



# Evaluation of hydroxyapatite crystallization in a batch reactor for the valorization of alkaline phosphate concentrates from wastewater treatment plants using calcium chloride



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## HIGHLIGHTS

- Hap was obtained by chemical precipitation using concentrated P(V) alkaline brines.
- Three stages were identified in the precipitation of phosphate as Hap.
- Higher precipitation rate of P(V) was obtained at constant pH of 11.5.
- Hap with higher degree of crystallinity was formed at higher P(V)<sub>0</sub> concentration.
- At higher Ca(II) dosing rate, mean size and degree of crystallinity were higher.

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## ABSTRACT

In this work, phosphorous recovery as hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}(s) = \text{Hap}$ ) from alkaline phosphate concentrates (0.25–1 g P- $\text{PO}_4^{3-}/\text{L}$ ) using calcium chloride (6 g/L) in a batch reactor was evaluated. Ca(II) solutions was continuously fed (0.1–0.3 mL/min) up to reaching a Ca/P ratio of ~1.67 (5/3) to promote Hap formation. Hap powders were characterized by structural form (using X-ray diffraction (XRD), laser light scattering (LS) and Fourier transform infrared spectroscopy (FTIR)); textural form (using Field Emission Scanning Electron Microscopy with Energy Dispersive System (FE-SEM/EDS) and Brunauer–Emmett–Teller (BET)) and thermally (using Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA)). When pH was kept constant in alkaline values (from 8 to 11.5), Hap precipitation efficiency was improved. At pH 11.5, higher phosphorous precipitation rate was registered compared to that obtained for pH 8 and 10, but lower degree of crystallinity was observed in the Hap powders. The increase of the total initial phosphate concentration lead to the formation of Hap powders with higher degree of crystallinity and crystal diameter, but also lower mean particle size. As Ca(II) dosing rate increased Hap precipitation rate was higher, and also the mean size and degree of crystallinity of the prepared particles increased.

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## 1. Introduction

Phosphorus management has been recently highlighted by the United Nations Environment Program as one of the main emerging problems to be faced in the next decades. The use of phosphorous needs to become more efficient and its recycling more widespread, since the demand for phosphorus is increasing and the available

phosphorous resources are scarce. For instance, the excessive phosphorus content in wastewaters should be removed for controlling eutrophication and maintaining a sustainable environment for future generations. Several physical, biological and chemical processes include adsorption/ion exchange, chemical precipitation/coagulation, crystallization and membrane filtration/reverse osmosis for the removal and/or recovery of dissolved phosphates (P(V)) in water and wastewaters have been investigated [1–3].

Different research efforts during the last decade, have probed that phosphorus recovery at low levels (e.g. 2–10 mg/L), from domestic and urban waste waters is not economically feasible,

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using conventional removal processes (coagulation, chemical precipitation, adsorption, ion-exchange) [2,4,5]. However, the introduction of new processes using P-selective sorbents (e.g. metal oxides sorbents or metal oxide impregnated ion exchange resins) will provide concentrated effluents of phosphate (e.g. from 0.1 to 2 g P-PO<sub>4</sub><sup>3-</sup>/L) typically at alkaline pH values (9–12) due to the requirements of the regeneration step using 2–5% NaOH solutions [6]. The alkaline P(V)-brines are suitable candidates to recover the phosphate content as (calcium, magnesium, ammonium) – phosphate by-products using Ca(II), Mg(II), NH<sub>4</sub><sup>+</sup> brines generated in many industrial effluents, especially in processes using membrane desalination technologies or using low-cost raw materials [1,7,8].

In alkaline solutions, calcium phosphates (Ca-P) are highly stable minerals [9] however involve the crystallization of many meta-stable precursor phases. Amorphous calcium phosphate (ACP, Ca/P(1.5), Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O), dicalcium phosphate dihydrate (DCPD, Ca/P(1), CaHPO<sub>4</sub>·2H<sub>2</sub>O, brushite), β-whitlockite (β-TCP, Ca/P(1.5), β-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) and octacalcium phosphate (OCP, Ca/P(1.33) Ca<sub>8</sub>H<sub>2</sub>(-PO<sub>4</sub>)<sub>6</sub>·5H<sub>2</sub>O). All of them are frequently precipitated at low pH values. Hydroxyapatite (Hap) (Ca/P(1.67), Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) is the less soluble phase, preferentially formed in neutral to basic solutions [10,11]. Hap, is a compound with a variable composition existing over Ca/P molar ratios from 1.67 for stoichiometric up to ≈1.5 for fully calcium-deficient Hap [12], and sometimes even outside this range [13]. Direct precipitation of Hap has only been observed for low reactants concentrations, that is, slightly supersaturated or under saturated aqueous solutions with respect to a precursor phase [14,15]. Thermodynamically, Hap is postulated to control the P(V) concentration in many natural and industrial aqueous streams; however, the remaining P(V) concentration appear to be controlled for lengthy periods by meta-stable phases [9].

Hap synthesis by a precipitation route stands out because of its simplicity, low cost, and easy application in industrial production [16,17], although other methods are also used. Different procedures and starting salts have been used as source of phosphate (P(V)) and Ca(II) ions. Boskey and Posner [15], Lagno et al. [10], and more recently Du et al. [18] formed Hap by adding a CaCl<sub>2</sub> solution of (pH 7.4–7.6) to a solution of Na<sub>2</sub>HPO<sub>4</sub> (pH 10–11), or vice versa at 25 °C for a Ca/P ratio varied between 1.0 and 1.67.

