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Low-Grade Phosphate Tailings Beneficiation via Organic Acid Leaching: Process Optimization and Kinetic Studies

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Abstract: In this paper, the beneficiation of rejected phosphate washing sludges (Ps) was investigated using acid leaching methods. Chemical analysis showed that these sludges are a low-grade ore (15.84% P2O5). The optimum milling parameters have helped to increase the P2O5 grade to 18.51%. Then, the effects of three different organic acids (acetic, lactic, and citric acid), acid concentrations, reaction temperatures, reaction times, and solid concentrations on the beneficiation of P2O5 were evaluated. Single-factor experiments indicate that with the optimal conditions: leaching for 60 min with an acetic acid concentration of 7%, a solid concentration of 25%, and a temperature of 40 °C, Ps could reach 30.1% P2O5 with a CaO/P2O5 ratio of 0.58. Taguchi experimental design, Pareto plot, desirability function, and Analysis of Covariance (ANCOVA) showed that the acid type has the most significant impact on the leaching and the optimized leaching conditions: 7% of acetic acid, a solid concentration of 30%, a reaction time of 100 min, and a temperature of 40 °C, helped to produce a Ps with 30.7% P2O5. The kinetic study showed that the leaching process was controlled by a chemical reaction, with an activation energy of 48.9 kJ/Mol, which confirms the chemical reaction’s control of the process.

Keywords: phosphate washing sludges; beneficiation; ball milling; organic acid leaching; Taguchi L9 design; desirability function; ANCOVA; leaching kinetics; kinetic models

1. Introduction

Phosphate rocks are essential in various industries, such as in the production of phosphoric acid and fertilizers. The total phosphate reserves in the world are up to 70 billion tons. The biggest phosphate resources are in Morocco with a reserve of 50 billion tons, accounting for 71.43% of the total amount [1]. Approximately 75% of phosphate resources have a sedimentary origin [2]. The marketable sedimentary phosphate ore usually has 28%~30% of P2O5 to be economical [3]. The requirements for phosphate concentrate used in the production of phosphoric acid are P2O5 content > 30%, CaO/P2O5 ratio < 1.6, MgO content < 1%, and Fe2O3 and Al2O3 content ≤ 2.5% [4]. However, with an increasing demand for phosphate and a reduction in phosphate reserves, it is necessary to enrich phosphate tailings (e.g., phosphate washing sludges) to concentrate phosphate to be used in the production of phosphoric acid.

Phosphate washing sludges (Ps) constitute a considerable amount of tailing, which are not exploitable by simple washing because they have a low content of P2O5 and an abundant amount of carbonates and silica. Moreover, these tailings are becoming a critical issue for the mining industry because of environmental concerns. They need to be processed by separation techniques to remove the problematic portions (e.g., carbonates) and recover the valuable parts (e.g., phosphates). Good beneficiation of Ps can be achieved by various processes, depending on the liberation size of phosphate and gangue minerals. Different processes like screening, scrubbing, milling, washing, calcination, leaching, and flotation...
may be used. Milling is an important stage in the beneficiation of low-grade phosphates. Indeed, it helps in the liberation of the phosphate grains from the gangue [5]. In our case, phosphate is recovered from the carbonated gangue.

The calcareous Ps can be also enriched by organic acid leaching. In this process, the carbonates are dissolves by the dilute acid solution, and the phosphates remain in the leached residues. Thus, the beneficiation of the low-grade phosphate is achieved. Strong acids can attack the phosphate minerals when used to selectively remove calcareous material in low-grade Ps. However, according to the literature, most of the organic weak acids show an interesting degree of selective leaching [6]. The liquid phase can be easily separable after leaching for regeneration and recycling of the acid. The commonly used organic acids are acetic acid [7], lactic acid [8], and citric acid [9]. According to Fei et al. [10], after leaching optimization of low-grade phosphate ore with a $P_2O_5$ content of 17.45% using Lactic and Acetic acid, the following optimum conditions were maintained: 11% of Lactic Acid, at a temperature of 55 °C for a 120 min leaching period, and 5% of Acetic acid, at a temperature of 40 °C for a 30 min leaching period. A concentrate of $P_2O_5$ content above 30% was obtained. In another study, by using 15% of Acid Acetic for leaching a phosphate ore of 10% $P_2O_5$, Gharabaghi et al. [7], obtained a concentrate of 32.14% $P_2O_5$ at a temperature of 40 °C, a reaction time of 60 min, and a solid concentration of 15%. Zafar et al. [8] have also reported in their study that with 8% of lactic acid, a temperature of 45 °C, a liquid/solid ratio of 7, and a reaction time of 45 min, it was possible to increase the content of $P_2O_5$ from 22.3% to 35%. Moreover, organic acids are effective and economical for the enrichment of low-grade calcareous phosphates. Organic acid leaching is a very selective process, ecological, and can produce high purity products [10].

The main purpose of this research is to upgrade a Moroccan low-grade Ps through organic acid leaching by using three organic acids acetic acid, lactic acid, and citric acid as a leaching agent for carbonates. A single-factor experiment was carried out to investigate the influence of various operational factors such as reaction temperature, reaction time, organic acid concentration, solid concentration, and acid type on the concentration and recovery of $P_2O_5$ and to optimize the process parameters for maximum beneficiation. Then Taguchi L9 orthogonal array, Signal-to-noise ratio, Desirability function, and Analysis of Covariance ANCOVA were used to determine optimal conditions and the main influence factors on the enrichment of low-grade Ps by leaching. Dissolution kinetics was studied using two reaction models. The dissolution kinetics model that best fit the experimental data was determined, and the activation energy was calculates using Arrhenius’ law.

