



ELECTROFLOTATION OF PRECIPITATED PHOSPHATE FROM SYNTHETIC SOLUTION

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ABSTRACT – The phosphate recovery from a 20 mg L⁻¹ Na₂HPO₄ solution through precipitation with Ca(OH)₂ followed by electroflotation was evaluated. X-ray diffraction and particle size measurements indicated that the precipitates were a mixture of hydroxyapatite and calcium-deficient hydroxyapatite, with size ranging from 3 to 10 μm. Electroflotation with Na-oleate as surfactant was used to recover the precipitates. The surfactant adsorption was evaluated through zeta potential measurements. The influence of Na-oleate concentration, pH and bubble size on phosphate recovery was investigated. In the absence of Na-oleate, a phosphate recovery of 50% was achieved, while in the presence of 20 mg L⁻¹ of Na-oleate it was increased to 90%, at pH 11. The phosphate recovery also increased with Ca(OH)₂ concentration increase and bubble size decrease, reaching 100% at 300 mg L⁻¹ Ca(OH)₂ and bubble size around 39 μm.

Keywords: Phosphate recovery, precipitation, electroflotation.

INTRODUCTION

Industrial and agricultural expansion currently demands a growing exploitation of phosphorus sources in the environment to supply human needs. This wide utilization of phosphates leads to a considerable amount of phosphorus-containing wastes being discharged into water bodies, demanding previous treatment to avoid eutrophication. Additionally, rainwater can wash the soil, removing phosphate fertilizers which can exacerbate still further the eutrophication issue, a phenomenon characterized by algae overpopulation and the rapid growth of aquatic plants, which impair the penetration of light in the water, thus reducing photosynthesis reactions and, consequently, the amount of dissolved oxygen in the water, suffocating aquatic animals and converting the water body into an open sewer (Hosni et al., 2008). Thus, the development of phosphorus management strategies in

the environment has been considered an important issue for quality of life support, leading to the search for new technologies to recover this element (Cordell et al., 2009), offering opportunities for its recycling, and contributing to phosphorus sustainability (Morse et al., 1998). At the present time, chemical and biological processes are the most used for phosphate removal from wastewaters. Among the biological processes, activated sludge is considered the most versatile and efficient, while among the chemical processes, precipitation through the use of aluminum, iron and calcium salts has been widely employed (Jenkins and Ferguson, 1971; Morse et al., 1998). Aluminum and iron salts present the disadvantage of generating sludge, which cannot be reused or reclaimed (Urano and Tachikawa, 1991). This problem does not occur with calcium salts, as they react with phosphate to generate precipitates such as hydroxyapatite, monetite, brushite and amorphous calcium phosphate, among others, which are compounds normally

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exploited in phosphate rock mining for fertilizer production and present the potential for reuse and recycling. However, calcium phosphate precipitates are difficult to settle, requiring the use of flocculants (Liu and Chang, 2009). Thus, there is a need to employ other solid/liquid separation techniques, such as flotation, which is a well established technique for minerals separation and is also commercially used for wastewater treatment (Hoseinian et al., 2015; Matis, 1995; Rubio et al., 1996; Rubio, 1998a,b; Rubio et al., 2002; Voronin and Dibrov, 1999). This technique is based on the different hydrophobicity of the particles to be separated. Thus, hydrophobic particles can be captured by gas bubbles and float to the liquid surface. To be effective, flotation requires the use of surfactants to render the particle surface more hydrophobic. The efficiency of this process depends on the probability of particle–bubble collision and attachment. For small particles there is a need for small bubbles such as those produced by dissolved air flotation or by electrolysis, which produce even smaller bubbles (Venkatachalam et al., 1992; Burns et al., 1997). Electroflotation is a process where particulate matter and/or polluting substances are floated through their adhesion on tiny hydrogen and oxygen (and other gases, depending on the electrolyte) bubbles generated electrolytically as a result of water decomposition. The application of this technique to ore fines recovery has been the object of investigation since 1946 (Miettinen et al., 2010). Bhaskar Raju and Khangaonkar (1984) studied the electroflotation of chalcopyrite ultrafines ($\sim 4 \mu\text{m}$) in a modified Hallimond tube with platinum anodes and copper cathodes. The authors observed that electrolytically generated bubbles rendered better floatability ($\sim 81.3\%$) compared to the floatability with an oxygen cylinder in a conventional Hallimond tube ($\sim 39.1\%$). Ketkar et al. (1991) studied the electroflotation of fine and ultrafine quartz particles ($< 20 \mu\text{m}$) in a modified Hallimond tube, with a stainless steel cathode and platinum as anode, and reported a recovery of 94% of the particles. Sarkar et al. (2010) compared the flotation of silica ultrafines ($\sim 13 \mu\text{m}$) in a Denver flotation cell using both air and hydrogen as the sparged gases with an electroflotation cell, and reported that much higher recoveries ($\sim 95\%$) were achieved when the electroflotation cell was used.

The feasibility of electroflotation applied to water and industrial wastewaters treatment has been demonstrated by several authors (Aoudj et al., 2015; Casqueira et al., 2006; Nahui et al., 2008; Vu et al., 2014); however, there is little information in the literature about the use of electroflotation for phosphate recovery from aqueous solutions. Vlyssides et al. (2002) studied the electrolytic treatment of domestic wastewater with an electrolytic cell with a Ti/Pt anode and an AISI 304 stainless steel cathode. The authors reported that the phosphate concentration decreased by 98% of its initial value (17.5 mg L^{-1}) in 60 minutes.

The electrocoagulation process has already reported by several authors as an alternative wastewater treatment

(Brahmi et al., 2015a,b; Bouguerra et al., 2015a,b; Kuokkanen et al., 2015). The main difference between electrocoagulation and electroflotation lies in the electrode type. In electrocoagulation soluble anodes of aluminum or iron are used, while insoluble anodes, such as RuO₂ coated titanium, are used in electroflotation. The technique used in this study has the advantage of generating more and smaller bubbles than those generated by electrocoagulation (Chen, 2003). Furthermore, electrocoagulation generates a more complex sludge, with aluminum or iron hydroxides, turning its reuse and recycling more difficult.