Koutsoukos et al. [19] also studied the precipitation of Hap at 37 °C. Recently, Castro et al. [17] prepared Hap in a batch reactor by neutralization between a saturated Ca(OH)<sub>2</sub> solution with orthophosphoric acid solution, using several mixing Ca/P molar ratios (namely, 1, 1.33 and 1.67) at 37 °C and a agitation speed of 270 rpm.

Continuous Stirred-Tank Reactor (CSTR), Plug Flow Reactor (PFR) and Batch Reactors (BR) have been set up to study phosphate crystallization. Some researchers have demonstrated that BR have the advantage of providing extreme flexibility of operation and at the same time being physically simple, since all the treatment operations (i.e. flow equalization, precipitation reactions and solids settling) take place in one single tank. Castro et al. [20] also studied the continuous flow precipitation of Hap performed in a meso oscillatory flow reactor at laboratory and pilot-scale at 37 °C, at a molar ratio Ca/P of 1.33.

Phosphorous recovery is a topic of great concern nowadays and Hap precipitation has been reported as a suitable process to recover phosphate in a BR, thus, the integration of different technologies (sorption/ion exchange-precipitation) in a waste water treatment scheme can provide an alternative solution for phosphorous recovery. In view of that, the main objective of this work was to assess the recovery of phosphate P(V) from alkaline brines by using Ca(II) solution to precipitate Hap under different experimental conditions in a BR. The alkaline brines were obtained from a P(V) concentration process from waste waters using iron-oxide impregnated ion-exchange resins. The Hap precipitation process

was evaluated as a function of pH, as well as the Ca(II) dosing rate, the stirring speed and phosphate initial concentration. The Hap precipitates obtained under these operation conditions were properly characterized through the degree of crystallinity, the crystal diameter, the particle size distribution and the thermal analysis.

## 2. Materials and methods

### 2.1. Experimental set-up and procedures

The precipitation of phosphate from aqueous solutions was performed in a two liters lab-scale batch reactor made of glass as can be seen in Fig. 1. Agitation in the reactor was provided by a mechanical stirrer (IKA RW 20 and Heidolph RZR) and the stirring speed was ranged from 50 to 250 rpm. pH was monitored on-line by using a pH potentiometer (Crison pH 28). When pH was 0.1 units above or below the set point, strong acid (HCl 1 M) or strong base (NaOH 1 M) were dosed using a peristaltic pump (Master flex console drive). Experiments batch tests were carried out mixing a volume of NaH<sub>2</sub>PO<sub>4</sub> solution (with an initial phosphate concentration between 0.25 and 1.0 g P-PO<sub>4</sub><sup>3-</sup>/L) with a CaCl<sub>2</sub> solution (6.0 g Ca(II)/L) added at a flow rate ( $Q_{Ca}$ ) between 0.1 and 0.3 mL/min (by means of a peristaltic pump Gilson Minipuls 3). The reaction time was ranged between 6 and 24 h depending on the initial phosphate concentration, the flow rate and in order to reach at the end of the test a molar ratio Ca/P of 1.67, suitable for Hap precipitation. Experiments were performed at room temperature. Three different types of experiments were performed: (i) experiments to study the influence of pH (at 8, 10 and 11.5) at constant initial phosphate concentration (1.0 g P-PO<sub>4</sub><sup>3-</sup>/L), calcium dosing rate (0.1 mL/min) and stirring speed (250 rpm); (ii) experiments to study the influence of the total initial phosphate (P(V)) concentra-

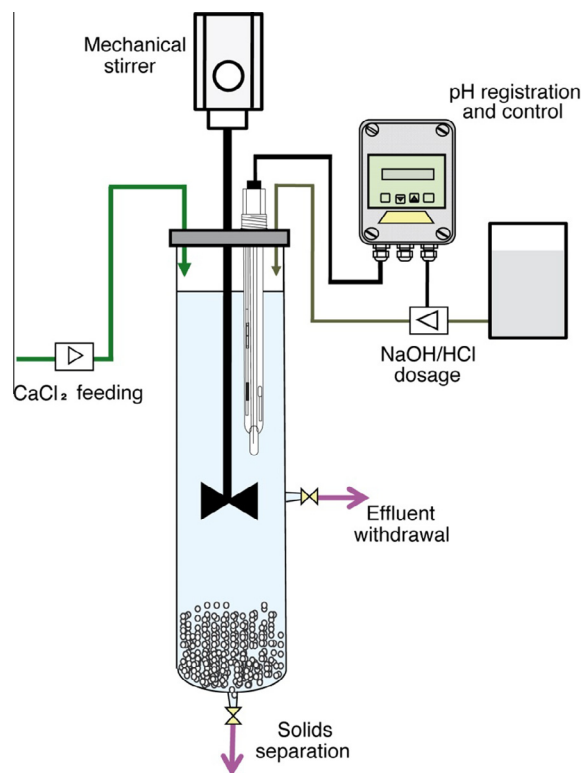


Fig. 1. Experimental set up of the batch reactor for phosphate precipitation with calcium including a CaCl<sub>2</sub> dosing pump, mechanical stirrer, the NaOH and HCl dosing pumps and the pH controller. Solids are removed at the bottom part of the reactor.

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