2. Materials and Methods

In our experiments, we used Ps coming from Khouribga’s washing plant. Ps samples are collected from ponds by chip sampling technique according to the international standard ISO 18400. Then the samples were dried in an electric oven at about 105 °C, cooled to room temperature, homogenized, and quartered through a riffle sampler to obtain a representative sample.

2.1. Characterization Techniques

All the analyses were conducted following quality assurance and analytical quality control program NM ISO/IEC 17025. For the Mineralogical Structure determination, we used X-ray diffraction of Rigaku (XRD) monochromatized CuKα radiation ($\lambda = 1.54 \text{ Å}$) using the international standard (EN 13925-2:2003). Microscopic observation was made on different size fractions of a milled sample to determine the percentage of liberated phosphate mineral in each size range. Sieving was carried out before mineral characterization. Wet sieving is carried out on a set of 5 sieves (NM EN 12948): 160, 100, 71, 53, and 20 μm. The elemental composition of Ps was determined by the X-ray fluorescence spectrometry (XRF) technique using a Philips spectrometer (Philips Industrial Electronics, Almelo, Netherlands, ISO 18227:2014). International standards were used to determine the $P_2O_5$ content by a colorimetric method (Spectrophotometer, SECOMAM, Alès, France) using
ammonium molybdate and ammonium metavanadate and applying a filter of 430 nm. Atomic Absorption Spectrophotometer (AAS) A-1800 Hitachi (Hitachi, Tokyo, Japan) was used to determining the Ca\(^{2+}\) content in the leach solution.

2.2. Ball Milling

A milling process was carried out on the laboratory scale in a planetary Mono Mill PULVERISETTE 6 classic line (FRITSCH, Idar-Oberstein, Germany) consisting of a metal cylindrical milling bowl of 225 mL capacity with media and rotated on its axis, and the milling load is made up of balls of same size 0.1 mm. The milling bowl and milling balls are made of agate.

2.3. Acid Leaching

The organic leaching experiments were carried out in a 500 mL glass reactor on a hot plate with a magnetic stirrer. A known amount of Ps (30–120 g) was leached with 300 mL of an acid solution with different concentrations (1–15\% in mass) at different temperatures. A digital thermometer was used to control the temperature. Moreover, during leaching experiments, all temperatures were ± 3 °C taking into account thermometer error. The leaching mechanism experimental setup is shown in Figure 1. During the experiments, the stirring speed was fixed at 300 rpm to ensure no sediment at the bottom of the reactor. The stirring intensity effects on leaching were not studied because they are not so significant [7]. Finally, after the sample reacted completely, the solid phase was separated from the reaction solution by filtration and dried at 105 °C before analysis. In the filtrate, the P\(_2\)O\(_5\) content was determined by the colorimetric method and the Ca\(^{2+}\) content in the leach solution was determined by AAS.

![Figure 1. Leaching experimental setup. 1: Acid solution, 2: Glass reactor, 3: magnetic stirrer, 4: Thermostatic magnetic stirrer, 5: Digital thermometer.](image)

In the analysis, after grinding and leaching, for each experiment, the recovery of P\(_2\)O\(_5\) (%) was calculated as follows:

\[
\%\text{P}_2\text{O}_5 \text{ recovery} = \left[ \frac{C \times c}{P \times p} \right] \times 100
\]  

(1)

where C is the weight of the concentrate, \(c\) is P\(_2\)O\(_5\) concentration (%) in the concentrate, \(P\) is the weight of original Ps, and \(p\) is P\(_2\)O\(_5\) concentration (%) in original Ps.
The dissolution fraction of calcareous material was calculated by Equation (2):

\[ \alpha = \frac{\text{calcium content in the solution}}{\text{Total calcium content in the original sample}} \]  

(2)

2.4. Taguchi Experimental Design

The Taguchi Parameter method is an experimental design technique that allows reducing the number of experiments by using orthogonal arrays. It reduces time and cost. This had an effect that substitutes the full factorial design of an experiment. Considering four experimental parameters and three levels, the total numbers of combinations of possible experiments are \(3^4\). It is difficult to determine the best combination among the \(3^4\) combinations due to the lengthy experimentation required. Taguchi’s method affirms that we need to try out only 9 out of \(3^4\) experiments, which will help us to achieve the best solution where every factor is varied, one at a time, while all of the other factors remain constant [11].

In this study Taguchi L_9 (\(3^4\)) experimental design was generated using JMP software (Version 11, SAS Institute, Inc., Cary, NC, USA). Each experiment was repeated only three times due to a lack of raw material. The signal-to-noise (S/N) ratio corresponding to each combination is calculated. The (S/N) ratio is a measure of robustness that identifies the control factor settings for the minimum impact of noise on response [12]. Various types of (S/N) ratios have been developed, e.g., smaller-is-better, larger-is-better, and nominal-is-best. The greater S/N ratio corresponds to better quality characteristics [11]. As the aim of the present study is to enrich sludges with \(P_2O_5\) and to obtain the highest possible % \(P_2O_5\), the larger-is-better ratio was selected and calculated using JMP software according to the following Equation (3):

\[ (S/N) = -10 \log\left(\frac{1}{n} \sum_{i=0}^{n} \frac{1}{y_i^2}\right) \]  

(3)

where \(y_i\) is the experimental response and \(n\) is the experiment replication number.