Considering the need for alternative treatments to recover phosphate from wastewaters and the success of flotation for apatite separation from other minerals, the objective of this paper was to assess the viability of recovering phosphate from a dilute synthetic solution, simulating a polishing stage of a municipal sewage treatment station by precipitation with calcium hydroxide followed by electroflotation.

MATERIALS AND METHODS

Calcium phosphate precipitate was obtained from a synthetic solution with 20 mg L^{-1} of Na₂HPO₄ and 50 mg L^{-1} of Ca(OH)₂. The precipitating agent Ca(OH)₂ concentration range was previously determined through a Jar test equipment. The precipitate was analyzed by X-ray diffraction (Shimadzu model XRD-6000), with CuK α radiation. The zeta potential was determined with a Zetasizer Nano Series (Nano-ZS). The particle size of the precipitate and the average bubble diameter were determined with a Malvern Instruments Mastersizer 2000SM capable of analyzing particles with diameters between 0.1–2000 μm .

The average bubble diameter was determined with the help of a specially designed acrylic cylindrical cell with a volume of 1 liter, to fit in a Malvern Instruments Mastersizer 2000SM device. The cathode was a stainless steel mesh and the anode an RuO₂ coated titanium grid. A constant electrical current was applied to the electrodes using a DC power supply. The influence of pH and current density on the bubble diameter in a 0.1 mol L^{-1} NaCl solution was evaluated.

Electroflotation tests were carried out in a 1-liter volume acrylic cell, with an AISI 316 stainless steel cathode and RuO₂ coated titanium as anode, as shown in Figure 1. A cathode–anode potential of 3.5 V, producing a cathodic current density of 6.25 mA cm^{-2} , was used in all the electroflotation experiments. Sodium oleate (CH₃(CH₂)₇CH=CH(CH₂)₇COO–Na⁺) was used as surfactant for the phosphate precipitate.

The influence of Na-oleate concentration, pH, calcium hydroxide concentration and bubble size on the phosphate recovery and on the zeta potential of the precipitate was evaluated. The solution used in the electroflotation tests

was 20 mg L⁻¹ of Na₂HPO₄, 50 mg L⁻¹ of Ca(OH)₂ and 0.1 mol L⁻¹ NaCl as electrolyte with 0.1 mol L⁻¹ HCl or NaOH as pH regulators. All reagents used were obtained from VETEC and were analytical grade.

For each experiment, a phosphate solution with a definite concentration of Ca(OH)₂ was fed into the electroflotation cell. After 20 minutes the phosphate concentration of the residual solution was determined by the photometric method (HI 83099, HANNA Instruments).

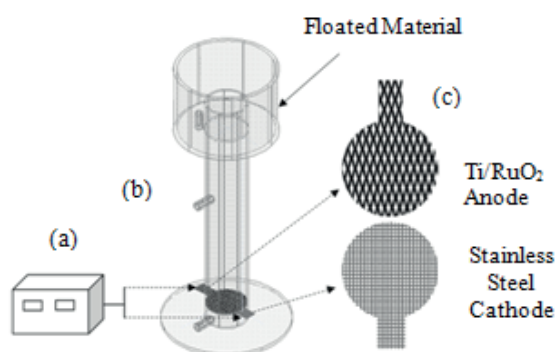


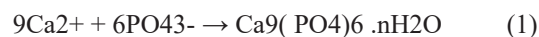
Figure 1. Schematic of the electroflotation system: (a) DC power source; (b) electroflotation cell; (c) electrodes.

RESULTS AND DISCUSSION

Precipitate characterization.

The X-ray diffractogram of the precipitate obtained from a solution containing 20 mg L⁻¹ of Na₂HPO₄ and 50 mg L⁻¹ of Ca(OH)₂ at pH 11 is presented in Figure 2. It can be observed that the precipitate is composed of a mixture of hydroxyapatite [hydroxide calcium phosphate, Ca₅(PO₄)₃(OH)] and a calcium-deficient hydroxyapatite [hydroxide calcium hydrogen phosphate Ca₉HPO₄(PO₄)₅OH] which is a non-stoichiometric hydroxyapatite. According to some authors (Abbona et al., 1986; Musvoto et al., 2000; Liu et al., 2009), hydroxyapatite precipitation starts at pH > 5; however, the precipitation reaction kinetics is not favored and other species, such as amorphous calcium phosphate, octacalcium phosphate and brushite, act as precursors of the hydroxyapatite precipitation. Gray and Schwab (1993) reported that calcium phosphate precipitation is almost complete at pH values higher than 9.8. A convenient method to classify the calcium phosphates is through their [Ca]:[P] molar ratio, which ranges from 0.5 to 2.0. The stoichiometric hydroxyapatite has a [Ca]:[P] molar ratio 1.67, while this molar ratio for non-stoichiometric hydroxyapatite can be 1.5 ≤ [Ca]:[P] < 1.67 (Stoia et al., 2008). Zawacki et al. (1990) proposed a two-step mechanism for the precipitation of calcium-deficient hydroxyapatite, as shown in the reactions 1 and 2:

Precipitation of amorphous calcium phosphate



Hydrolysis of PO₄³⁻



resulting in the final product (Ca_{10-x}(HPO₄)_x(PO₄)_{6-x}(OH)_{2-x}), 0 < x ≤ 1. For X=1, [Ca]:[P]=1.5, the product found was hydroxide calcium hydrogen phosphate, Ca₉(HPO₄)(PO₄)₅OH, as shown in the diffractogram of Figure 2.

The precipitate size distribution is presented in Figure 3. Among the information generated by the particle size analyzer is the cumulative curve that corresponds to the result accumulated below a given diameter, and the frequency characteristic curve is represented in the chart by the curve with a peak obtained by derivation of the cumulative curve. It can be observed that 10% of precipitates in the sample have diameters below 3 mm, 50% of precipitates in the sample have diameters below 5 mm (generally regarded as the average particle size of the sample) and 90% of precipitates in the sample have diameters below 8 mm, a size small enough to justify the use of electroflotation to recover the phosphates, since this technique produces bubbles smaller than those produced in the regular flotation process or even in dissolved air flotation.

