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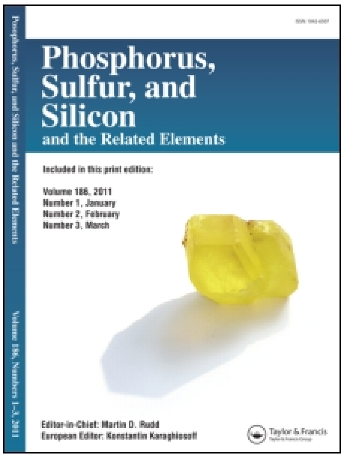

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Bases of the production of phosphoric fertilizers are classical methods involving acid dissolution of rock phosphates. The development of new methods applicable both to high-quality and low-quality phosphates is important for solving technological and ecological problems and to increase the economical effectiveness of phosphorus fertilizer technologies. In this respect, the bioconversion of rock phosphates in order to obtain phosphorus fertilizers is very promising. The basic principle of the biotechnological processing of natural phosphates is the production of organic acids, mainly citric, oxalic, and gluconic acid, that attack and dissolve the phosphates, converting the phosphorus to a form utilizable for the plants. The aim of this research is to optimize the process of Tunisian phosphorite solubilization with citric, oxalic, and gluconic acids in relation to the following main factors: the acid concentration, reaction time, solid/liquid phases ratio, and natural phosphate fraction. Two objective functions have been investigated: the quantity of the available acid in the system and the extent of phosphate dissolution. The research data has been processed according to the standard statistical tests. A mathematical model describing the phosphate decomposition process by organic acids has been obtained. A multicriteria optimization has been performed to determine the optimum levels of the examined factors. It was established that the different factors have a different effect on the goal parameters. A maximum degree of 91.89% of phosphorus extraction has been reached at phosphate solubilization by citric acid.

Keywords Natural phosphate; optimisation; organic acids; phosphate-solubilizing microorganisms; regression analysis

INTRODUCTION

Phosphorus is one of the most important nutrients for plant growth. The traditional P-containing fertilizers are produced by chemical processing of rock phosphate ore. The application of a phosphorus fertilizer to the

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soil results in chemical reactions between the phosphate, soil, and nonphosphatic fertilizer components, which immediately remove phosphorus from the solution phase, making it unavailable for plant growth.[1] Many microorganisms were found to solubilize insoluble calcium orthophosphate and to convert it into a nutritionally available form for plants.[1–12] It is generally accepted that the most common mechanism for the mineral phosphate-solubilizing phenomenon with respect to calcium phosphates is the acidification of the medium via biosynthesis and the release of organic acids (citric, oxalic, gluconic, formic, acetic, etc.). The effectiveness of the organic acids to dissolve the rock phosphate depends on the nature of the phosphates,[13] the number of acidic protons biochemically generated, and the pK_a values of the acids.[10,14] On the availability of organic acids in the cultural liquid, the extraction of the phosphorus from rock phosphate can be considered like a process of acid solubilization. The principal factors affecting the acid dissolution are the size of the particles, acid concentration, temperature, solid to liquid phases ratio, agitation, and the nature of the material.[15]

In previous studies, we have established the possibility of biological mobilization of the phosphorus contained in various phosphorites (Bulgarian, Moroccan, Tunisian) using *Aspergillus niger* fungi.[16,17,18] It has already been proved that a maximum degree of 90% of the phosphorus extraction in a water and citrate-soluble form can be reached.[18]

In the available sources,[10,19] the solubilization of the various rock phosphates was considered a biochemical process. The bioconversion of the rock phosphates was performed in a complex heterogeneous system with simultaneously occuring biosynthetic and chemical reactions, which have different rates depending on the various mutually affected parameters. The acid dissolution is one of the basic stages from the total solubilizing process. It should be useful to explain completely the chemistry of the rock phosphate solubilization.

