# Fluidized-bed crystallization of iron phosphate from solution containing phosphorus

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## ABSTRACT

This work demonstrates the recovery of phosphorus from a solution (150 mg-P/L) using ferrous salts ($FeSO_4$) and hydrogen peroxide ($H_2O_2$) as precipitants through the fluidized bed crystallization (FBC) process. Jar-test experiments were conducted to investigate effective pH and molar ratios of $H_2O_2$/Fe(II) and Fe(II)/P in the removal of phosphate. The pure ferric phosphate crystal was then recovered using the FBC process and the effluent $pH_e$ and surface loading (L, kg-P/$m^2$ h) were tested. The results of XRD revealed that the FBC pellets were composed of the mixtures of rodolicoite and giniite, with a Fe/P molar ratio of approximately 1.1, based on elemental analysis. Under conditions $pH_e = 2.6$, an $H_2O_2$/Fe(II) molar ratio of 0.6, an Fe(II)/P molar ration of 1.2, and $L = 0.3$–0.89 kg/$m^2$ h, a crystallization ratio of 86% and a removal efficiency of 95% were achieved.

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## 1. Introduction

As the demand for electronic products has increased over the past decade, the thin-film transistor liquid crystal display (TFT-LCD) industry has developed [1] to become one of the most important industries in Taiwan. The TFT-LCD manufacturing industry generates a significant amount of wastewater with various levels of organic [2] and inorganic [3] compounds. A solution that contains a high concentration of phosphate is generated from the etching process, in which phosphoric acid is used as an agent [4]. Phosphorus is one of the main elements that causes water eutrophication, which causes the overgrowth of plants and algae in water bodies [5]. Phosphorus is important in aquatic systems because aquatic life depends on it [6]. However excessive amounts of phosphorus can accelerate the production of phytoplankton, causing oxygen depletion, and the death of fish and aquatic organisms [7]. Nowadays, most phosphorus is used in fertilizer [8] to increase food production [9]. Phosphorus is a limited resource that is abundant in the Earth's crust [10]. The Taiwan Environmental Protection Agency has set a standard limit of 1.4 mg-P/L on phosphorus levels in wastewater [11]. Techniques for recovering phosphate from the

wastewater include biological treatment [12], chemical precipitation [13], adsorption [14], electrocoagulation [15] and crystallization [16]. Biological treatment requires long-term operation and monitoring. Chemical precipitation has been proved to be more highly efficient than biological methods [17], but it typically generates sludge with a high water content. The efficiencies of adsorption and the electrochemical method are low owing to scaling and fouling.

Fluidized bed crystallization (FBC) has been developed since the 1970s. It is extensively used to treat wastewaters that contain heavy metal, hardness and phosphate [18]. Most of the pellets that are produced by FBC are reused as raw materials in agriculture [19]. Calcium or magnesium salts are the preferred precipitants for removing phosphate in the FBC process. Crystallization of the target compound within an FBC reactor depends on hydraulic conditions that cause particles to collide with each other sufficiently and the subsequent repulsion of most of the water from the fine nuclei [16]. Meanwhile, the aquatic condition that controls the supersaturation as a solute exceeds the solubility limit determines the efficiency of crystal growth. Ferric phosphate is a raw material in the synthesis of lithium iron phosphate ($LiFePO_4$) s, which is a cathode material in rechargeable lithium batteries; Satyavani et al. have demonstrated a methodology that prepared a mixture of chemical compounds – $FePO_4.xH_2O$, $Li_2CO_3$ and oxalic acid – as the precursor of the following thermal treatment and successfully fabricated the lithium iron phosphate [20]. The recovery of phosphate as ferric phosphate is a potential

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alternative to chemical precipitation for the sustainable reuse of phosphorus. In related most studies, struvite ($NH_4MgPO_46H_2O$) and hydroxyapatite ($Ca_5(PO_4)_3(OH)$), which are common fertilizers, are reclaimed from a phosphorus-containing solution. Few investigations have involved the use of ferric salt in the crystallization of ferric phosphate ($FePO_4$) in an FBC reactor. Based on stoichiometry, the amount of Fe(III) salt that is required to reduce phosphorus in solution in the precipitation of $FePO_4$ is less than that of Fe(II) salt for creating vivianite ($Fe_3(PO_4)_28H_2O$), and both can be used as precursors in the fabrication of Li ion secondary batteries [21, 22]. Considering the cost-effect and recoverability of phosphorus in wastewaters, this investigation examines the removal of phosphate in synthetic wastewater in an FBC reactor by forming valuable $FePO_4$ crystals. The experimental parameters herein include the effluent pH, molar ratios of $H_2O_2$/Fe and Fe/P, and the surface loading, which were evaluated to optimize the aquatic conditions based on the phosphorus removal, PR (%), and crystallization ratio, CR (%).

## 2. Materials and methods

### 2.1. Chemicals

The phosphorus-containing solution was synthesized by dissolving monopotassium phosphate ($KH_2PO_4$, Sigma-Aldrich Co. LLC., USA) in deionized water. Ferrous sulfate heptahydrate ($FeSO_4\bullet8H_2O$, Sigma-Aldrich Co. LLC., USA) was used as the iron source, and hydrogen peroxide ($H_2O_2$ 35 wt%, Sigma-Aldrich Co. LLC., USA) was used as an oxidizing agent. The reaction pH was adjusted by sodium hydroxide (NaOH, Merck KGaA, Germany) and nitric acid ($HNO_3$, Sigma-Aldrich, USA). The water applied to prepare all stock solution of chemicals was doubly deionized using a laboratory-grade RO-ultrapure water system (resistance > 18.3 MΩ/cm). All reagents were of analytical grade, and used without further purification.