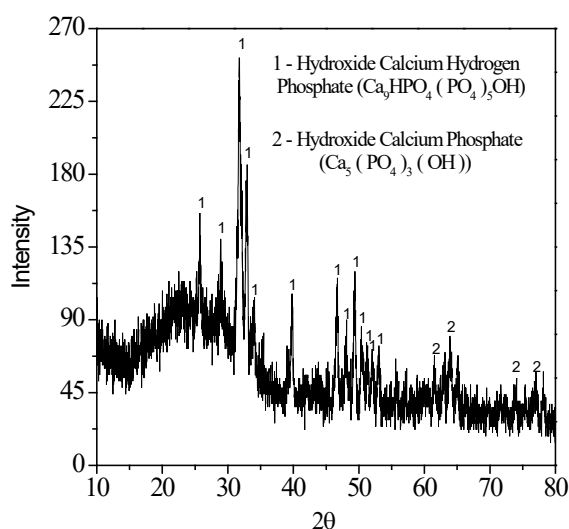


Figure 2. Precipitate X-ray diffractogram obtained from a solution containing 20 mg L⁻¹ of Na₂HPO₄ and 50 mg L⁻¹ of Ca(OH)₂ at pH 11.

Effect of sodium oleate on the phosphate recovery

The effect of Na-oleate concentration on the phosphate recovery by electroflotation and on the zeta potential of the precipitate particles is presented in Figure 4. It can be observed that, in the absence of Na-oleate, a phosphate recovery of 50% was achieved. The precipitates formed are sparingly soluble species, hydrophilic and with an average diameter around 5.5 μm . Therefore, it is suggested that the phosphate recovery is a function of entrainment (Warren, 1985). According to this author, in the entrainment mechanism there is no discrimination between hydrophobic and hydrophilic particles. This phenomenon occurs when the particles enter the base of the froth column suspended in the water occupying the spaces between the bubbles. Some of the inter-bubble water and some of the larger particles are drained back into the pulp, but the remainder is carried upwards and is ultimately recovered in the concentrate. The finer the particle ($<10 \mu\text{m}$), the more likely it is to remain suspended in the inter-bubble water and to be recovered by entrainment rather than by true flotation, a process that occurs only with hydrophobic particles.

In the presence of Na-oleate, it is possible to observe an increase of phosphate recovery in the range of less concentrated surfactant (2–20 mg L^{-1}) and a decrease of phosphate recovery for concentrations above 20 mg L^{-1} .

The zeta potential of the precipitate is around -7 mV in the absence of Na-oleate. In the presence of Na-oleate, it can be observed that the zeta potential of the precipitate assumes more negative values in the concentration range studied, as shown in Figure 4B, which suggests the surfactant adsorption on the precipitate. According to the oleate adsorption isotherm on apatite reported by Lu et al. (1998), in the less concentrated range of Na-oleate (2–20 mg L^{-1}), the adsorption occurs by means of a chemisorption mechanism: the interaction between the dissociated ions ($\text{O}1^-$ ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}^-$) and $\text{O}122^-$) of the oleate with the precipitate surface cations (Ca^{2+} e CaOH^+), forming hemimicelles and rendering the surface hydrophobic. This kind of chemical interaction is a specific adsorption, and therefore of difficult desorption, which justifies the increase of phosphate recovery in this concentration range, achieving the maximum recovery of 90% in the presence of 20 mg L^{-1} of Na-oleate.

In the more concentrated range, the adsorption occurs due to the surface precipitation mechanism. The interaction of the oleate ions with the surface cations leads to the formation of insoluble salts at the surface of the precipitate (hydroxyapatite). This interaction can be represented by a specific reaction between the surface cations of the precipitate and the $\text{O}1^-$ anionic groups of the surfactant, forming calcium oleate on the precipitate surface. In this type of mechanism, the adsorption is weak once the calcium oleate is attached to the mineral surface by attractive Van der Waals forces, and therefore of

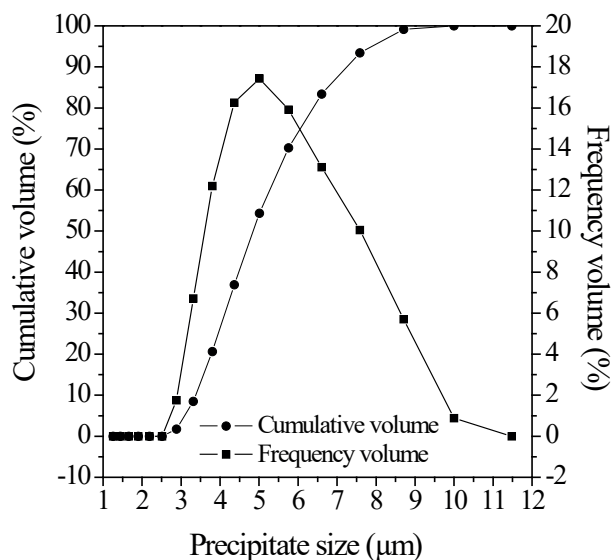


Figure 3. Precipitate size distribution obtained from a solution containing 20 mg L^{-1} of Na_2HPO_4 and 50 mg L^{-1} of $\text{Ca}(\text{OH})_2$ at pH 11.

