

# Recovery of different types of hydroxyapatite by precipitation of phosphates of wastewater from anodizing industry

Lorena Delgadillo-Velasco<sup>a</sup>, Virginia Hernández-Montoya<sup>a,\*</sup>, Miguel A. Montes-Morán<sup>b</sup>, Rigoberto Tovar Gómez<sup>a</sup>, Francisco J. Cervantes<sup>c</sup>

<sup>a</sup> TecNM/Instituto Tecnológico de Aguascalientes, Av. Adolfo López Mateos, No. 1801 Ote, C.P. 20256, Aguascalientes, Ags, México

<sup>b</sup> Instituto Nacional del Carbón, INCAR-CSIC, Apartado, 73, E-33080, Oviedo, Spain

<sup>c</sup> Laboratory for Research on Advanced Processes for Water Treatment, Instituto de Ingeniería, Unidad Académica Juriquilla, Universidad Nacional Autónoma de México, Blvd. Juriquilla 3001, 76230, Querétaro, México

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## ABSTRACT

Recovery of phosphates from an anodizing industry wastewater was studied by chemical precipitation. Samples of wastewater were selected attending to the highest phosphate concentration observed during 1 year of weekly sampling. Different types of precipitant agents were analyzed in batch systems. Results showed that it is possible to remove 100 % of phosphates when  $\text{Ca}(\text{OH})_2$  is used as precipitant agent. The best conditions of precipitation were found following a  $L_9$  orthogonal array design of the Taguchi method. For an initial concentration of phosphates of 4336 mg/L, these best conditions were a Ca/P molar ratio of 5.77, pH 2, stirring time of 15 min and settling time of 1 h. Additionally, it was demonstrated that the factors with more influence in the precipitation of phosphates with  $\text{Ca}(\text{OH})_2$  were the pH of the wastewater and the stirring time. When the phosphate removal was performed at pH 6 and 10, hydroxyapatite  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  was found in the precipitate, whereas other crystalline hydroxyapatite with a more complex structure  $(\text{Ca}_{3.36}\text{Na}_{0.08})(\text{Ca}_{5.04}\text{Na}_{0.72})(\text{PO}_4)_{3.6}(\text{CO}_3)_{2.4}(\text{OH})_2$  was identified in the experiment performed at pH 2. The present study provides valuable information to recover phosphate from industrial effluents.

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## 1. Introduction

Phosphorous (P) is an important constituent of living organisms, which is essential for plants, but natural P resources (e.g. phosphate rock) are depleting (Marshall et al., 2017; Krishna Veni et al., 2017; Amann et al., 2018; Muhmood et al., 2019; Pradel and Aissani, 2019). According to the Mineral Commodity Summaries 2016, mine production of phosphate rock was 223 ktons worldwide, while the remaining reserves are approximately 69 Mtons (Vasenko and Qu, 2018). Moreover, easily exploitable deposits will be exhausted at a more rapid pace since the remaining low-grade deposits are now considered difficult to exploit and are contaminated with cadmium and uranium (Franz, 2008). In this context, the recovery of phosphates from wastewater is an important strategy to provide alternative sources of P and several technologies have been applied with this purpose in the last decades including

precipitation, crystallization, ion exchange-precipitation, wet-chemical extraction, supercritical water oxidation, acidic/alkaline leaching, thermo-chemical and thermo-electric methods and biological treatments (Huang et al., 2017; Amann et al., 2018; Shiba and Ntuli, 2016; Sepehri and Sarrafzadeh, 2018, 2019). Precipitation is the most widely method used for P recovery and the main precipitation chemical agents are metallic salts of calcium ( $\text{Ca}^{2+}$ ), iron (either  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) or aluminum (either alum,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  or sodium aluminate,  $\text{Na}_2\text{Al}_2\text{O}_4$ ). Chloride and sulfate salts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are also used as precipitants (Mohammed and Shanshool, 2009).

Today, different types of wastewater have been studied for removing or recovering P since the discharge of untreated P-rich effluents leads to the eutrophication of aquatic ecosystems (Mor et al., 2016; Rabiul Awual, 2019; Li et al., 2018; Santos et al., 2019). For example, recovery and potential reuse of P from

\* Corresponding author.

E-mail address: [virginia.hm@aguascalientes.tecnm.mx](mailto:virginia.hm@aguascalientes.tecnm.mx) (V. Hernández-Montoya).

agricultural wastewater was studied using tomato plant roots as a capture matrix and carboxymethyl cellulose (CMC) as an eluent and enhancer of P precipitation. Results obtained indicated that it is possible to remove 226.5  $\mu\text{g/L}$  per day (Ure et al., 2019). Also, fosfomicin pharmaceutical wastewater was studied with the purpose to remove and recover phosphorous. In this case, an induced crystallization process, combined with schorl/ $\text{H}_2\text{O}_2$  (Fenton) system was used. In a first step, the organic phosphorous present in wastewater is transformed into inorganic phosphorous that is recovered as hydroxyapatite in a second step. Results showed that most of the recovered P was in the form of hydroxyapatite in the 10–11 pH range (Yang et al., 2019).