The aim of this research is to optimize the process of natural phosphate solubilization with citric, oxalic, and gluconic acid in relation to the following main factors: the acid concentration (x_1), the reaction time (x_2), the solid/liquid phases ratio (x_3), and the rock phosphate fraction (x_4). Two objective parameters have been investigated: the quantity of the available acid in the system (y_1) and the rate of phosphate solubilization (y_2). Statistical analysis has been applied using the standard statistical tests.

EXPERIMENTAL

Tunisian Phosphorite

The commercial Tunisian Phosphorite (TP) contains apatite mineral, carbonates, alumosilicates, glauconite, limonite, and clay minerals.

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Three fractions (below 0.2 mm, from 0.2 to 0.4 mm, and from 0.4 to 0.63 mm) were used. The chemical composition of the TP (3 fractions) is shown in Table I. The P_2O_5 content was determined spectrophotometrically using a vanado-molybdate yellow complex.[20] The TP was analyzed for the content of the total P_2O_5 ($P_2O_{5\,\mathrm{tot}}$) and assimilable P_2O_5 estimated by its solubility in 2% citric acid ($P_2O_{5\,\mathrm{c.s.}}$), neutral ammonium citrate solution ($P_2O_{5\,\mathrm{a.s.}}$), and 2% formic acid ($P_2O_{5\,\mathrm{f.s.}}$). A complexometric method[21] was used for CaO, Fe_2O_3, and Al_2O_3 determination; Atom Absorption Spectrophotometry (AAS) for magnesium; flame spectrophotometry for potassium and sodium; weight analysis for silicon; the ion selective electrode method for fluorine; and volumetric analysis for CO_2.

Experimental Methods

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The necessary quantities of organic acids were added to 250-mL measuring flasks each containing 1 g of TP. These quantities were estimated following Eqs. (1) and (2) and according to the P_2O_5 content in the phosphorite and the acid concentration. The solid-liquid phases ratio became 1:140, 1:170, and 1:200, respectively, so at the lowest ratio the quantity of organic acid is equivalent to the stoichiometric quantity.

$$2\ Ca_5\ F(PO_4)_3 + 20\ (HX) = 10\ CaX_2 + 6\ H_3PO_4 + 2\ HF \qquad (1)$$

$$2\ Ca_5\ F(PO_4)_3 + 14\ (HX) = 7\ CaX_2 + 3\ Ca(H_2PO_4)2 + 2\ HF \qquad (2)$$

where HX is
citric acid ($C_6H_8O_7$)
oxalic acid ($C_2H_2O_4$)
gluconic acid ($C_6H_{12}O_7$)

The flasks were put into a shaking water bath at 30°C for a fixed reaction time (30, 60, and 90 min). The content of the flasks was filtered, and the quantity of the available acid (y_1, g/dm^3) as well as the content of P_2O_5 (% w/w) were determined through titration with 0.1 N NaOH. On the basis of the results obtained for P_2O_5-concentration available in the liquid, the extraction degree y_2 (α, % w/w) was calculated, compared to the total content of P_2O_5 in the TP, and expressed as follows:

$$\alpha P_2O_5 = \frac{P_2O_{5\ \mathrm{f.}}}{P_2O_{5\ \mathrm{tot.}}} 100(\%) \qquad (3)$$

where $P_2O_{5\ \mathrm{f.}} = P_2O_5$ content in the filtrate (% w/w);
$P_2O_{5\ \mathrm{tot.}}$ = the total content of P2O5 in TP (% w/w).