2.5. Statistical Analysis

In this section, the statistical approach to determine factors influencing the two responses, namely % \(P_2O_5\) mean values and S/N ratio, is discussed. By evaluating statistical analysis tools such as the Pareto plot and Desirability function for each response, the most influential factors and optimum conditions are determined. The Pareto plot is a plot of scaled estimates. The most important factor has the longest horizontal bar [13]. The desirability function analysis is used for the determination of optimum conditions of different variables that determine optimum performance for different responses [14].

Analysis of Covariance (ANCOVA) is performed to determine the most effective parameters using the commercial statistics software package IBM SPSS version 25.0 (IBM, New York, U.S.A) for Windows.

3. Results and Discussion

3.1. Characterization of Phosphate Washing Sludges

The X-ray diffraction patterns of the Phosphate Sludge sample are shown in Figure 2. The results achieved show the dominance of quartz, calcite, and dolomite. Fluorapatite phases are also present in phosphate sludge.
Chemical analysis of Ps sample is presented in Table 1. The Ps represent a large amount of CaO (35.2%). The content of P\textsubscript{2}O\textsubscript{5} in the Ps is 15.84% with a CaO/P\textsubscript{2}O\textsubscript{5} ratio of 2.34.

### Table 1. Mean concentrations (in wt.%) of major elements of the Ps sample.

|       | CaO % | P\textsubscript{2}O\textsubscript{5} % | SiO\textsubscript{2} % | Al\textsubscript{2}O\textsubscript{3} % | MgO % | Fe\textsubscript{2}O\textsubscript{3} % | SO\textsubscript{3} % |
|-------|-------|-----------------|----------------|-----------------|------|----------------|----------------|
| Ps    | 35.2  | 15.84           | 9.6           | 2.3             | 1.01 | 0.4            | 1.38           |

The pure phase is determined using a dense media separation at a laboratory scale through heavy-liquid separation (HLS) test work. Bromoform (density (d) = 2.82 g/cm\textsuperscript{3}) was used to separate Ps (d > 2.82 g/cm\textsuperscript{3}) from silicate and carbonates (d < 2.82 g/cm\textsuperscript{3}). This analysis is followed by the identification of the concentration of elements under XRF and colorimetry analyses and the results are shown in Table 2. The maximum content of P\textsubscript{2}O\textsubscript{5} is 33.1%. It is the maximum concentration that can be obtained by any separation process. The CaO content is high (41.2%) with a CaO/P\textsubscript{2}O\textsubscript{5} ratio = 1.23.

### Table 2. Mean concentrations (in wt.%) of major elements of the Ps pure phase.

|       | CaO % | P\textsubscript{2}O\textsubscript{5} % | SiO\textsubscript{2} % | MgO % | Fe\textsubscript{2}O\textsubscript{3} % |
|-------|-------|-----------------|----------------|------|----------------|
| Ps    | 41.2  | 33.1            | 1.6            | 1.89 |

After sieving, the chemical analysis of the different particle size fractions is shown in Table 3. The grananulo-chemical distribution shows that the 160, 100, and 71 μm fractions (9.09%, 12.32%, and 18.59% by weight, respectively) bear the highest amounts of P\textsubscript{2}O\textsubscript{5} (20.01%, 19.6%, and 17.24% P\textsubscript{2}O\textsubscript{5}, respectively). Furthermore, this fraction presents 40% of the total weight. All the analyzed fractions are rich in CaO (CaO concentrations vary from 30.4 to 37.2%).
Table 3. Chemical results percentage of liberated phosphate minerals in different particle size fractions of Ps.

| Fraction (µm) | Weight (%) | P_2O_5 % | CaO % | CaO/P_2O_5 | SiO_2 % | Liberated Phosphate Particles (%) |
|---------------|------------|----------|-------|-------------|---------|----------------------------------|
| 160           | 9.09       | 20.01    | 37.2  | 1.85        | 5.2     | 76                               |
| 100           | 12.32      | 19.6     | 35.6  | 1.81        | 7.8     | 80                               |
| 71            | 18.59      | 17.24    | 31.5  | 1.82        | 8       | 88                               |
| 53            | 33.3       | 14.6     | 33.2  | 2.27        | 10      | 94                               |
| 20            | 15.1       | 12.3     | 30.4  | 2.47        | 13.4    | 94                               |
| <20           | 11.6       | 11.8     | 35.6  | 3           | 12.5    | 94                               |

The results of the microscopic observation presented in Table 3 show that the liberated phosphate particles amount increased as the particle size increases, but there was no significant change after −53 µm. To achieve high-quality phosphate concentrate, the sample has to be milled to −53 µm for liberating maximum phosphate from gangue minerals.

3.2. Milling Experiments

Milling is an important stage in the enrichment of phosphate tailings; it allows the phosphate grains to be released from the gangue [5]. In this study, apatite is recovered from the gangue. A series of milling tests were conducted to determine the milling time to achieve sufficient liberation. Three milling parameters are studied and optimized to determine their impact on the product fineness: solid concentration (30%, 40%, and 50%), milling time (3, 4, and 5 min), and charge ratio (3/1, 4/1, and 5/1). The rotation speed was fixed at 100 rpm.