Wastewaters derived from electropainting industries generally have high concentrations of phosphates and sulfates and the recovery of these chemical species is an interesting topic currently undertaken by several research groups around the world. Anodizing is an electrochemical process by which an oxide film is formed over aluminum alloys to provide hardness and corrosion resistance. This process includes several steps, such as rinsing, etching, desmutting, anodizing, coloring and sealing. Anodizing is a fundamental step and it is performed in an acid solution. Depending on the aluminum surface finishing, several typical electrolytes such as sulfuric acid, phosphoric acid or hydrochloric acid are used under different conditions (Tramontin-Souza et al., 2019). To our best knowledge, there are not previous publications related to the removal and recovery of phosphates from wastewater generated in anodizing industries. Furthermore, intensive production in the automotive sector and related auxiliary industries generate large quantities of wastewater from anodizing processes, thus it is very important to explore strategies for recovery of phosphates from these effluents. The purpose of the present work is to study the recovery of phosphates from anodizing wastewater by precipitation method. The best conditions of precipitation have been determined following the Taguchi methodology. The response variable selected was the removal of phosphates from wastewater of an anodizing industry. The precipitates obtained were characterized using different analytical techniques with the purpose to visualize the type of chemical species formed during the precipitation reaction and the possible recovery of phosphates from those waters.

## 2. Materials and methods

### 2.1. Chemical precipitation of phosphate from wastewater

The removal of phosphate from wastewater was studied using

chemical precipitation in batch systems at room temperature ( $\sim 30^\circ\text{C}$ ). The wastewater used in this work was collected from an anodizing industry located in the Aguascalientes State (Mexico). Two samples of wastewater with high concentration of phosphates were selected after 1 year of weekly sampling. The first sample of wastewater was collected on September 20 (2017) with a phosphate concentration of 5119 mg/L and the second sample was collected on August 31 (2018) with a concentration of 4336 mg/L.

The chemical precipitation studies were conducted in three different ways as follows:

#### 2.1.1. Comparison of precipitants

Five reagents were tested as phosphate precipitants: Red-Oxy is a patented product from Watch Water México Company, whereas  $\text{KAl}(\text{SO}_4)_3$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{FeCl}_3$  were used as chemical reagents with analytical grade. The experiments of precipitation were performed in batch systems using a Precipitant/P molar ratio of 1.79, in which the precipitant was added to 250 ml of wastewater with an initial concentration of phosphates of 5119 mg/L. Then, the wastewater was stirred for 5 min, followed by a settling period of 120 h. After this time, the supernatant was separated from the precipitate with a micropipette and, subsequently, the phosphate concentration and pH were measured in the solution. Afterwards, the precipitates were dried at  $110^\circ\text{C}$  for 24 h and characterized with different analytical techniques (see section 2.2). The pH value of the initial and treated wastewater in all experiments of precipitation was measured with an UB-10 pH-meter from Denver Instruments; and phosphate concentration was determined using the colorimetric method 8114 (Molybdovanadate Method) of standard HACH procedures, using a HACH DR-5000 spectrophotometer.

#### 2.1.2. Taguchi methodology

The chemical reagent showing the highest precipitation of phosphate in test 2.1.1. ( $\text{Ca}(\text{OH})_2$ ) was selected for the optimization of the precipitation process using the Taguchi method. Specifically, a  $\text{L}_9$  orthogonal array of the Taguchi method was used to find the best conditions of precipitation to increase the phosphate removal (response variable). The factors studied were: A: Ca/P molar ratio, B: pH of the wastewater, C: Stirring time (min) and D: Settling time (h). The levels of each factor are shown in Table 1. For each experiment the pH adjustment was made by adding either 1 M  $\text{H}_2\text{SO}_4$  or 1 M NaOH. This set of experiments was carried out using 1 L of wastewater with an initial phosphate concentration of 4336 mg/L and batch reactors. Phosphates concentration was measured as

**Table 1**  
 $\text{L}_9$  orthogonal array of the Taguchi method used in the removal of phosphates from anodizing wastewater using  $\text{Ca}(\text{OH})_2$  as precipitant.

Levels	Factor			
	A (Ca/P molar ratio)	B (pH of wastewater)	C (Stirring time, min)	D (Settling time, h)
Level 1	1.92	2	2.5	0.5
Level 2	3.86	6	5	1
Level 3	5.77	10	15	3

Experiment	Factors			
	A (Ca/P molar ratio)	B (pH of waste water)	C (Stirring time, min)	D (Settling time, h)
1	1.92	2	2.5	0.5
2	1.92	6	5	1
3	1.92	10	15	3
4	3.85	2	5	3
5	3.85	6	15	0.5
6	3.85	10	2.5	1
7	5.77	2	15	1
8	5.77	6	2.5	3
9	5.77	10	5	0.5

described in section 2.1.1. The precipitates obtained in these experiments were dried at 110 °C for 24 h, for later analysis.

### 2.1.3. Scaling up of the precipitation reactor

Chemical precipitation studies were carried out in batch reactors of 0.2, 2 and 20 L using the best experimental conditions according to the Taguchi methodology and the wastewater with an initial phosphate concentration of 4336 mg/L. This scaling up of the reactor was made with the purpose to observe the variations in the removal of phosphate with respect to the volume of treated wastewater. Phosphate concentration and pH were analyzed similarly to experiment 2.1.1.