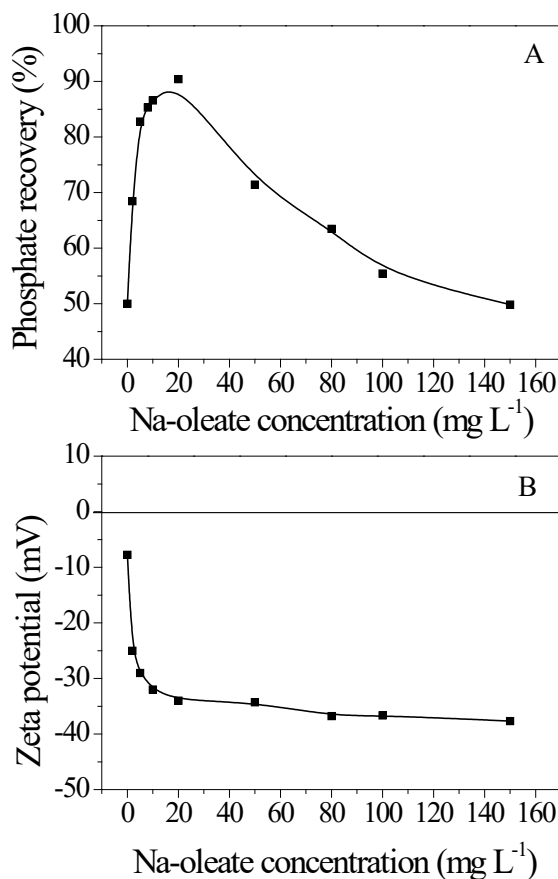


Figure 4. Phosphate recovery (A) and zeta potential of precipitate (B) as a function of the Na-oleate concentration in a 0.1 mol L^{-1} NaCl solution as electrolyte at pH 11.

easy desorption, justifying the decrease of the phosphate recovery in this concentration range. Furthermore, some studies (Antti and Forsberg, 1989; Hanumantha Rao et al., 1990; Hanumantha Rao and Forsberg, 1991) have reported that in pH 11 the oleate adsorption isotherm on the apatite surface corresponds to the formation of an oleate bilayer on the same surface. The second layer of surfactant is formed by the bond between the two hydrocarbon chains of the reagent, leaving the polar head groups toward the water solution and rendering the precipitate surface again hydrophilic, causing a decrease of the phosphate recovery. It can be concluded that, in the more concentrated range, the floatability of precipitated hydroxyapatite decreases as a result of oleate dimer adsorption and precipitation of CaO12.

Effect of pH on the phosphate recovery

The effect of pH on the phosphate recovery and on the zeta potential of precipitated hydroxyapatite in the absence and in the presence of Na-oleate is presented in Figure 5. It can be observed that, in the absence of Na-oleate, the phosphate recovery was possible at high pH, being increased from 20% to 50% when the pH is increased from 4 to 12. This increase can be attributed to the stability of hydroxyapatite at high pH. Diagrams of the total calcium and total phosphorus concentration as a function of pH for hydroxyapatite, as described by Chander and Fuerstenau (1979), confirm that the solubility of the hydroxyapatite decreases with the pH increase, which can contribute to the increasing phosphate recovery as a function of entrainment.

In the presence of Na-oleate an increase of the phosphate recovery in the whole pH range studied was observed. This increase can be attributed to the adsorption of Na-oleate on the precipitate surface and, with that, the phosphate recovery can become a function of the true flotation.

In Figure 5B, it can be observed that, in the absence of surfactant, the zeta potential of the precipitate is negative in the whole pH range, due to the prevalence of negatively charged species in the Stern layer of the electrical double layer of hydroxyapatite, as proposed by Vucinic et al. (2010). In the presence of 20 mg L⁻¹ Na-oleate, the precipitate charge became more negative in the whole pH range studied.

According to the distribution diagram of phosphoric acid, the predominant species in the solution are H₂PO₄⁻ ions in the pH range from 2.4 to 7.2, HPO₄²⁻ ions from 7.2 to 12, and PO₄³⁻ ions above pH 12. With regard to calcium, Ca²⁺ ions are the main species up to pH 12.5. The monohydroxy complex CaOH⁺ is present in notable concentrations above pH 11, while calcium hydroxide precipitates above pH 13.3 (Somasundaran et al., 1985).

Vucinic et al. (2010) evaluated the electrokinetic properties of hydroxyapatite and presumed that the surface ions Ca²⁺, PO₄³⁻ and OH⁻ are the species that participate

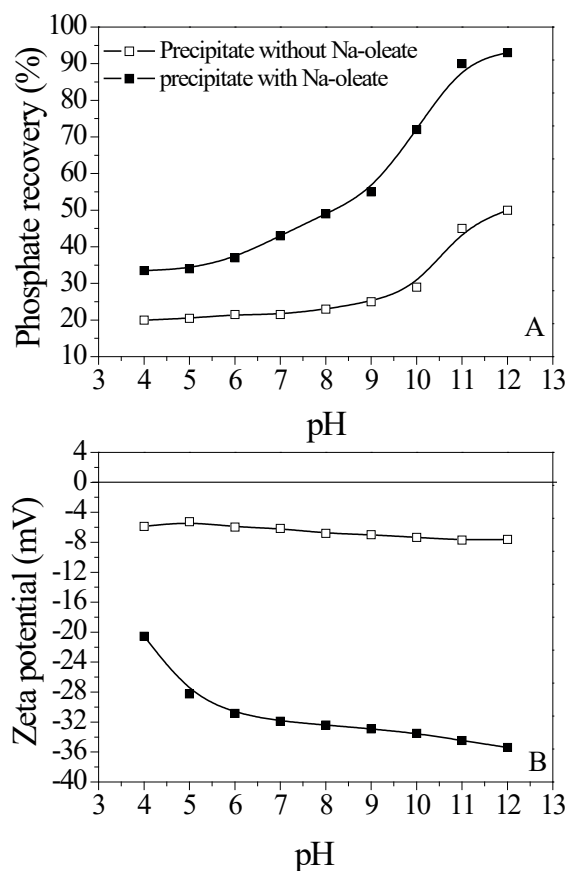


Figure 5. Phosphate recovery (A) and zeta potential of precipitate (B) as a function of pH in the absence and presence of 20 mg L⁻¹ Na-oleate in a 0.1 mol L⁻¹ NaCl solution as electrolyte.

in the surface reactions, similar to those reactions that occur in the bulk.