3.2.1. Variation in Milling Time

In this study, three milling times were evaluated: 3, 4, and 5 min, with a solid concentration of 30%, and a charge ratio of 4/1. Results in Table 4 show that the best P_2O_5 grade and recovery were obtained at a milling time of 4 min. This period was maintained for the rest of the tests.

Table 4. Milling tests results after variation of different parameters.

| Parameters       | Milling Time | Charge Ratio | Solid Concentration | P_2O_5       | Wt (%) Passing −53 µm |
|------------------|--------------|--------------|---------------------|--------------|-----------------------|
|                  |              |              |                     | Grade (%)    | Recovery (%)          |
| Miling Time (min)| 3            | 4/1          | 30                  | 16.19        | 46.61                 | 50.01 |
|                  | 4            | 4/1          | 30                  | 18.2         | 55.8                  | 88.12 |
|                  | 5            | 4/1          | 30                  | 18.01        | 49.1                  | 88.03 |
| Charge Ratio     | 4            | 3/1          | 30                  | 16.81        | 44.51                 | 50.26 |
|                  | 4, 4/1       | 30           | 18.2                | 58.1         | 88.12                 |       |
|                  | 4, 5/1       | 30           | 17.65               | 46.32        | 76.22                 |       |
| Solid Concentration (%) | 4, 4/1 | 30 | 18.2 | 45.7 | 88.12 |
|                  | 4, 4/1       | 40           | 18.51               | 58.2         | 99.07                 |       |
|                  | 4, 4/1       | 50           | 17.89               | 44.82        | 74.43                 |       |

3.2.2. Variation in Charge Ratio

Three charge ratios were investigated in those tests: 3/1, 4/1, and 5/1, with a solid concentration of 30%. The results obtained in Table 4 show that by using a charge ratio of 4/1, the highest grade and recovery were obtained. This ratio was maintained for the rest of the tests.

3.2.3. Variation in Solid Concentration

To evaluate the impact of solid concentration, three tests of 30%, 40%, and 50% solids were chosen with a milling period of 4 min and a charge ratio of 4/1. Table 4 shows that the best results were obtained for 40% solid concentration.
The optimal test (rotation speed of 100 rpm, charge ratio of 4/1, solid concentration of 40%, and a milling period of 4 min) has shown an improvement in \( \text{P}_2\text{O}_5 \) content, from 15.84% (before milling) to 18.51% with a recovery of 58.20%. These conditions also make it possible to produce a 99.07% passing 53 \( \mu \text{m} \) size fraction for a maximum phosphate liberation (Table 4).

However, milling is not sufficient as a separation method due to the high amount of carbonates. Thus, it should be supplemented by organic acid leaching as an appropriate separation technique. Moreover, it is reported that organic acid leaching can be more efficient by grinding the phosphate feed [15]. The decrease in particle size increases the leaching efficiency; this is due to the increased surface area of the sample and the liberation of more carbonates from the apatite matrix attributed to an increase in the degree of size reduction [16].

The \( \text{Ps} \)s under the optimal conditions of milling with a size fraction \( -53 \mu \text{m} \) was used as the feed for the leaching process, and they are majority composed of phosphate, carbonate, and silicates.

### 3.3. Acid Leaching Experiments

#### 3.3.1. Single-Factor Experiment

The effects of acid type, solid concentration, reaction temperature, acid concentration, and reaction time on the enrichment of \( \text{Ps} \) were evaluated by single-factor experiments. The fixed conditions of the experiments are a reaction time of 50 min, solid concentration of 30%, and a reaction temperature of 40 °C. All the experimental conditions were selected according to the literature [4].

#### 3.3.2. Effect of Organic Acid Type

Acid concentration is one of the most important factors in organic acid leaching of carbonates in low-grade \( \text{Ps} \). The results of leaching tests under different concentrations of the three different organic acids, a reaction time of 50 min, a solid concentration of 30%, and a reaction temperature of 40 °C are shown in Table 5.

**Table 5.** The leaching results of three types of organic acids at different acid concentrations.

| Acid Concentration (%) | Acid Type Grade of \( \text{P}_2\text{O}_5 \) (%) |
|------------------------|-----------------------------------------------|
|                        | Acetic Acid | Lactic Acid | Citric Acid |
| 1                      | 21.6        | 20.3        | 19.8        |
| 3                      | 25.8        | 22.5        | 20.9        |
| 5                      | 27.9        | 24.1        | 22.6        |
| 7                      | 27.7        | 27.01       | 24.8        |
| 9                      | 27.5        | 27.7        | 26.6        |

The results show that the three tested organic acids have good selectivity for the leaching of carbonates. The three acids can upgrade the \( \text{P}_2\text{O}_5 \) content from 18.5% to 27.9%. However, acid acetic shows very good results at only a 5% concentration. Indeed, dilute acetic acid shows significant potential as leaching agents for the beneficiation of \( \text{P}_2\text{O}_5 \) in low-grade phosphates [17]. Further analyses were done using acetic acid.

