainly caused by the loss of

crystallization water. The total mass loss calculated was 24.33 %, which, based on the total moles of iron and phosphorus in the precipitate, does not correspond to the expected loss of 2 mol of water per mole of Fe or P and that may be caused by the loss of free water in the tested sample. The corresponding DTA curve (Fig. 3b) shows one endothermic peak at 115.01  $^\circ\text{C}$ , which shows it is the characteristic peak of  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  and the result is in agreement with previous reports (Scaccia et al. 2002, 2004). At higher temperatures, two small peaks (at 389.27 and 479.12  $^\circ\text{C}$ ) corresponding to weight losses of approximately 1.54 % are observed in the DTA and DTG curves. These weight loss events may be associated with the



transition phase of minor impurities in the synthesized  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , as observed in the XRD curves.

Although the total mass loss from the synthesized  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  was not equal to the theoretical value (i.e., 2 mol of water for each mole of  $\text{FePO}_4$ ), from the TG/DTG/DTA analysis, it could also be concluded that the major component of the prepared product was  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , with small quantities of other  $\text{FePO}_4$  hydrates as impurities.

## Conclusion

The electrocoagulation sludge, which was produced during the removal of phosphorus from source-separated urine by electrochemical method with iron electrodes, was successfully converted into a white precipitate,  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , by treatment with HCl,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_3\text{PO}_4$ , and NaOH, and was later converted to the crystalline quartz-like anhydrous  $\text{FePO}_4$  by heating at 750 °C for 10 h. Both the hydrate and the calcined forms of  $\text{FePO}_4$  were analyzed by SEM and XRD, demonstrating that differences in structure existed between the two species, with the particles of the anhydrous form being larger than those of the hydrate. The XRD results showed that the main structure of calcined  $\text{FePO}_4$  was crystalline in nature, with the major reflections attributed to a trigonal quartz-like structure. Thermal analysis of  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  showed that mass loss occurred upon heating to 235 °C, corresponding to the elimination of water from the crystals. The results presented here are important for providing a new method to resource utilization of electrocoagulation sludge that produced in the removal of phosphorus from source-separated urine.

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