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TABLE I The Chemical Composition of Different Fractions of Tunisian Phosphorite (% w/w)

											P_2O_5			
Value of fraction (mm)	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SiO_2	F	CO_2	H_2O	tot.	c.s.	f.s.	a.s.
Below 0.2	48.9	0.2	<0.1	0.5	0.1	1.3	1.1	3.2	5.0	1.1	29.6	10.1	14.1	5.0
From 0.2 to 0.4	49.1	0.3	<0.1	0.3	0.1	1.4	1.0	3.4	4.9	1.1	30.2	10.0	16.9	5.0
From 0.4 to 0.63	49.2	0.4	<0.1	0.3	0.1	1.4	1.0	3.5	4.8	1.2	31.4	9.9	16.4	5.1

Statistical Analysis and Optimisation

Statistical analysis was conducted using the standard statistical tests. The verification for the goodness of fit of the mathematical models was carried out by the coefficient of determination R^2. The significance test of R^2 was made by a comparison between the calculated value F and the critical value of Fisher's criterion (Fc) from the Fisher's distribution at defined significance level α and degrees of freedom (ν_M, ν_R). A multicriteria optimisation was performed to determine the optimum values of the objective functions.[22]

Independent variables and limits of the main factors x_1 (g/dm^3), x_2 (min), and x_3 and x_4 (mm) for the investigations with citric, oxalic, and gluconic acids are given in Table II.

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RESULTS AND DISCUSSION

Using statistical analysis and following the method of experiment design, the experimental results for the objective functions (y_1 and y_2) were obtained (Table III). The second order polynomials model was used (Eq. (4)) to derive a mathematical model to describe the solubilization of TP with citric, oxalic, and gluconic acid:

$$\hat{y} = b_0 + \sum_{i=1}^{4} b_i x_i + \sum_{i=1}^{3}\sum_{j=i+1}^{4} b_{ij} x_i x_j + \sum_{i=1}^{4} b_{ii} x_i^2 \qquad (4)$$

Table IV presents the values of the coefficients of the regression equations for objective functions (y_1 and y_2) after the elimination of the insignificant part. The coefficients of determination R^2, the adjusted coefficient of determination R^2(adj), the calculated values of Fisher's criterion (F), and the values of the critical Fisher's criterion (Fc) for investigations with citric, oxalic, and gluconic acid are shown in Table V.

TABLE II Independent Variables and Limits of the Main Factors

	Citric Acid				Oxalic Acid				Gluconic Acid			
Levels	x_1^a	x_2^b	x_3^c	x_4^d	x_1^a	x_2^b	x_3^c	x_4^d	x_1^a	x_2^b	x_3^c	x_4^d
Base levels (0)	40	90	1:170	0.4	35	90	1:170	0.4	23	90	1:170	0.4
Low levels (−1)	20	60	1:140	0.2	14	60	1:140	0.2	8	60	1:140	0.2
High levels (+1)	60	120	1:120	0.63	56	120	1:120	0.63	38	120	1:120	0.63

[a] Acid concentration (g/dm^3).
[b] Reaction time (min).
[c] Solid–liquid phases ratio.
[d] Rock phosphate fraction (mm).

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TABLE III The Experimental Design and Results from the TP Solubilization Using Citric, Oxalic, and Gluconic Acid