According to the distribution diagram of oleate (Somasundaran et al., 1999), the predominant species below pH 5 are neutral acid molecules (HOI). In the pH range from 5 to 9, oleate ions (OI⁻) and ion-molecule complexes H(OI)₂ are the dominant species, whereas at pH >9 the dominant ions are OI⁻ and dimers OI₂²⁻. Based on the distributions of the species mentioned above, in the pH range from 4 to 6, the increase in the negative zeta potential of the precipitate indicates the chemisorption of oleate ions and neutral molecules, oriented with head groups toward the solid, and with hydrocarbon chains toward the water solution, forming hemimicelles and rendering the surface hydrophobic, and therefore more floatable (Nunes et al., 2011; Vucinic et al., 2010). In the pH range from 7 to 9, the oleate ions and the ion molecule complex, oriented with head groups toward the solid and associated due to the chain-chain interaction into hemimicelles make the precipitate surface more hydrophobic and more floatable (Vucinic et al., 2010). The maximum zeta potential difference with and without Na-oleate addition

was observed above pH 10. This can be attributed to the adsorption of oleate ions, dimers, as well as OH⁻ on the precipitate surface. It is believed that the high phosphate recovery above pH 10 can be explained by the formation of the monohydroxy complex (CaOH⁺), which adsorbs on the negatively charged precipitate, forming reactive sites available for the surfactant adsorption and allowing an increase of the floatability of minerals. Therefore, the phosphate recovery around 90% can be explained by the adsorption of oleate ions and dimers at the positive surface sites of the negatively charged precipitate surface.

Effect of the calcium hydroxide concentration on the phosphate recovery

The effect of the calcium hydroxide concentration on the phosphate recovery and on the zeta potential of precipitates in the absence and presence of Na-oleate is presented in Figure 6. In Figure 6A it can be observed that, in both the presence and absence of Na-oleate, the phosphate recovery slightly increases as the concentration of Ca(OH)₂ is increased. In the absence of Na-oleate the phosphate recovery increased from 50% to 80% when the Ca(OH)₂ concentration was increased from 50 mg L⁻¹ to 300 mg L⁻¹. This increase can be attributed to the increase of phosphate precipitation with increasing concentration of the precipitating agent, which may suggest the generation of a calcium phosphate mineral that is less soluble at higher pH levels.

According to some studies, phosphate precipitation from wastewater is significantly increased by calcium concentrations higher than 50mg.L⁻¹ and water pH higher than 8 (Ferguson et al., 1973; Jenkins et al., 1971; Arvin, 1983; Diaz et al., 1994). Jenkins et al. (1971) reported that a calcium concentration of 80mg.L⁻¹ and a water pH higher than 8 were needed to precipitate 80% of the phosphate from the wastewater. Diaz et al. (1994) reported that an effective phosphate precipitation requires a calcium concentration higher than 100 mg L⁻¹ and pH 8. However, higher pH levels (>9) may be needed to form a more stable calcium phosphate mineral. According to the theoretical solubility isotherms for calcium phosphate minerals reported by the same authors, the species beta tricalcium phosphate, octacalcium phosphate, dicalcium phosphate dehydrate and calcite are formed at high calcium concentration (>50 mg L⁻¹) and high pH (>9) conditions. These species of calcium phosphate formed are less soluble than hydroxyapatite, and therefore more stable, which may contribute to increase the phosphate recovery as a function of entrainment.

In the presence of Na-oleate the phosphate recovery increased from 90% to 100% when the Ca(OH)₂ concentration was increased from 50 mg L⁻¹ to 300 mg L⁻¹. This increase can be attributed to an increase of the Ca²⁺ and CaOH⁺ ion concentrations on the precipitate surface, activating the adsorption of oleate ions. Horta et al. (2015)

reported that apatite floatability increases with the rise of the initial dissolution rate and consequent increase of available Ca²⁺ ions.

In Figure 6B it can be observed that, in the absence of Na-oleate, the zeta potential of the precipitate becomes less negative with increasing Ca(OH)₂ concentrations and the particle charge is changed to positive values for a Ca(OH)₂ concentration around 90 mg L⁻¹. These results can be attributed to an increase of the Ca²⁺ and CaOH⁺ ion concentrations in solution, which adsorb on the precipitate surface forming reactive sites for the surfactant adsorption. It can be observed that, in the presence of 20 mg L⁻¹ Na-oleate, the precipitate charge is negative for all of the concentration range studied. The zeta potential difference, with and without Na-oleate addition, was increased with the increase of Ca(OH)₂. The increased adsorption of oleate ions on the mineral surface in the presence of dissolved calcium ions was reported by Bibawy and Yousef (1985) and Sis and Chander (2003). The increase of phosphate

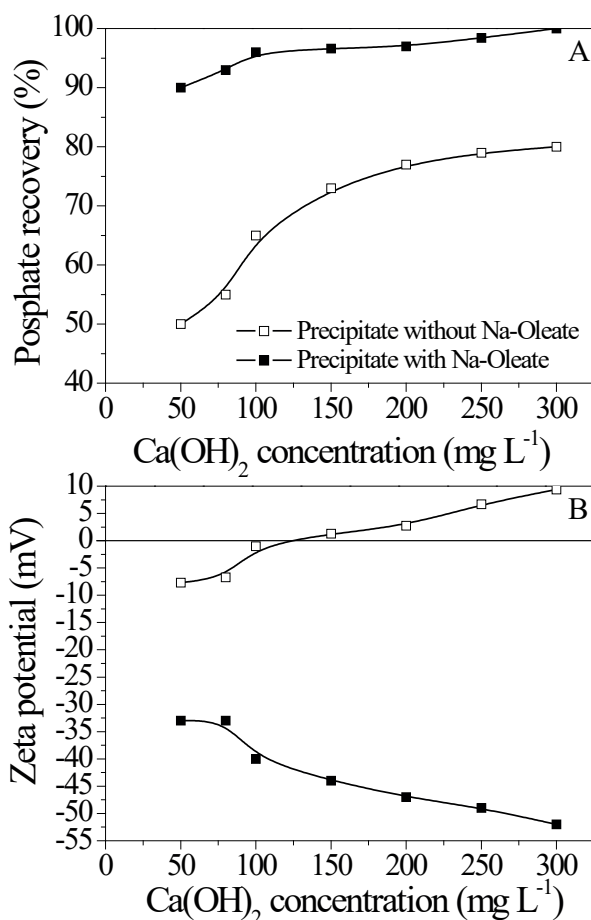


Figure 6. Phosphate recovery (A) and zeta potential of precipitates (B) as a function of the calcium hydroxide concentration in the absence and presence of 20 mg L⁻¹ Na-oleate in a 0.1 mol L⁻¹ NaCl solution as electrolyte at pH 11.