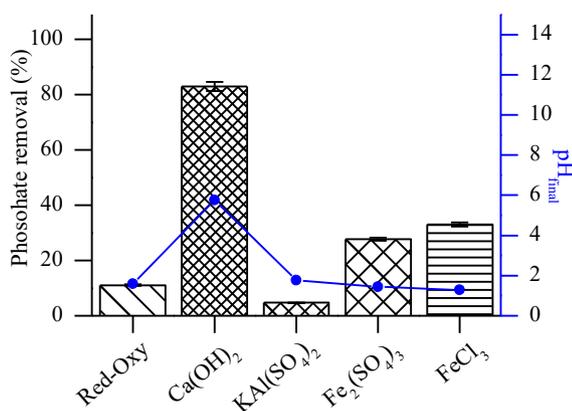
## 2.2. Characterization of precipitates

The original  $\text{Ca}(\text{OH})_2$  and some precipitates were selected and characterized using different analytical techniques. The functional groups were determined by FT-IR spectroscopy using a Thermo Scientific Nicolet iS10 spectrometer equipped with an ATR accessory. The crystalline phases in the precipitates were analyzed by X-ray diffraction in a Bruker D8 Advance diffractometer equipped with a  $\text{Cu K}\alpha$  X-ray source operated at 40 kV and 40 mA. A single Göbel mirror configuration was used to monochromatize and focus X-rays on samples, attaining a highly efficient parallel beam geometry. Diffraction data were collected by step scanning with a step size of  $0.02^\circ 2\theta$  and a scan step time of 5 s. Also, to get an insight of the composition of the precipitates, they were analyzed by SEM/EDX analyses using a Quanta FEG 650 FE-SEM system, from FEI.

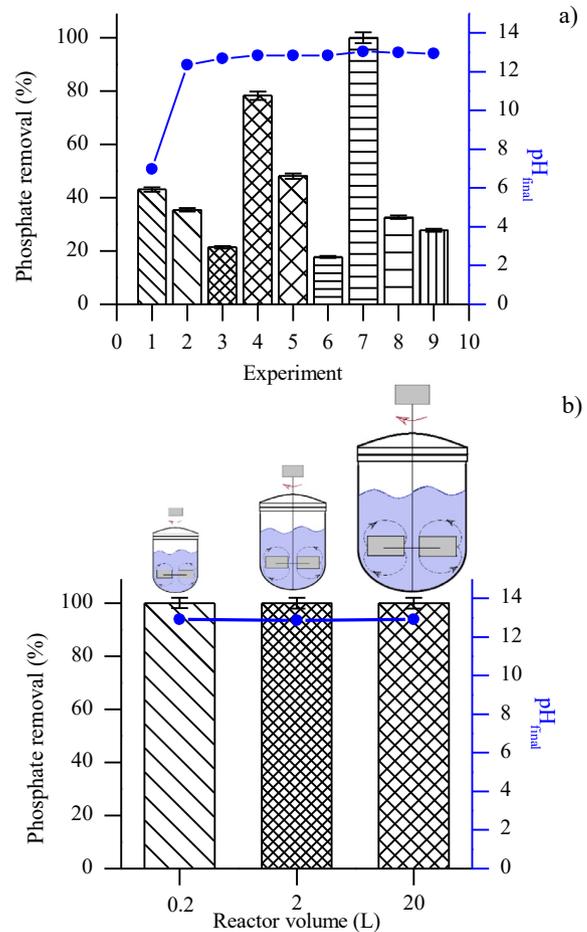
## 3. Result and discussions

### 3.1. Comparison of precipitant agents and assessment of best precipitation conditions

Phosphate removal from anodizing wastewater using different types of precipitant agents is shown in Fig. 1. The initial concentration of phosphates in the wastewater sample used in this experiment was 5119 mg/L (sample 1). Results point out that it is possible to remove up to a 83% of phosphates from this wastewater using  $\text{Ca}(\text{OH})_2$  as precipitant, in contrast with other agents for which the removal was less than 35%. Accordingly,  $\text{Ca}(\text{OH})_2$  was selected as the most effective precipitant for the Taguchi optimization of the precipitation process. A total of 9 experiments were performed in batch reactors of 1 L using a wastewater with an

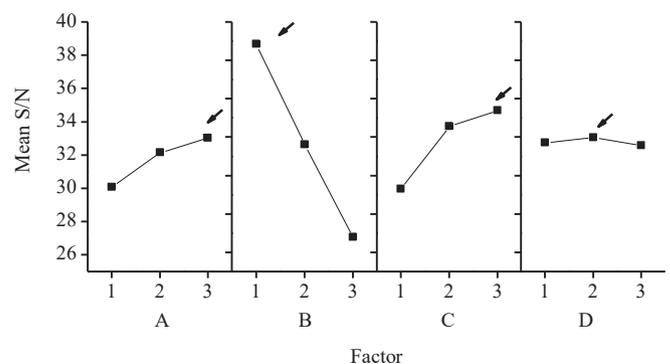


**Fig. 1.** Phosphate removal by chemical precipitation using different chemical reagents in batch systems and final pH of each experiment. Experimental conditions: Phosphate concentration of waste water: 5119 mg/L, sample volume: 250 ml, Precipitant/P molar ratio: 1.79, pH of waste water: 1.86, stirring time: 5 min, settling time: 120 h.