No.	x_1	x_2	x_3	x_4	Citric Acid		Oxalic Acid		Gluconic Acid	
					y_1^a	y_2^b	y_1^a	y_2^b	y_1^a	y_2^b
1	−1	−1	−1	−1	10.3	44.1	8.8	13.9	3.4	28.0
2	+1	−1	−1	−1	33.2	79.9	34.4	3.0	16.9	67.6
3	−1	+1	−1	−1	10.6	48.2	8.8	19.5	3.8	32.7
4	+1	+1	−1	−1	33.8	91.9	34.7	16.7	17.5	83.2
5	−1	−1	+1	−1	15.7	23.0	12.8	13.1	5.0	15.2
6	+1	−1	+1	−1	49.0	29.0	49.5	3.4	25.0	24.5
7	−1	+1	+1	−1	16.3	29.8	13.8	18.6	5.0	17.4
8	+1	+1	+1	−1	51.3	48.4	48.8	7.9	25.0	39.7
9	−1	−1	−1	+1	10.8	41.0	12.2	9.9	3.8	25.8
10	+1	−1	−1	+1	33.8	73.0	35.7	3.5	18.2	62.0
11	−1	+1	−1	+1	11.3	47.9	9.4	17.4	6.3	33.3
12	+1	+1	−1	+1	34.4	79.6	35.1	6.2	18.8	75.7
13	−1	−1	+1	+1	16.0	15.9	13.5	12.1	5.3	14.1
14	+1	−1	+1	+1	49.5	28.5	50.4	6.1	23.8	26.2
15	−1	+1	+1	+1	16.6	21.9	12.5	17.3	5.6	17.1
16	+1	+1	+1	+1	50.7	46.5	50.7	7.2	26.3	25.5
17	−1	0	0	0	13.8	24.6	9.7	21.2	5.0	11.5
18	+1	0	0	0	42.9	38.4	41.3	9.3	22.5	38.6
19	0	−1	0	0	27.5	33.4	26.3	4.9	13.2	20.0
20	0	+1	0	0	26.3	39.3	28.2	8.2	12.5	32.6
21	0	0	−1	0	21.6	66.1	21.9	9.9	10.6	47.5
22	0	0	+1	0	33.2	24.7	31.6	9.9	16.9	18.1
23	0	0	0	−1	27.5	30.0	26.3	11.5	17.5	24.6
24	0	0	0	+1	27.5	37.5	25.7	10.8	13.8	24.1
25	0	0	0	0	27.9	42.1	26.9	10.2	13.8	25.3

[a] The quantity of the available acid in the system (g/dm^3).
[b] The rate of phosphate solubilization (% w/w).

The lowest concentration of the available citric acid (10.3 g/dm^3), oxalic acid (8.8 g/dm^3), and gluconic acid (3.4 g/dm^3) was achieved at the low levels of the 4 examined factors. This concentration does not change essentially when the time of reaction (x_2) was increased from 60 min to 120 min at constant values of the other three factors.

As seen from the data (Table IV), the highest coefficients value b_1 were observed for the objective function y_1 independently of the organic acid used. From the other coefficients, b_3 has a value of 5.46 for an investigations with citric acid and of 4.58 for an investigation with oxalic acid, followed by b_{13} with values of 2.47 and 2.93, respectively. This fact shows that the acid concentration (x_1) and the solid/liquid phases ratio (x_3) have an essential influence on the reactivity of the citric and

TABLE IV Values of the Coefficients for Deduced Regression Equations

	Organic acid					
	Citric acid		Oxalic acid		Gluconic acid	
Coefficient	y_1^a	y_2^b	y_1^a	y_2^b	y_1^a	y_2^b
b_0	27.70	35.00	26.70	10.50	14.30	25.20
b_1	14.30	12.20	15.50	4.43	8.38	13.80
b_2	0.31	4.76	—	2.74	2.16	4.10
b_3	5.46	16.90	4.58	—	—	14.30
b_4	—	—	0.49	0.95	—	1.61
b_{12}	—	—	—	—	—	1.67
b_{13}	2.47	5.10	2.93	—	1.56	7.29
b_{14}	—	—	—	—	—	1.42
b_{23}	—	—	—	0.83	—	—
b_{24}	—	—	—	—	—	—
b_{34}	—	—	—	0.99	—	—
b_{11}	—	—	—	4.56	—	—
b_{22}	—	—	—	4.08	1.23	—
b_{33}	—	11.60	—	—	—	11.10
b_{44}	—	—	—	—	—	—

[a] The quantity of the available acid in the system (g/dm^3).
[b] The rate of phosphate solubilization (% w/w).

oxalic acid. For the investigations with gluconic acid, b_2 is the second coefficient with an essential value after b_1. This is different compared to the other two organic acids and proves that the reactivity of gluconic acid depends on the acid concentration (x_1) as well as on reaction time (x_2).