recovery from 90 to 100% at 300 mg L⁻¹ Ca(OH)₂ was attributed to the adsorption increase of oleate ions on the precipitate surface, since the negative value of zeta potential increases with increasing Ca(OH)₂ concentration in the presence of 20 mg L⁻¹ Na-oleate.

Effect of bubble size on the phosphate recovery

The influence of the pH and current density on the average bubble size and phosphate recovery, in the presence of 20 mg L⁻¹ Na-oleate, is presented in Table 1.

It can be observed that the phosphate recovery increases and the bubble size decreases as the pH and current density increase. The conditions for high phosphate recovery can be attributed to the increase of the collision efficiency between the precipitates and the generated bubbles.

According to the studies reported by Nguyen et al. (2006) and Sarrot et al. (2007), the collision efficiency of particles with diameters between 1 and 10 μm is increased with decreasing size of the bubbles. The capture efficiency of a particle by a rising air bubble is given by the product between collision efficiency, attachment efficiency and the particle-bubble aggregate stability efficiency as shown in Equation 1.

$$E_{cap} = E_c E_a E_s \quad (1)$$

where E_c is the collision efficiency, E_a is the attachment efficiency and E_s is the particle-bubble aggregate stability efficiency.

Dai et al. (2000) considered attachment and stability efficiencies equal to 1 for small and hydrophobic particles interacting with microbubbles, both being conditions met for the electroflotation of the phosphate particles used. Therefore, the capture efficiency is equal to the collision efficiency and can be expressed by Equation 2.

$$E_{c=} = \frac{3}{2} \left(\frac{d_p}{d_b} \right)^2 \quad (2)$$

The relationship between the bubble size and the collision efficiency described by Equation 2 with a value of particle size fixed at 5.5 μm is presented in Figure 7. It can be observed that the particle-bubble collision efficiency is increased as the bubble size decreases. It is concluded that the smaller bubbles generated in the alkaline pH range and high current density resulted in a higher collision efficiency, explaining the recoveries above 90% of the fines precipitates.

Table 1. Phosphate recovery and bubble average Sauter's diameter as a function of pH and current density. Cell with stainless steel (AISI 316) mesh cathode and ruthenium-oxide coated titanium anode. 20 mg L⁻¹ of sodium oleate used as surfactant in phosphate electroflotation and 0.1 mol L⁻¹ NaCl solution as electrolyte.

Phosphate recovery as a function of pH. current density = 14mA cm-2		
pH	Average bubble size (μm)	Recovery (%)
4.0	52.2	33.5
5.0	48.5	34
6.0	45.5	37
7.0	43.2	43
8.0	41.7	49
9.0	40.8	55
10.0	40.2	72
11.0	39.6	90
12.0	38.8	93
Phosphate recovery as a function of current density.pH=11		
Current density (mA cm-2)	Average bubble size (μm)	Recovery (%)
14	39.678	90
23	34.18	92
40	32.267	94,5
60	31.35	95
77	30.96	95

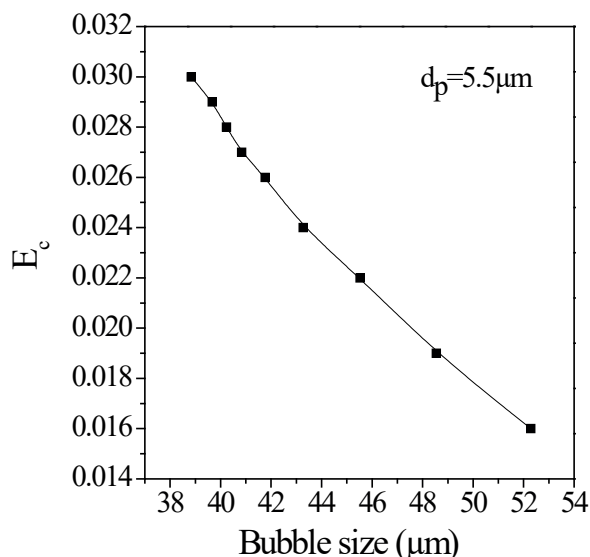


Figure 7. Variation of collision efficiency as a function of bubble size. Particle size fixed at 5.5 μm.

CONCLUSIONS

The results demonstrated that phosphate precipitation with calcium hydroxide and electroflotation can be used to recover phosphate from the synthetic solution. Hydroxyapatite and calcium-deficient hydroxyapatite with particle sizes ranging from 3 to 10 μm were obtained with 50 mg L⁻¹ of Ca(OH)₂. A recovery of 50% of fine precipitates was achieved in the absence of surfactant. The addition of Na-oleate favored phosphate recovery. The increase in phosphate recovery was attributed to the adsorption of oleate ions on the precipitate surface, rendering its surface hydrophobic, and therefore more floatable. A phosphate recovery around 90% was achieved with 20 mg L⁻¹ of Na-oleate at pH 11 and bubble sizes around 39 μm. An increase in the calcium hydroxide concentration led to an increase in the phosphate recovery, reaching a recovery of 100% at 300 mg L⁻¹.

These results indicate that electroflotation can be an effective alternative treatment for wastewater with phosphate concentrations above that established by legislation and, at the same time, recover the phosphates present in the wastewater. Tests with real wastewaters should be the object of a future work.