### 2.2. Experimental procedure

The jar test was conducted to assess the influence of molar ratio of $H_2O_2$ to Fe(II) on the precipitation of iron phosphate in 1000 mL glass beaker (initial $P = 5$ mM, 155 mg-P/L). 500 mL of synthetic wastewater was added into 500 mL of ferrous sulfate solution which was conditioned by a specific amount of hydrogen peroxide. The pH of solution was adjusted to the target value with NaOH and $HNO_3$. The mixture was stirred at 100 rpm for 20 min, 30 rpm for 30 min, and then kept settling for 24 h. The sampling was filtrated using 0.22 μm filter, and the filtrate was directly digested with 1 mL $HNO_3$ (70%) (to stop the precipitation). The fluidized bed reactor is a cylindrical column made of Pyrex glass with a capacity of 500 mL (including main body of reactor and pipelines) as shown in Fig. 1. Two parts of fluidized-bed reactor are connected with a sudden enlarged joint constitute the main body of reactor. The lower part is 2 cm in inner diameter and 80 cm in height. The upper part is 4 cm in inner diameter and 15 cm in height. Such sudden expansion can reduce the hydraulic loading and prevent too much fines from being drained out. Two peristaltic pumps are used for pumping the mixing inflows of ferrous sulfate and hydrogen peroxide and wastewater, and one peristaltic pump is used to control the reflux flow rate. A preceding step was required to create fine seeds of the iron phosphate in the reactor. The aquatic conditions was properly adjusted by the mixed feeding of 1000 mg-P/L and ferrous sulfate/hydrogen peroxide, which yielded a molar ratio of [Fe]/[P] = 1 (pH = 2.5). At a low superficial velocity, the fine particles were not overflowed, favoring their growth into coarse particles. The seeds eventually descended and became fluidized in the reactor. Crystals of sizes that made them visible

to the naked eye were formed in 4–5 days. Afterwards, a regular run of FBC reaction was initiated by introducing the mixed feeds of ferrous sulfate and hydrogen peroxide solution and synthetic P-containing wastewater at given flow rates, the ratio of reflux ($Q_r$) and influx flows ($Q_t = Q_P + Q_{Fe}$). The ferric phosphate as the seed was filled into reactor to reach a static bed height of 30 cm. The pH of wastewater was controlled using NaOH and $HNO_3$. Typically, pH and aquatic measurements lasted at least 9 HRT after changing the parameters of whole system (such as pH, $H_2O_2$/$Fe^{2+}$). For every sampling, 10 mL solution was withdrawn at effluent twice: one was filtered with a 0.22 μm filter and the other was not. Both liquids with and without filtration were then acid digested with 1 mL $HNO_3$ (70%). Phosphate and iron ions in digests were $[P]_t$ and $[Fe]_t$, and in filtrates were $[P]_s$ and $[Fe]_s$. Two calculations were therefore used to verify the efficacy of FBC process, phosphorous removal, PR (%), and crystallization ratio, CR (%).

$$PR\% = \left(1 - \frac{[P]_s \times Q_t}{C_P \times Q_P}\right) \times 100 \tag{1}$$

$$CR\% = \left(1 - \frac{[P]_t \times Q_t}{C_P \times Q_P}\right) \times 100 \tag{2}$$

PR is used to evaluate the efficiency of FBC in reducing phosphorous from aqueous phase, while CR% refers to the recoverability of the iron phosphate as coarse pellets. At the end of the experiment the pellets were removed from the bottom of the bed and air-dried for further characterization.
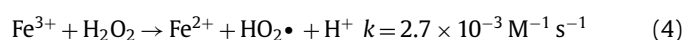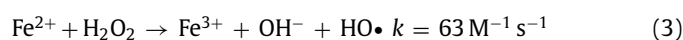
### 2.3. Analytical methods and characterization

Phosphorus and iron concentrations in samplings were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, ULTIMA 2000, HORIBA Ltd., Japan). Concentrations of ferrous ion and hydrogen peroxide was measured based on uv-spectrophotometer (Agilent 8453, United State of America); Fe were determined using the 1,10-phenanthroline method [23], and the hydrogen peroxide was measured using titanium sulfate method [24]. A scanning electron microscopy (SEM, JSM-6700F, JEOL Ltd., Japan) was used to observe the micro-morphology of FBC products. While the surface composition was analyzed by the attached energy dispersive spectrometer (EDS, LINKS AN10000/85S). X-ray diffraction (XRD, DX III, Rigaku Co., Japan) patterns determined the crystallographic structure was operated with Cu Kα radiation source ($\lambda = 1.5406$ Å), a scanning rate of 10° min$^{-1}$ in the incidence angle range of 10°–90° ($2\theta$) and the accelerating voltage and current were 40 kV and 20 mA.

## 3. Results and discussion

### 3.1. Jar-test of ferric phosphate precipitation

Since Fe(III) salt is very easily precipitated as $Fe(OH)_{3(s)}$ in weak acid to neutral solutions before it is introduced into the reactor, in this investigation, a solution of ferric salt (Fe(III)) is prepared by conditioning ferrous iron (Fe(II), $FeSO_4$) with $H_2O_2$ as an oxidant, according to a general Fenton reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \; k = 63 \, M^{-1} \, s^{-1} \tag{3}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \; k = 2.7 \times 10^{-3} \, M^{-1} \, s^{-1} \tag{4}$$

Although $Fe^{2+}$ acts as a catalyst when the solution pH is maintained around 3.0, the reduction of $Fe^{3+}$ (in a so-called Fenton-like reaction) is relatively slow [25]. This preconditioning of Fe(II) salt with $H_2O_2$ can provide an input stream of completely dissolved Fe(III) as a precipitant. The amount of ferric salt is affected