**Fig. 2.** Phosphate removal using  $\text{Ca}(\text{OH})_2$  as precipitant agent and the  $L_9$  orthogonal array of the Taguchi method (a), results of phosphate removal employing batch reactors of different volume (b) and final pH of each experiment (a,b). Phosphate concentration of waste water: 4336 mg/L.

initial concentration of phosphates of 4336 mg/L (sample 2). Fig. 2a shows the results of phosphate removal for each experiment. The conditions of precipitation in the experiment 7 (Ca/P molar ratio of 5.77, pH 2, stirring time of 15 min and settling time of 1 h) are clearly the best ones for the removal of phosphates from wastewater with a removal efficiency near 100%. Other experimental conditions such as those of experiment 4 (Ca/P molar ratio of 3.86, pH 2, stirring time of 5 min and settling time of 3 h) allowed us to



**Fig. 3.** Plot of the effect of each factor on the phosphate removal using  $\text{Ca}(\text{OH})_2$  as a precipitant agent according to the  $L_9$  orthogonal array of the Taguchi method.

**Table 2**  
Analysis of variance using the removal percentage of phosphates from water obtained from the chemical precipitation studies by Taguchi design.

Chemical precipitant	Factor	Mean S/N ratio			Degrees of freedom (v)	Sum of squares (SS)	Variance ( $\sigma_A$ )
		Level 1	Level 2	Level 3			
Ca(OH) <sub>2</sub>	A	30.1	32.2	33.0	2	13.8	6.9
	B	36.9	31.6	26.8	2	151.4	75.7
	C	29.3	32.6	33.4	2	28.1	14.0
	D	31.7	32.0	31.6	2	0.3	0.1
	Total				8	193.5	

reach a removal of 78%. In order to determine which factor has more effect in the precipitation reaction and consequently, in the removal of phosphates from wastewater, the removal data of the 9 experiments were analyzed in terms of signal-to-noise ratio (S/N) to maximize the phosphate removal using the equations of the Taguchi methodology described in the literature (Elizalde-González and Hernández-Montoya, 2009). Also, a variance analysis (ANOVA) was carried out, and the effect graphs were built (Fig. 3). Table 2 shows the variance and the mean S/N ratio for each factor and level. Results point out that the factors with more influence in the reaction of precipitation of phosphates from wastewater using Ca(OH)<sub>2</sub> are the pH (Factor B) and the stirring time (Factor C) because the variance was higher (75.7 and 14, respectively) in comparison with the other two factors. These results agree with the data reported in the literature for the removal of phosphates from synthetic wastewater using the precipitation method with calcium hydroxide as precipitant (Hosni et al., 2008). Additionally, the levels of factor B (pH) in the effect graphs show the greatest variation and the highest values of each factor in these graphs represent the best conditions of precipitation of phosphates from wastewater using Ca(OH)<sub>2</sub> as precipitant (See Fig. 3). Particularly, these conditions are identical to those established in experiment 7 of the L<sub>9</sub> orthogonal array, in which a removal percentage of 100% was obtained (See Fig. 2a).

On the other hand, in order to assess the scalability of the precipitation system, the reaction of precipitation was performed using the best conditions of precipitation for phosphates (Ca/P molar ratio of 5.77, pH 2, stirring time of 15 min and settling time of 1 h) with the same sample of wastewater (4336 mg/L), Ca(OH)<sub>2</sub> as precipitant and reactors of 0.2, 2 and 20 L. Results obtained (Fig. 2b) show a very similar removal percentage (~100%) regardless the size of the system, thus suggesting that this process could be easily scaled up. These results are comparable with the data reported in the literature for the removal of phosphates from anodizing aluminium wastewater using MgO as precipitant, where the initial phosphate concentration was 9937 mg/L and the final concentration decreased to levels lower than 20 mg/L (efficiency ~ 100%) (Chimenos et al., 2006).

Further analyses were performed to verify the quality of the treated wastewater with Ca(OH)<sub>2</sub> using the best conditions of precipitation according with the Taguchi methodology. Selected physicochemical parameters of wastewater in the reactor of 20 L were determined using standard procedures (See Table 3). In general, the raw wastewater was free of biological contaminants, oil and fats and the concentration of total nitrogen was relatively low (less than 4.1 mg/L). Also, phosphates and sulfates were found in high concentrations (4336 mg/L and 9347 mg/L, respectively), while sodium (4366 mg/L) was the most abundant cation. The concentration of Al is low (0.083 mg/L) and the presence of heavy metals such as Cd, Pb, Cu and Zn was not detected.