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REFERENCES

Abbona, E., Lundager Madsen, H. E. and Boistelle, R., The initial phases of calcium and magnesium phosphate precipitated

from solutions of high to medium concentrations, *Journal of Crystal Growth*, 74, No. 3, 581-590 (1986).

Antti, B. M. and Forssberg, E., Pulp chemistry in industrial mineral flotation. Studies of surface complex on calcite and apatite surfaces using FTIR spectroscopy, *Minerals Engineering*, 2, No. 2, 217-227 (1989).

Aoudj, S., Khelifa, A., Drouich, N., Belkada, R. and Miroud, D., Simultaneous removal of chromium(VI) and fluoride by electrocoagulation-electroflotation: Application of a hybrid Fe-Al anode, *Chemical Engineering Journal*, 267, 153-162 (2015).

Arvin, E., Observations supporting phosphate removal by biologically mediated chemical precipitation-a review. *Water Science and Technology*, 15, 43-63 (1983).

Bhaskar Raju, G. and Khangaonkar, P. R., Electroflotation of chalcopryrite fines with sodium diethyldithiocarbamate as collector, *International Journal of Mineral Processing*, 13, 211-221 (1984).

Bibawy, T. A. and Yousef, A. A., Adsorption behavior of precipitated tribasic calcium phosphate, *Tenside Detergents*, 22, 83-87 (1985).

Bouguerra, W., Barhoumi, A., Ibrahim, N., Brahmi, K., Aloui, L. and Hamrouni, B., Optimization of the electrocoagulation process for the removal of lead from water using aluminium as electrode material, *Desalination and Water Treatment*, 56, No. 10, 2672-2681 (2015a).

Bouguerra, W., Brahmi, K., Elaloui, E., Loungou, M. and Hamrouni, B., Optimization of electrocoagulation operating parameters and reactor design for zinc removal: application to industrial Tunisian wastewater, *Desalination and Water Treatment*, 56, No. 10, 2706-2714 (2015b).

Brahmi, K., Bouguerra, B., Hamrouni, B. and Loungou, M., Removal of zinc ions from synthetic and industrial Tunisian wastewater by electrocoagulation using aluminium electrodes, *Desalination and Water Treatment*, 56, N0.10, 2689-2698 (2015a).

Brahmi, K., Bouguerra, W., Hamrouni, B., Elaloui, E., Loungou, M. and Tlili, Z., Investigation of electrocoagulation reactor design parameters effect on the removal of cadmium from synthetic and phosphate industrial wastewater, *Arabian Journal of Chemistry*, (2015b). <https://doi.org/10.1016/j.arabjc.2014.12.012>

Burns, S. E., Yiacoumi, S. and Tsouris, C., Microbubble generation for environmental and industrial separation, *Separation and Purification Technology*, 11, No. 3, 221-232 (1997).

Casqueira, R. G., Torem, M. L. and Kohler, H. M., The removal of zinc from liquid streams by electroflotation, *Mineral Engineering*, 19, 1388-1392 (2006).

Chander, S. and Fuerstenau, D. W., Interfacial properties and equilibria in the apatite-aqueous solution system, *Journal of Colloid and International Science*, 70, No. 3, 506-516 (1979).

Cordell, D., Drangert, J. O. and White, S., The story of phosphorus: Global food security and food for thought, *Global Environmental Change*, 19, No. 2, 292-305 (2009).

Dai, Z., Fornasiero, D. and Ralston, J., Particle-bubble collision models - a review, *Advances in Colloid and Interface Science*, 85, No. 2-3, 231-256 (2000).