TABLE V Values of the Determination's Coefficients (R^2, R^2 adj) and Fisher's Criterion (F, Fc)

Organic acid	Equation	R^2	R^2 (adj)	F	Fc
Citric acid	y_1^a	0.998	99.80	3125.00	5.84
	y_2^b	0.950	0.937	72.76	4.60
Oxalic acid	y_1^a	0.997	99.60	1456.47	5.84
	y_2^b	0.914	0.879	25.89	3.49
Gluconic acid	y_1^a	0.982	97.90	273.34	5.84
	y_2^b	0.984	0.976	120.47	3.28

[a] The quantity of the available acid in the system (g/dm^3).
[b] The rate of phosphate solubilization (% w/w).

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The regression equations for the objective function y_1 obtained describe the data satisfactorily. This conclusion is confirmed by the values of coefficients of determination R^2 and R^2(adj) and the calculated values of F and Fc (Table V). The values of R^2 are very high (0.998, 0.997, and 0.996) and are equal to the R^2(adj) (0.998, 0.996, and 0.979) for citric, oxalic, and gluconic acid, respectively. The values of F are much higher compared with Fc, which indicate that determination coefficient R^2 is significant and the regression models for y_1 obtained for citric, oxalic, and gluconic acid describe the data well.

A maximum extent of P_2O_5 extraction (α, % w/w) with citric acid reaches a value of 91.9% at the highest level of the factors $x_1 = 60$ g/dm^3 and $x_2 = 120$ min and the lowest level of the remaining two factors: $x_3 = 1{:}140$ and $x_4 = 0.2$ mm (Table III). The results are similar when gluconic acid was used. At these conditions, α has a maximum of 83.2%. Comparing the results from the experiments obtained with citric and gluconic acid to those for oxalic acid, it can be concluded that a maximum value α (21.2%) is too low and can be achieved at some different conditions: concentration $x_1 = 14$ g/dm^3 and at the basic level of the other factors: $x_2 = 90$ min, $x_3 = 1{:}140$, and x_4 (from 0.2 to 0.4 mm).

The values of the objective function y_2 correlate with the values of the coefficients (b_i). As seen from the data, the solid/liquid phases ratio (x_3) and acid concentration (x_1) followed from reaction time (x_2) have a significant influence on the solubilization of TP with citric and gluconic acid. This conclusion can be made because of the fact that b_1, b_3, b_{13}, $b_{33,}$ and the b_2 coefficient have the highest values (Table IV). The experiments carried out with oxalic acid have the highest values for b_1, b_2, b_{11}, and $b_{22,}$ which indicated that in these conditions the oxalic acid concentration and the reaction time affect the phosphorite solubilization. The phosphate fraction (x_4) does not affect both the quantity of the unreacted acid and the extent of phosphate dissolution, independently of the organic acid used.

Optimisation in searching for a compromised decision for the objective function y_1 and y_2 using citric, oxalic, and gluconic acid on the basis of the deduced adequate regression models was done.[23] The indicated optimum values by the multicriteria optimisation of the examined factors (x_1, x_2, x_3, and x_4) and optimum values of the objective functions y_1 and y_2 are presented in Table VI. Our experimental data confirms the optimum values of the objective parameters after optimisation. The statistical error varies from 2 to 5%.

Figures 1, 2, and 3 present contour plots of y_1 as function of two factors having the highest influence at optimal constant values of the rest factors.

TABLE VI Results from the Multicriteria Optimisation

Organic acid	x_1^a g/dm^3	x_2^b min	x_3^c —	x_4^d mm	y_1^e g/dm^3	y_2^f % w/w
Citric acid	42	120	1:140	0.2	22.52	73.73
Oxalic acid	14	105	1:140	0.2	8.30	22.55
Gluconic acid	38	120	1:140	0.2	17.59	83.17

[a] Acid concentration.
[b] Reaction time.
[c] Solid–liquid phases ratio.
[d] Rock phosphate fraction.
[e] The quantity of the available acid in the system.
[f] The rate of phosphate solubilization.