After the precipitation of phosphates with Ca(OH)<sub>2</sub>, the value of the total alkalinity of the treated wastewater increases due to the rise in the concentration of calcium ions. Also, a significant decrease occurred in the concentration of the main contaminants, such as

**Table 3**  
Parameters of raw wastewater and the sample treated with Ca(OH)<sub>2</sub> in the reactor of 20 L.

Parameter	Water sample	
	Raw	After treatment with Ca(OH) <sub>2</sub>
pH	5.43	12.9
T (°C)	25	25
PO <sub>4</sub> <sup>3-</sup> (mg/L)	4336	3.69
Al <sup>3+</sup> (mg/L)	0.083	0
SO <sub>4</sub> <sup>2-</sup> (mg/L)	9347	7661
F <sup>-</sup> (mg/L)	0.75	0.2
Arsenic (mg/L)	<0.05	<0.05
Calcium (mg/L)	<1	787
Cadmium (mg/L)	0	0
Copper (mg/L)	0	0
Cyanide (mg/L)	<0.026	<0.026
Iron (mg/L)	0.4495	0.0799
Lead (mg/L)	0	0
Potassium (mg/L)	20	12.5
Sodium (mg/L)	4366	4023.31
Zinc (mg/L)	0	0
Total Nitrogen (mg/L)	<4.1	<4.1
Total alkalinity (mg/L)	<12	3902
Faecal coliforms (MPN/100 ml)	<300	<300
Helminth eggs (egg/L)	<1	<1
Oils and fats (mg/L)	<3	<3

phosphates, sulfates and sodium (See Table 3). Phosphate showed the largest concentration decrease thus confirming data reported in the literature in which Ca(OH)<sub>2</sub> has been identified as an efficient precipitant of phosphates. For example, the precipitation of phosphates was studied using synthetic solutions (NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O in deionized water) with an initial concentration of 245 mg/L and Ca(OH)<sub>2</sub> as precipitant agent (Hosni et al., 2008). Results obtained indicated that it was possible to remove 98% of phosphates. Also, a saturated Ca(OH)<sub>2</sub> solution was used to precipitate phosphates from leachates of slags of steelmaking, with results showing a recovery of 70% of P (Du et al., 2019). The P<sub>2</sub>O<sub>5</sub> content in the product obtained reached 20.2 mass%, i.e., a fertilizer grade. Additionally, Ca(OH)<sub>2</sub> has been mixed with natural zeolites to increase the adsorbed amount of phosphorus from aqueous solutions. Particularly, the pretreatment of natural zeolite (clinoptilolite) with 0.25 mol/L Ca(OH)<sub>2</sub> led to an increase of P removal from 1.7 to 97.6 % at an initial P concentration of 10 mg/L in aqueous solution, pH 7 and 25 °C (Mitrogiannis et al., 2017). The modification of natural clinoptilolite with Ca(OH)<sub>2</sub> also proved to be more efficient in the adsorption of P from real fresh urine than the raw zeolite (Mitrogiannis et al., 2018). This behavior was associated with an adsorption mechanism involving the adsorption and precipitation of P on the adsorbent surface.

### 3.2. Characterization of recovered hydroxyapatite

According with data reported in literature, the calcium ions can react with phosphates to form a precipitate of hydroxylapatite [Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)], following the reaction:

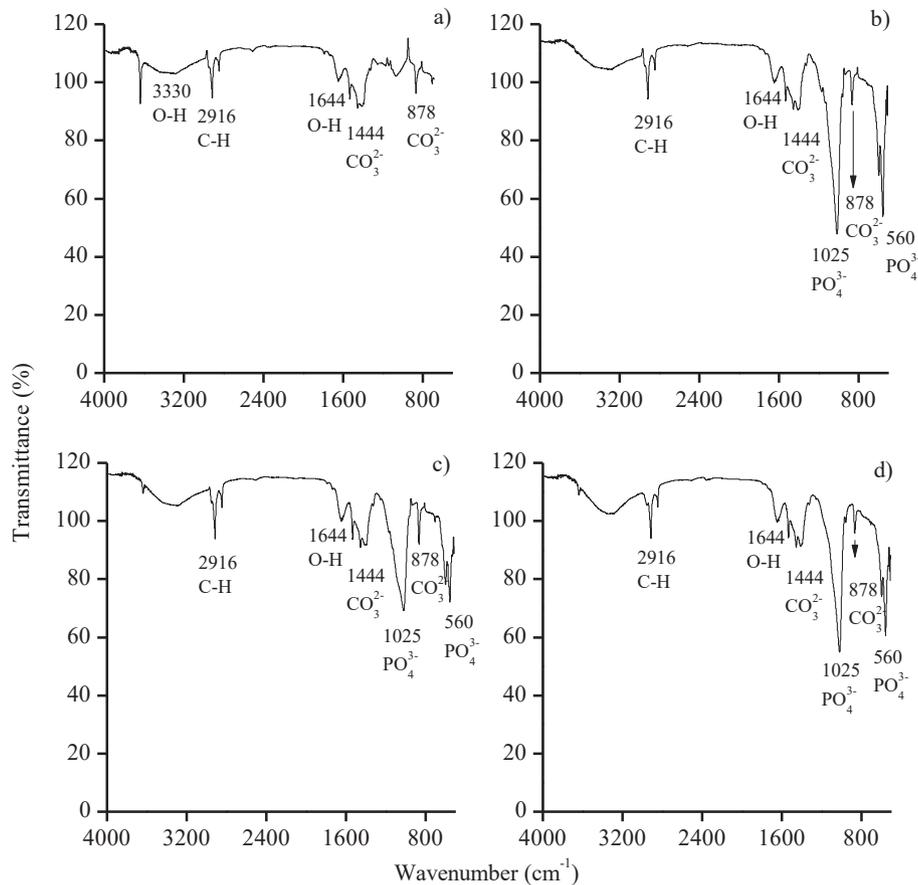


Fig. 4. FT-IR spectra of  $\text{Ca}(\text{OH})_2$  (a) and precipitates from experiments 5 (b), 7 (c) and 9 (d) of  $L_9$  orthogonal array of the Taguchi method.



The quality, purity, morphology and particle size distribution of hydroxyapatite as a precipitation product depends on different parameters involved in the precipitation reaction such as temperature, pH, presence of ionic contaminants, the reaction mixture stirring intensity, input rate of reactants, Ca/P molar ratio, among others (Cichy et al., 2019). In this context, it is important to emphasize that the aim of the present work was to remove the highest amount of phosphates from wastewater and to evaluate the possibility of hydroxyapatite recovering. Precipitates obtained in experiments 5, 7 and 9 were characterized to determine their chemical functionality and crystalline structure. These precipitates were selected because they were obtained a different pH (6, 2 and 10, respectively) and, according with the Taguchi results, pH was the most important factor in the reaction of precipitation of phosphates from wastewater using  $\text{Ca}(\text{OH})_2$  as precipitant.

Fig. 4 shows the FT-IR spectra of  $\text{Ca}(\text{OH})_2$  (a) and the precipitates obtained in the experiments 5 (b), 7 (c) and 9 (d) of the  $L_9$  orthogonal array of the Taguchi method. Not significant differences were detected in the FT-IR spectra of these three precipitates. Particularly, in the FT-IR spectrum of  $\text{Ca}(\text{OH})_2$  were identified peaks at 3330 and 1644  $\text{cm}^{-1}$  corresponding to O–H stretching and bending vibrations, respectively (See Fig. 4a). Also, the characteristics peaks of calcium carbonate ( $\text{CaCO}_3$ ) were observed at 1444 and 878  $\text{cm}^{-1}$  (Karimi et al., 2018; Kim et al., 2019; Plavšić et al., 1999), and finally, the signal corresponding to C–H stretching vibrations of methylene groups was identified at 2916  $\text{cm}^{-1}$  due to organic impurities (Parolo et al., 2017). All the peaks of  $\text{Ca}(\text{OH})_2$

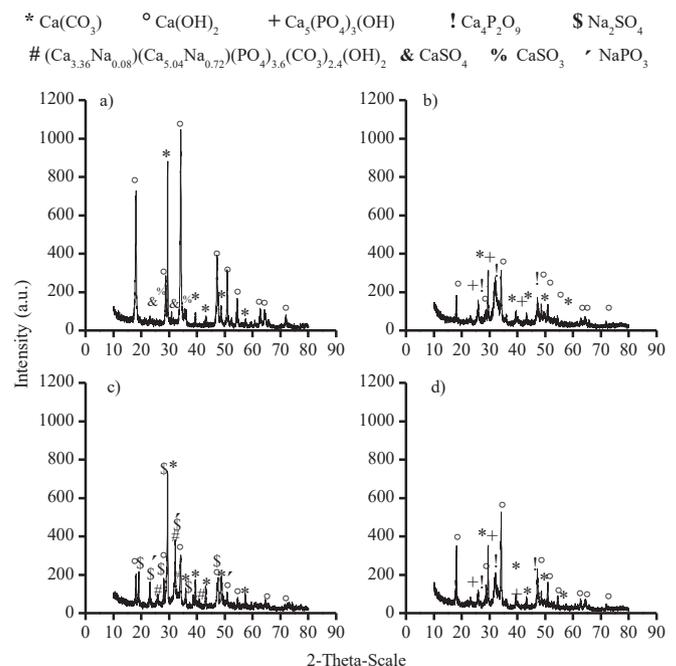


Fig. 5. XRD patterns of  $\text{Ca}(\text{OH})_2$  (a) and precipitates from experiments 5 (b), 7 (c) and 9 (d) of  $L_9$  orthogonal array of the Taguchi method.