- Diaz, O. A., Reddy, K. R. and Moore, P. A., Solubility of inorganic phosphorus in stream water as influenced by pH and calcium concentration, *Water Research*, 28, No. 8, 1755-1763 (1994).
- Ferguson, J. F., Jenkins, D. and Eastman, J., Calcium phosphate precipitation at slightly alkaline pH values, *Journal of the Water Pollution Control Federation*, 45, 620-631 (1973).
- Gray, C. A. and Schwab, A. P., Phosphorus-fixing ability of high pH, high calcium, coal- combustion, waste materials. *Water Air Soil Pollut*, 69, No. 3-4, 309-320 (1993).
- Hanumantha Rao, K., Britt-Marie, A. and Forsberg, E., Mechanism of interaction on salt-type minerals, Part II: Adsorption and electrokinetic studies of apatite in the presence of sodium oleate and sodium metasilicate, *International Journal of Mineral Processing*, 28, 59-79 (1990).
- Hanumantha Rao, K. and Forsberg, K. S. E., Mechanism of fatty acid adsorption in salt-type minerals flotation, *Minerals Engineering*, 4, No. 7-11, 879-890 (1991).
- Horta, D., Monte, M.B.M. and Leal Filho, L.S., The effect of dissolution kinetics on flotation response of apatite with sodium oleate, *International Journal of Mineral Processing*, 146, 97-104 (2015).
- Hoseinian, F. S., Irannajad, M. and Nooshabadi, A. J., Ion flotation for removal of Ni(II) and Zn(II) ions from wastewaters, *International Journal of Mineral Processing*, 143, 131-137 (2015).
- Hosni, K., Ben Moussa, S., Chachi, A. and Ben Amor, M., The removal of PO₄³⁻ by calcium hydroxide from synthetic wastewater: optimisation of the operating conditions, *Desalination*, 223, No. 1-3, 337-343 (2008).
- Jenkins, D. and Ferguson, J. F., Review paper chemical process for phosphate removal. *Water Research*, 5, 369-389 (1971).
- Ketkar, D. R., Mallikarjunan, R. and Venkatachalam, S., Electroflotation of quartz fines. *International Journal of Mineral Processing*, 31, No. 1-2, 127-138 (1991).
- Kuokkanen, V., Kuokkanen, T., Ramo, J., Lassi, U. and Roininen, J., Removal of phosphate from wastewaters for further utilization using electrocoagulation with hybrid electrodes - Techno-economic studies, *Journal of Water Process Engineering*, 8, 50-57 (2015).
- Liu, J. C. and Chang, C. J., Precipitation flotation of phosphate from water, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 34, 215-219 (2009).
- Lu, Y., Drellich, J., Miller, J. D., Oleate adsorption at an apatite surface studied by ex-situ FTIR internal reflection spectroscopy, *Journal of Colloid and Interface Science*, 476, No. 202, 462-476 (1998).
- Matis, K. A. (Ed.), *Flotation Science and Engineering*. Marcel Dekker, New York (1995).
- Miettinen, T., Ralston, J. and Fornasiero, D., The limits of fine particle flotation, *Minerals Engineering*, 23, No. 5, 420-437 (2010).
- Morse, G. K., Brett, S. W., Guy, J. A. and Lester, J. N., Phosphate removal and recovery technologies, *The Science of the Total Environment*, 212, 69-81 (1998).
- Musvoto, E. V., Wentzel, M. C. and Ekama, G. A., Integrated chemical-physical process modeling. II: Simulation aeration treatment for anaerobic digester supernatant, *Water Research*, 34, No. 6, 1868-1880 (2000).
- Nahui, F. N. B., Nascimento, M. R., Cavalcanti, E. B. and Vilar, E.O., Electroflotation of emulsified oil in industrial wastes evaluated with a full factorial design, *Brazilian Journal of Chemical Engineering*, 25, 435-442 (2008).
- Nguyen, A. V., George, P. and Jameson, G. J., Demonstration of a minimum in the recovery of nanoparticles by flotation: theory and experiment, *Chemical Engineering Science*, 61, 2494-2509 (2006).
- Nunes, A. P. L., Peres, A. E. C., Araujo, A. C. and Valadão, G. E. S., Electrokinetic properties of wavelite and its floatability with cationic and anionic surfactants, *Journal of Colloid and Interface Science*, 361, 632-638 (2011).
- Rubio, J., Schneider, I. A. H. and Aliaga, W., New processes for heavy metals separations from wastewater streams in the mining industry, *Proceedings of Clean Technologies for the Mining Industry*, p. 85-98 (1996).
- Rubio, J., Environmental applications of flotation. In: Castro, S. H., Vergana, F., Sanchez, M. (Eds.), *Effluent Treatment in the Mining Industry*. University of Concepción, Chile, p. 335-364 (1998a).
- Rubio, J., Flotation applied to effluent treatment. In: Castro, S. H., Vergana, F., Sanchez, M. (Eds.), *Environment and Innovation in Mineral Technology, IV International Conference on Clean Technologies for the Mining Industry*. University of Concepción, Chile, p. 353-366 (1998b).
- Rubio, J., Souza, M. L. and Smith, R. W., Overview of flotation as a wastewater treatment technique, *Minerals Engineering*, 15, 139-155 (2002).
- Sarkar, M. S. K. A., Donne, S. W. and Evans, G. M., Hydrogen bubble flotation of silica, *Advanced Powder Technology*, 21, No. 4, 412-418 (2010).
- Sarrot, V., Huang, Z., Legendre, D. and Guiraud, P., Experimental determination of particles capture efficiency in flotation, *Chemical Engineering Science*, 62, 7359-7369 (2007).
- Sis, H. and Chander, S., Adsorption and contact angle of single and binary mixtures of surfactants on apatite, *Minerals Engineering*, 16(9), 839-848 (2003).
- Somasundaran, P., Ananthapadmabhan, K. P. and Ofori Amankonah, J., Mineral solution equilibria in sparingly soluble mineral system, *Colloids and Surfaces*, 15, 309-333 (1985).
- Somasundaran, P. and Zhang, L. in: P. Zhang, H. El-Shall, R. Wiegel (Eds.), *Beneficiation of Phosphates, Advances in Research and Practice*, Society of Mining, Metallurgy, and Exploration, Inc., Littleton, CO, Chapter 12 (1999).
- Stoia, M., Ionescu, M., Stef, O., Murgan, R. and Stefanescu, M., Preparation of β -Tricalcium Phosphate from Precursors Obtained by a Wet Precipitation Method, *Chemical Bulletin of Politehnica University of Timisoara*, 53, No. 3, 1-2 (2008).
- Urano, K. and Tachikawa, H., Process-development for removal and recovery of phosphorus from wastewater by a new adsorbent. Preparation method and adsorption capability of a new adsorbent, *Industrial & Engineering Chemistry Research*, 30, No. 8, 1893-1896 (1991).
- Venkatachalam, S., Electrogenerated gas bubbles in flotation, *Mineral Processing and Extractive Metallurgy Review*, 8, 47-55 (1992).

- Vlyssides, A. G., Karlis, P. K., Rori, N. and Zorpas, A. A., Electrochemical treatment in relation to pH of domestic wastewater using Ti/Pt electrodes, *Journal of Hazardous Materials*, 95, 215-226 (2002).
- Voronin, N. N. and Dibrov, I. A., Classification of flotation processes in wastewater decontamination, *Journal of Environmental Engineering*, 124, No. 5, 469-472 (1999).
- Vu, T. P., Vogel, A., Kern, F., Platz, S., Menzel, U. and Gadow, R., Characteristics of an electrocoagulation–electroflotation process in separating powdered activated carbon from urban wastewater effluent, *Separation and Purification Technology*, 134, 196-203 (2014).
- Vucinic, D. R., Radulovic, D. S. and Deusic, S. D., Electrokinetic properties of hydroapatite under flotation conditions, *Journal of Colloid and Interface Science*, 343, 239-245 (2010).
- Warren, L. J., Determination of the contributions of true flotation and entrainment in batch flotation tests, *International Journal of Mineral Processing*, 14, 33-44 (1985).
- Zawacki, S. J., Eughebaert, J. C. and Nancollasz, G. H., The growth of nonstoichiometric apatite from aqueous solution at 37°. II: Effects of pH upon the precipitated phase, *Journal of Colloid and Interface Science*, 135, 33-44 (1990).