#### 3.3.3. Effect of Reaction Time

The effects of reaction time in the range from 10 min to 80 min on leaching performance using acetic acid have been investigated using an acid concentration of 5%, a solid concentration of 30%, and a reaction temperature of 40 °C. The results obtained are represented in Figure 3. With the increase of reaction time, the % \( \text{P}_2\text{O}_5 \) content increases along with the corresponding increase in \( \text{P}_2\text{O}_5 \) recovery. As presented in literature, the time required for carbonate leaching depends on the particle size and the nature of the adherent materials existing in the \( \text{Ps} \)s and other process conditions [4]. In our study, the reaction equilibrium is reached after 60 min. Indeed, many investigators mentioned that for effective carbonate
leaching, the reaction time should range from 45 to 60 min \[7,8\]. Thus, the maintained optimum leaching time is 60 min.

\[\text{Figure 3. Effect of reaction time on P}_2\text{O}_5 \text{ content and recovery (5\% Acid acetic; 30\% solid concentration; 40 °C).}\]

3.3.4. Effect of Acid Concentration

The effects of acid concentration in the range from 1\% to 15\% were studied for a reaction time of 60 min, a solid concentration of 30\%, and a temperature of 40 °C. Figure 4 shows that the P\(_2\)O\(_5\) content increased and reached a maximum of 29.9\% with increasing the acid concentration up to 7\%. This increase is due to the dissolution of carbonate minerals. Then, above an acid concentration of 7\%, P\(_2\)O\(_5\) content decreases and remains almost constant with a recovery of 74\%. Indeed, at higher acid concentrations, the acetic acid did not leach the remaining carbonates and tends to attack phosphate minerals and decreases P\(_2\)O\(_5\) content.

\[\text{Figure 4. Effect of acid concentration on P}_2\text{O}_5 \text{ content and recovery (60 min; 30\% solid concentration; 40 °C).}\]

3.3.5. Effect of Solid Concentration

The results of leaching with different solid concentrations, a reaction time of 60 min, an acid concentration of 7\%, and a temperature of 40 °C are represented in Figure 5. The \% P\(_2\)O\(_5\) increased with the increasing solid concentration and at the higher percent solids, the P\(_2\)O\(_5\) content decreased with a reduction in P\(_2\)O\(_5\) recovery. The increase in solids concentration leads to an increase in the consumption of acetic acid; thus, with constant initial acid concentration, the P\(_2\)O\(_5\) recovery decreases. Moreover, high solid concentration tends to decrease the dissolution of carbonates, which explains the decrease in P\(_2\)O\(_5\) content. As confirmed by Zafar et al. [16], the optimum solid concentration varied between 25\% and 15\%. Taking into consideration the process performance and economy, 25\% is maintained as the optimum solids concentration.
3.3.6. Effect of Temperature

The effect of temperature was examined in the range of 20 °C to 70 °C for a reaction time of 60 min, a 7% acetic acid, and a solid concentration of 25%. Figure 6 shows that the P2O5 content increased and reached 30.1% with 80% recovery at 40 °C, but then these parameters remain almost constant beyond this temperature. Higher temperatures improve the reaction efficiency and acid selectivity and may contribute to a slight increase in P2O5 content, but the most refractory carbonates remain unreacted above 40 °C [8]. The dissolution of carbonates is not much higher. However, leaching at temperatures higher than 80 °C can only lead to organic acids and water evaporation [4]. There is no benefit in leaching at a temperature >40 °C. As reported in different studies, the optimum leaching temperature varied from 40 to 60 °C [7,10]. By using the optimized leaching parameters, it was possible to achieve a marketable product from Ps with 30.1% P2O5 and recovery of 80%.

Figure 5. Effect of solid concentrations on P2O5 content and recovery (60 min; 7% Acid acetic; 40 °C).

3.3.7. Taguchi Orthogonal Experiment

To explore the optimized conditions for the leaching of Ps and to study the effects of four different factors on the P2O5 content, the Taguchi orthogonal experiments are made. Based on the single-factor optimization experiment, the main factors of reaction time, acid type, solid concentration, and acid concentration were selected for the orthogonal experiment investigation. A four-factor three-level L9 (3^4) orthogonal experiment table was designed as shown in Table 6 while the reaction temperature is fixed at 40 °C.
Table 6. The design of the orthogonal experiment.

| Code | Factor’s Name       | Level 1   | Level 2   | Level 3   |
|------|---------------------|-----------|-----------|-----------|
| A    | Acid type           | Acetic acid | Lactic acid | Citric acid |
| B    | Solid concentration (%) | 20     | 25      | 30       |
| C    | Acid Concentration (%) | 5      | 7      | 9        |
| D    | Reaction Time (min) | 60       | 100     | 120      |

The orthogonal experiment design generated by JMP is shown in Table 7.

Table 7. The result of the orthogonal experiment.

| Level | A     | B      | C      | D      | %P2O5 | P2O5 Recovery (%) |
|-------|-------|--------|--------|--------|-------|-------------------|
| 1     | Acetic acid | 20    | 5      | 60     | 28.5  | 70.01             |
| 2     | Acetic acid | 25    | 7      | 100    | 30.7  | 80.05             |
| 3     | Acetic acid | 30    | 9      | 120    | 30.2  | 80.02             |
| 4     | Lactic acid | 20    | 7      | 120    | 29.2  | 76.50             |
| 5     | Lactic acid | 25    | 9      | 60     | 28.7  | 72.10             |
| 6     | Lactic acid | 30    | 5      | 100    | 27.4  | 68.61             |
| 7     | Citric acid  | 20    | 9      | 100    | 27.9  | 69.80             |
| 8     | Citric acid  | 25    | 5      | 120    | 26.5  | 76.05             |
| 9     | Citric acid  | 30    | 7      | 60     | 24.8  | 63.03             |