**Table 4**  
Crystalline structures identified in the XRD analysis shown in Fig. 5.

Symbol	Crystalline structure	Name	Number JCPDS cards
*	Ca(CO <sub>3</sub> )	Calcite	01-071-3699
o	Ca(OH) <sub>2</sub>	Portlandite	00-044-1481
+	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	Hydroxylapatite	01-086-0740
!	Ca <sub>4</sub> P <sub>2</sub> O <sub>9</sub>	Calcium phosphate	01-073-1731
\$	Na <sub>2</sub> SO <sub>4</sub>	Thenatdite	00-011-0232
#	(Ca <sub>3.36</sub> Na <sub>0.08</sub> )(Ca <sub>5.04</sub> Na <sub>0.72</sub> )(PO <sub>4</sub> ) <sub>3.6</sub> (CO <sub>3</sub> ) <sub>2.4</sub> (OH) <sub>2</sub>	Hydroxylapatite	01-074-2036
%	CaSO <sub>3</sub>	Calcium Sulfite	01-074-2680
&	CaSO <sub>4</sub>	Calcium Sulfate	00-004-0599
'	NaPO <sub>3</sub>	Sodium Phosphate	00-037-0184
			00-003-0680

**Table 5**  
Principal elements identified by EDX in the original precipitant Ca(OH)<sub>2</sub> and the precipitates obtained in the experiments 5, 7 and 9.

Element	Ca(OH) <sub>2</sub>	Experiment 5	Experiment 7	Experiment 9
C	02.04	04.96	04.72	03.53
O	23.83	34.71	34.92	35.06
Na	–	2.185	16.37	05.56
P	–	12.25	04.59	06.36
S	01.10	03.88	10.80	02.91
Ca	71.36	42.01	28.60	46.58

were also identified in the FT-IR spectra of precipitates obtained in experiments 5, 7 and 9. But, additionally, peaks corresponding to phosphates were observed at 1025 and 560 cm<sup>-1</sup>, which are characteristics of P–O stretching and bending vibration, respectively (Jastrzębski et al., 2011).

On the other hand, further analyses were performed by X-ray diffraction to identify the crystalline structures of the precipitant reagent, as well as selected precipitates recovered. Fig. 5 shows the X-ray diffraction patterns of Ca(OH)<sub>2</sub> and the precipitates obtained in experiments 5, 7 and 9 of the Taguchi method. Additionally, Table 4 summarizes the main crystalline structures identified in the diffraction patterns. Essentially, the XRD pattern of Ca(OH)<sub>2</sub> is consistent with the 00-044-1481- Portlandite- Ca(OH)<sub>2</sub> pattern and with 01-071-3699 - Calcite- Ca(CO<sub>3</sub>) pattern (JCPDS cards). Additional compounds with crystalline structure were also identified as CaSO<sub>3</sub> and CaSO<sub>4</sub> (Fig. 5a).

In the analysis of the precipitates by X-ray diffraction some interesting structures were observed. For example, the crystalline structure of common hydroxyapatite or hidroxyapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)) was identified in the precipitate obtained in experiments 5 and 9 (carried out at pH 6 and 10). Specifically, several reflections in the XRD patterns of the precipitates obtained in experiments 5 and 9 are consistent with 01-086-0740 (A) - Hydroxylapatite - Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH) and 01-073-1731 (I) - Hydroxylapatite - Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH) patterns (JCPDS cards) (See Fig. 5b and 5d). According to data reported in the literature, the precipitation of hydroxyapatite is predominant in solutions with pH 4–12 because this compound is the most stable and durable form of bonds between calcium and orthophosphate ions (Cichy et al., 2019; Oubagha et al., 2016). However, in experiment 7, which was carried out at pH 2, a hydroxylapatite with a more complex structure was observed: (Ca<sub>3.36</sub>Na<sub>0.08</sub>)(Ca<sub>5.04</sub>Na<sub>0.72</sub>)(PO<sub>4</sub>)<sub>3.6</sub>(CO<sub>3</sub>)<sub>2.4</sub>(OH)<sub>2</sub>, corresponding to the 01-074-2680 JCPDS card (See Table 4 and Fig. 5). Also, Na was found in this precipitate forming part of other crystalline structures such as Na<sub>2</sub>SO<sub>4</sub> and NaPO<sub>3</sub>. The presence of significant amounts of sodium and sulfates in this precipitate is due to the composition of the raw wastewater, as detailed above; and the low pH of this experiment (pH = 2). These results were corroborated by EDX analysis, where the main elements identified

in the precipitate of experiment 7 were O (34.9%), Na (16.3%), P (4.6%), Ca (28.6%) and S (10.8%) (See Table 5). In this context, it is important to note that the contents of Na and S in the precipitates of experiments 5 and 9 were lower than in experiment 7 and, probably for this reason, it was not possible to find by XRD any crystalline structure containing Na and S (See Fig. 5 and Table 4).

The morphology of Ca(OH)<sub>2</sub> and the precipitates of experiments 5, 7 and 9 were irregular and heterogeneous and the main elements observed in the original Ca(OH)<sub>2</sub> were Ca (71.3%) and O (23.8%). Other impurities such as S (1.10%) and C (2.0%) are present in minor amounts (See Fig. 6 and Table 5). This information is congruent with the results obtained by FT-IR spectroscopy and X-ray diffraction, where the presence of carbon and impurities of sulfur were identified in the original Ca(OH)<sub>2</sub>.