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The quantity of the unreacted citric acid increases with an increase the acid concentration (x_1) and the solid–liquid phases ratio (x_3), which was also observed in the case of oxalic acid (Figures 1 and 2). Figure 3 presents the results from the investigations regarding the solubilization with gluconic acid and in particular the changes of y_1 as a function of x_2 and x_4 at optimal constant values of x_1 and x_3.

Figures 4, 5, and 6 present contor plots of y_2 as a function of two factors having the highest influence at optimal constant values of the rest factors. As seen from Figures 4 and 6, when citric and gluconic

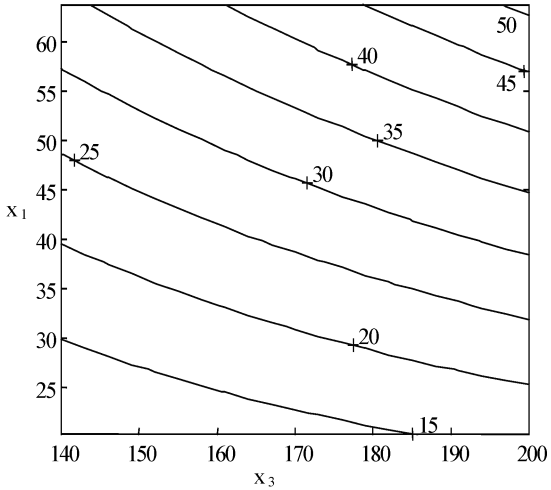

FIGURE 1 The contour plot of y_1 at the optimal constant value of $x_2 = 120$ min and $x_4 = 0.2$ mm.

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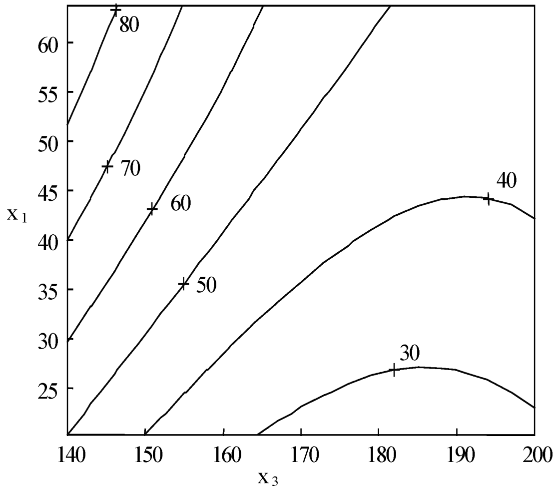

FIGURE 2 The contour plot of y_1 at the optimal constant value of $x_2 = 105$ min and $x_4 = 0.2$ mm.

acid concentration (x_1) increases and with a decrease of the solid/liquid phases ratio (x_3), the extent of P_2O_5 solubilization (y_2) increases.

The oxalic acid concentration (x_1) and reaction time (x_2) have an insignificant influence on y_2 (Figure 5) compared with the results for citric

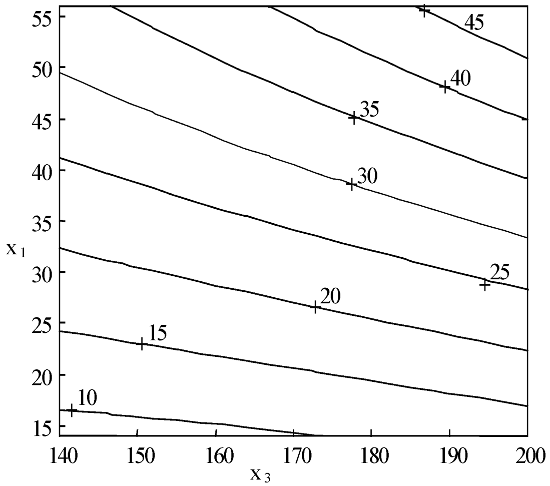

FIGURE 3 The contour plot of y_1 at the optimal constant value of $x_1 = 38$ g/dm^3 and $x_3 = 1{:}140$.