After the generation of the Taguchi model, P2O5’s concentrations and recovery mean values are calculated. Then, the S/N ratio is calculated using % P2O5 and a Pareto Plot is designed using JMP software (Figure 7). Figure 7 shows that acid type is the most significant factor in the leaching reaction. However, reaction time, acid concentration, and solid concentration did not play an important role in the leaching process. Similar behavior has been observed by Fei et al. [10]. The cumulative percentage line has been made to evaluate the contribution of each parameter. We can remark in Figure 7 that a total of 90%, 79%, and 69% of the mean values effect, Global effect, and S/N ratio effect, respectively, are related to Acid Type.

![Figure 7. Pareto Plot of (a) P2O5’s concentrations mean values effect, (b) (S/N) ratio effect, and (c) Global effect.](image-url)
The desirability function method has been used to determine the best leaching parameters to achieve the maximum \( P_2O_5 \) grade with maximizing the signal-to-noise ratio. Figure 8 shows that the maximum desirability is achieved with 7% of acetic acid, 30% of solid concentration, and a reaction time of 100 min. Therefore, the optimum leaching conditions are \( A_1B_3C_2D_2 \). It seems that the strongest acid (Acetic acid, \( pK_a = 4.76 \)) has the highest efficiency in leaching carbonates. Moreover, leaching is less effective at high organic acid concentration due to the polarity of the O-H bond [18]. According to Taguchi results, a higher solid concentration leads to achieving the desired grade in the low-grade Ps. It also appears that acid acetic required more time to release phosphate.

![Figure 8. Desirability function graph.](image)

**3.3.8. Analysis of Covariance (ANCOVA)**

To explore the data collected from the Taguchi orthogonal experimental design, the Analysis of Covariance (ANCOVA) is used. ANCOVA is a general linear model carried out to evaluate the degrees of dependence of the mean values of the response \( P_2O_5 \) concentration with the four independent variables of our experiment, which are solid concentration, acid concentration, leaching time, and acid type. The results are given in Table 8. The R-squared value of our model 96.3% means that all the variability of the response \( P_2O_5 \) concentration mean values are completely explained by movements in the four independent variables. The \( p \)-Value <0.05 was always the accepted value for statistical significance with a confidence level >95%, and smaller \( p \) values refer to a larger significance of the respective coefficient [19]. As shown in Table 8, a significant effect (\( p < 0.05 \)) was observed for acid type. In contrast, no significant differences (\( p > 0.05 \)) were found for the other variables.
Table 8. Analysis of covariance for %P$_2$O$_5$ as a dependent variable.

| Source          | Sum of Squares | df | Mean Square | F-Value | p-Value | R-Squared |
|-----------------|----------------|----|-------------|---------|---------|-----------|
| Corrected Model | 26.718 a       | 5  | 5.344       | 15.578  | 0.023   | 0.963     |
| Intercept       | 87.951         | 1  | 87.951      | 256.404 | 0.001   | 0.988     |
| Solid concentration | 2.046    | 1  | 2.046       | 5.963   | 0.092   | 0.665     |
| Acid concentration | 3.212    | 1  | 3.212       | 9.364   | 0.055   | 0.757     |
| Reaction Time   | 3.297         | 1  | 3.297       | 9.613   | 0.053   | 0.762     |
| Acid Type       | 18.163        | 2  | 9.081       | 26.475  | 0.012   | 0.946     |
| Error           | 1.029         | 3  | 0.343       | -       | -       | -         |
| Total           | 7196.944      | 9  | -           | -       | -       | -         |
| Corrected Total | 27.747        | 8  | -           | -       | -       | -         |

*a R-Squared = 0.963 (Adjusted R Squared = 0.901); df: Degree of freedom.

We can conclude that the acid type may affect the P$_2$O$_5$ grade significantly, but leaching time, solid concentration, and acid concentration slightly, which confirms results obtained by Taguchi experimental design analysis. To assess the economic feasibility of the Ps leaching, we should consider sustainable development more than the benefits and costs. The development and feasibility of this beneficiation technique are justified for other reasons, such as environmental benefits, i.e., water consumption; like other conventional beneficiation techniques, leaching is not a hazardous technique and the final product has a very good quality. Hence, for the objective evaluation of this leaching process, economic feasibility studies should take into count both costs and benefits. Nevertheless, it is important to highlight that the organic acid price is high, and they are generally expensive for utilization in practice in the phosphate beneficiation industries. However, it is possible to recover the whole of the organic acids and reuse it in the process. The recovery of organic acid can be achieved by different methods [6,8]. Their recovery using sulfuric acid is known as the best organic acid recovery technique. Moreover, acid leaching plants have low investment costs. Therefore, the proposed process is economically feasible.

3.3.9. Final Optimum Experiment

By using the optimal leaching parameters obtained using the Taguchi Technique (Table 9), the final test showed that it was possible to achieve a marketable product with a P$_2$O$_5$ content of 30.70% and a recovery of 81.01%.