#### 4. Conclusions

This is, to our knowledge, the first study related with the removal and recovery of phosphates from anodizing plants wastewaters and represents a water treatment alternative for this type of companies. Particularly, the results obtained point out that Ca(OH)<sub>2</sub> is an effective precipitant agent of phosphates for these wastewaters. That removal efficiency was almost 100% when using the optimal experimental conditions for precipitation of phosphates, as determined by the Taguchi methodology. The best conditions for the precipitation of phosphates were obtained when using a Ca/P molar ratio of 5.77 at pH 2 with a stirring time of 15 min and a settling time of 1 h. In addition, the ANOVA results indicated that the factors with more influence in the precipitation of phosphates were the pH and the stirring time (Factor B and Factor C). Finally, two types of crystalline hydroxyapatite were identified as precipitation products, with the most complex structure ((Ca<sub>3.36</sub>Na<sub>0.08</sub>)(Ca<sub>5.04</sub>Na<sub>0.72</sub>)(PO<sub>4</sub>)<sub>3.6</sub>(CO<sub>3</sub>)<sub>2.4</sub>(OH)<sub>2</sub>) being obtained at pH 2. These results are congruent with the data reported in the literature, where Ca(OH)<sub>2</sub> has been used as precipitant agent of phosphates in synthetic waters, and also as a natural zeolites modifier to increase the adsorption of phosphates from water.

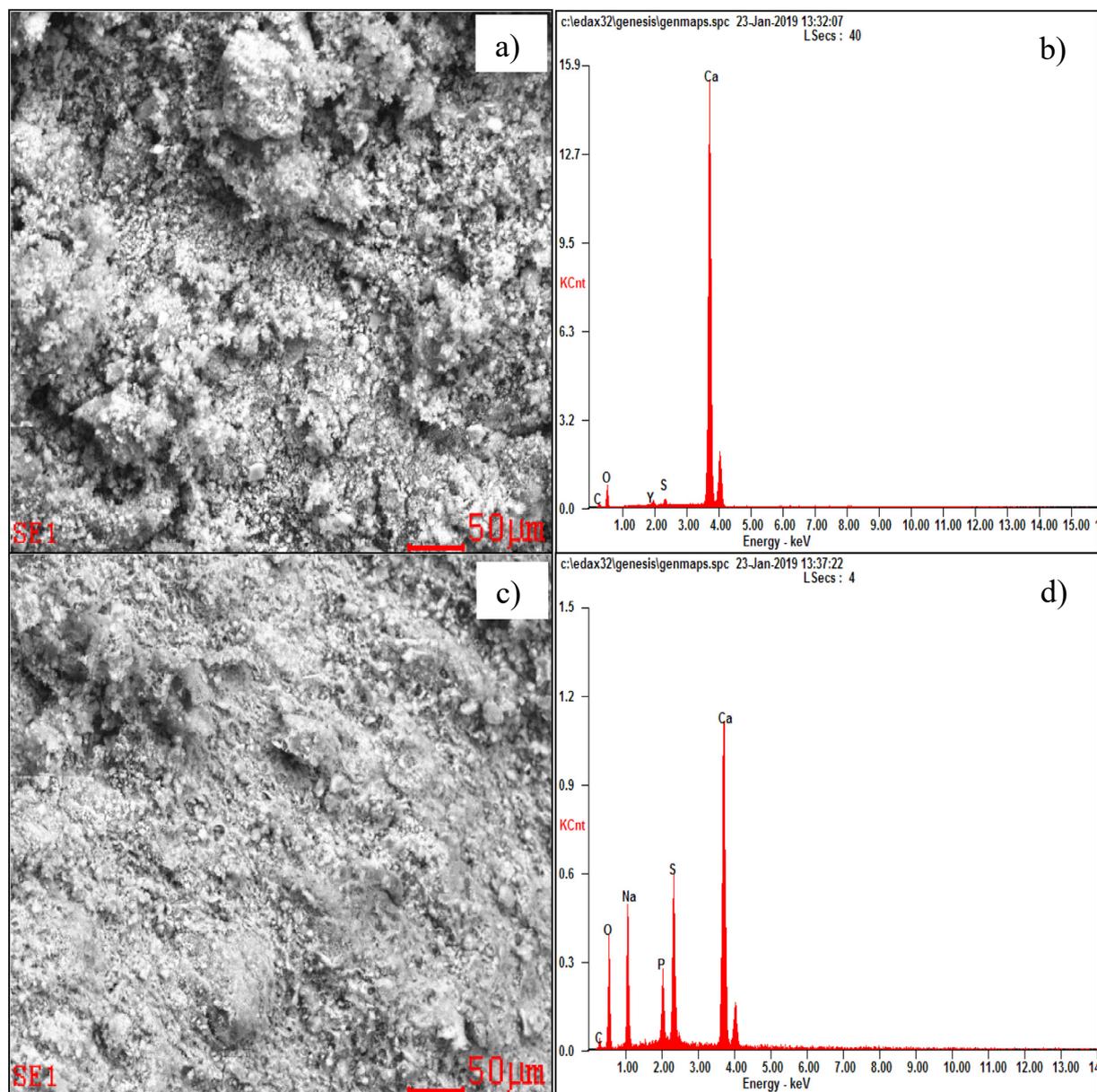


Fig. 6. SEM images and EDX analysis of  $\text{Ca(OH)}_2$  (a, b) and precipitate from experiment 7 (c, d) from the Taguchi method.

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