Table 9. Optimized conditions for leaching experiments.

| Acid Type      | Solid Concentration (%) | Acid Concentration (%) | Reaction Time (min) | Temperature (°C) |
|----------------|-------------------------|------------------------|---------------------|-----------------|
| Acetic acid    | 30                      | 7                      | 100                 | 40              |

3.4. Kinetic Analysis

3.4.1. Leaching Mechanism

Take Acetic acid to illustrate the reaction process. The reaction that occurs between acetic acid and calcareous materials is:

$$\text{CaCO}_3 + 2\text{CH}_3\text{COOH} \rightarrow \text{Ca(CH}_3\text{COO)}_2 + \text{CO}_2 + \text{H}_2\text{O}$$ (4)

This reaction continues to completion depending on acetic acid concentration, leaching temperature, leaching time, and other process conditions. After the complete dissolution of carbonates, the acid begins to dissolve the phosphorus content of the ore. However, the dissolution kinetics controls the overall rate of leaching of carbonates in the low-grade Ps. The acid selectivity indicates that the acid does not leach the phosphate minerals.
3.4.2. Reaction Models

In general, the rate of the leaching reaction is controlled by the slowest steps [6]. In a fluid-solid reaction system, the reaction rate is controlled by one of the following sequential steps: diffusion through the fluid film, diffusion through the ash/product layer, or the chemical reaction at the surface of the core of unreacted particles [20]. The experimental data can be analyzed using the heterogeneous reaction models to investigate the kinetic parameters and rate-controlling step for the dissolution of carbonates in low-grade Ps using Acetic acid [21]. The shrinking core model has been commonly used to model the leaching systems, it confirms that the leaching reaction is controlled by fluid film diffusion or chemical reaction control.

The equations of the shrinking core model when the diffusion or the surface chemical reactions are the slowest steps is expressed as follows, respectively:

\[ 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = K_d t = K \exp \left( -\frac{E_a}{RT} \right) t \]  \hfil (5)

\[ 1 - (1 - \alpha)^{\frac{1}{3}} = K_r t = K \exp \left( -\frac{E_a}{RT} \right) t \] \hfil (6)

In the kinetics experiments, activation energy is calculated using the Arrhenius Equation (7) [22]:

\[ K = K_o e^{-\frac{E_a}{RT}} \] \hfil (7)

where \( \alpha = \) fraction reacted; \( K_d \) and \( K_r \) = rate constants calculated from Equations (5) and (6), respectively; \( t = \) reaction time; \( K = \) kinetic constant; \( T = \) absolute temperature; \( K_o = \) the Arrhenius constant; \( R = \) universal constant of gas; \( E_a = \) activation energy.

The plot of \( \ln k \) versus \( 1/T \) gives a straight line with a slope of \( -E_a/RT \) and an intercept of \( \ln k_0 \). In the diffusion-controlled process, the activation energy is <25 kJ/mol and the activation energy for a chemically controlled process is >40 kJ/mol [20].

3.4.3. Kinetics Experiments

In the optimal conditions, several experiments were performed at different temperatures and times to determine the leaching kinetics of the Ps. After doing the tests at optimal conditions, a sample of the obtained solid was sent to the AAS chemical analysis to determine Ca\(^{2+}\) content to obtain \( \alpha \), the fraction reacted according to Equation (2), in each test. Experimental results and equations of the shrinking core model are given in Table 10.

Table 10. Characteristics of experiments of the shrinking core model.

| Time (min) | \( \alpha \ (%) \) | \( 1 - (1 - \alpha)^{\frac{1}{3}} \) | \( 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} \) |
|-----------|----------------|---------------------|---------------------|
| 30        | 0              | 0                   | 0                   |
| 40        | 5 10           | 0.017               | 0.035               |
| 50        | 11             | 0.038               | 0.068               |
| 60        | 17             | 0.072               | 0.114               |
| 70        | 27             | 0.083               | 0.152               |
| 80        | 30             | 0.100               | 0.191               |
| 90        | 35             | 0.114               | 0.230               |
| 100       | 40             | 0.126               | 0.275               |
| 110       | 42             | 0.142               | 0.326               |

The variation in the carbonate content in the Ps according to the reaction time at different temperatures is shown in Figure 9. As shown in Figure 9, by increasing the time and temperature, carbonate solubility increased and the reaction was almost completed.
Figure 9. The effect of time and temperature on carbonate dissolution.

Figures 10 and 11 show the relationships between the experimental data obtained from the suggested kinetic models (Table 10) and leaching time (min) at different leaching temperatures.

Figure 10. The plot of $1 - (1 - \alpha)^{1/3}$ vs. $t$ versus temperature for the recovery of P$_2$O$_5$. 
Figure 11. The plot of $1 - \frac{2}{3} \alpha - \left(1 - \alpha\right)^{\frac{2}{3}}$ vs. $t$ versus temperature for the recovery of $P_2O_5$.

The values of the apparent rate constant $K_r$ and $K_d$ were calculated as the slopes of the straight lines obtained in Figures 10 and 11 and summarized in Table 11.

Table 11. Values for $k_r$ and $k_d$ and correlation coefficients $R^2$ various temperatures.

| Temperature (°C) | $k_r$ (min$^{-1}$) | $k_d$ (min$^{-1}$) | $R^2$ | $k_r$ | $k_d$ |
|------------------|-------------------|-------------------|-------|-------|-------|
| 30               | 0.0009            | 0.0001            | 0.99  | 0.95  | 0.95  |
| 40               | 0.0016            | 0.0003            | 0.98  | 0.87  | 0.87  |
| 50               | 0.00334           | 0.0009            | 0.982 | 0.89  | 0.89  |
| 60               | 0.0049            | 0.0017            | 0.983 | 0.97  | 0.97  |

We can conclude that the experimental data fit with the chemical reaction control models $1 - (1 - \alpha)^{\frac{1}{3}}$ leaching processes of Ps by Acetic acid. These models’ equations have been chosen depending on the highest value of $R^2$. This shrinking core model $(1 - (1 - \alpha)^{\frac{1}{3}})$ gives a straight line with plotting vs. leaching time ($t$) at different leaching temperatures with a good correlation of $R^2 \geq 0.98$.

The activation energy ($E_a$) of the leaching reaction using the acetic acid under the optimum conditions was calculated using the Arrhenius equation (Equation (7)).

Equation (7) can be expressed as follows:

$$\text{Ln} K = \text{Ln} K_0 - \frac{E_a}{RT}$$ (8)

A graph of $\text{Ln} K$ versus $1000/T (1/K_0)$ resulted in a straight line with a slope of $-E_a/RT$ and a width of the origin of $\text{Ln}K_0$ (Figure 12).
Figure 12. Arrhenius plot for the selective dissolution of carbonates.

The activation energy $E_a$ of the reaction is calculated from the slope of the line ($E_a/R = 5.89$). This value, which is 48.9 kJ/mol, confirms that the dissolution rate was controlled by the chemical reaction as $E_a$ is greater than 40 kJ/mol, further verifying the suitability of this kinetic model. This value is consistent with the values obtained in most of the studies on the dissolution of carbonates in low-grade phosphate ores; it has been concluded that the overall rate of dissolution is controlled by chemical reactions [4].

The Arrhenius constant was also calculated:

$$\ln K_0 = 12.42 \frac{1}{min} \rightarrow K_0 = 247.7 \times 10^{-3} \frac{1}{min} = 4.12 \times 10^{3} \frac{1}{s}$$

The leaching kinetics model for this study can be described by Equation (9):

$$1 - (1 - \alpha)^\frac{3}{4} = 4.12 \times 10^{3} \exp\left(\frac{-48.9}{RT}\right) t$$

4. Conclusions

Phosphate washing sludges from the Khouribga washing plant have, so far, been rejected as non-profitable material. These low-grade sludges (15.84% $P_2O_5$), non-recoverable by the washing process, are enriched with organic acid leaching for upgrading. Ball-milling under optimum conditions (rotation speed of 100 rpm, charge ratio of 4/1, a solid concentration of 40%, and a grinding time of 4 min) increases the content of $P_2O_5$ up to 18.51%. After studying the influence of the operating parameters (acid type, acid concentration, solid concentration, Temperature, and reaction time) on organic acid leaching of Ps through single-factor experiments and Taguchi orthogonal experiments, we conclude that optimum parameters obtained from single-factor experiments are leaching for 60 min using acetic acid with a concentration of 7%, solid concentration of 25%, and a temperature of 40 °C. Single-factor analysis results helped to improve the grade of $P_2O_5$ to 30.1% with a recovery of 80%. It is important to highlight that increasing the Acid concentration above 7% may have a negative influence on phosphate minerals. It tends to attack phosphate minerals besides dissolving carbonates. Moreover, we can affirm that increasing leaching temperature has a good influence on leaching efficiency, and acid selectivity, but the most refractory carbonates remain unreacted above 40 °C; there are no benefits at leaching above this temperature. Then, the Taguchi $L_9$ ($3^4$) orthogonal array experimental design is generated and % $P_2O_5$ mean values and the signal-to-noise ratio (larger the better) are calculated. Pareto
plot of the two responses shows that acid type is the most significant factor in leaching and according to the desirability function, the optimum conditions were measured to be 7% of acetic acid, a solid concentration of 30%, a reaction time of 100 min, and a temperature of 40 °C. By optimization of the leaching parameters, the final test results showed that it was possible to produce a marketable phosphate concentrate with 81.01% recovery and 30.7% of P₂O₅ content. According to the ANCOVA analysis, the most important factor affecting the % P₂O₅ of phosphate washing sludges is the organic acid type at a reliability level of 95%, while it did not show effects for all the other leaching factors. These results are considered satisfactory as long as they have allowed the beneficiated low-grade phosphate washing sludges to reach the levels of marketable grades (≥30%). The dissolution kinetics by two different kinetic models of the calcareous material with acetic were proven to fit the shrinking core model for a chemically controlled process. The activation energy was determined to 48.9 kJ/mol, which is consistent with a chemically controlled reaction.

Author Contributions: Conceptualization, L.A., and M.E.; methodology, L.A. and M.E.; software, L.A. and M.A.; validation, M.E., and A.Z.; formal analysis, L.A.; investigation, L.A.; resources, M.E.; data curation, L.A., M.A. and M.E.; writing—original draft preparation, L.A.; writing—review and editing, L.A., M.E., M.A., and A.Z.; visualization, M.E.; supervision, M.E. and A.Z.; project administration, M.E. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Not applicable.

Funding: This research received no external funding.

Acknowledgments: The authors gratefully thank Reminex Managem laboratories in Marrakech, Morocco, for the chemical analyses, as well as the Center of Analysis and Characterization (CAC) at Cady Ayyad University, Marrakech, Morocco.

Conflicts of Interest: The authors declare no conflict of interest.

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