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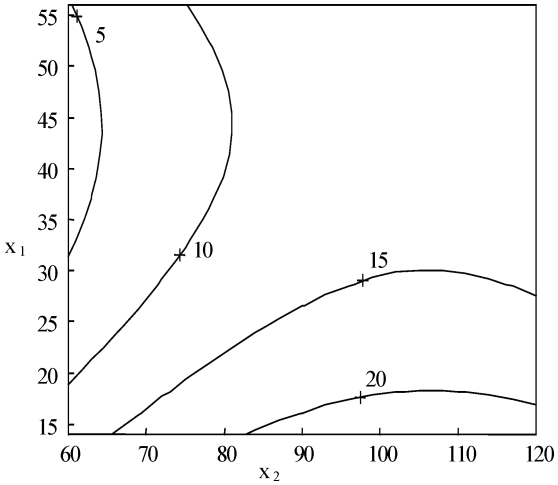

FIGURE 4 The contour plot of y_2 at the optimal constant value of $x_2 = 120$ min and $x_4 = 0.2$ mm.

and gluconic acid. This fact correlates with the values of the regression equations coefficients b_1 and b_2 (Table IV).

The present study shows that all selected factors, which can be considered main factors in a process of acid dissolution, have an influence

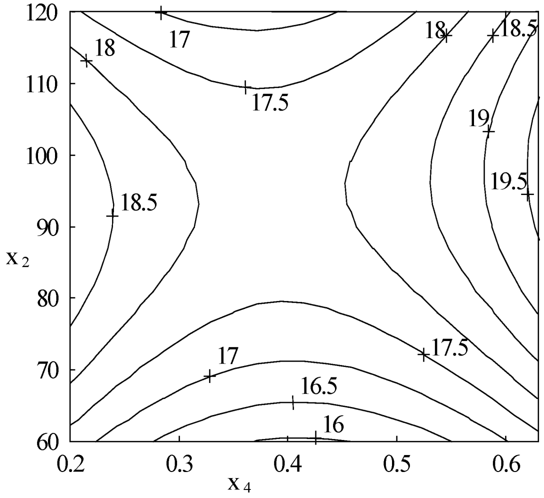

FIGURE 5 The contour plot of y_2 at the optimal constant value of $x_3 = 1{:}140$ and $x_4 = 0.2$ mm.

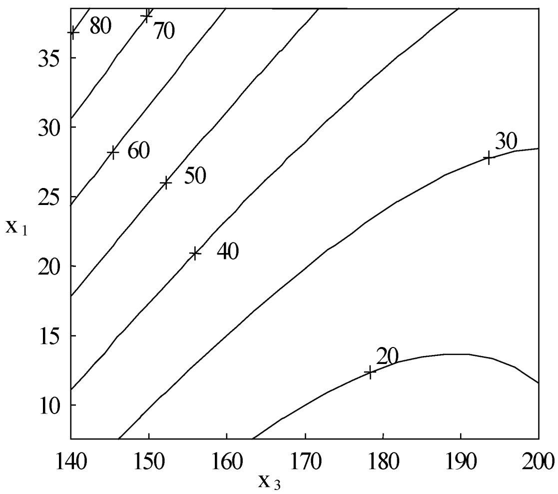

FIGURE 6 The contour plot of y_2 at the optimal constant value of $x_2 = 120$ min and $x_4 = 0.2$ mm.

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on the solubility of TP with citric, oxalic, and gluconic acid. Acid dissolution was performed in a complex heterogeneous system with simultaneously occurring chemical reactions. The availability of the H^+ ions in the liquid, which depends on the dissociation constant (pK_a) of the organic acids,[10] has an essential influence on the acid solubilization. Citric acid has the highest value of pK_a (4.13), followed by gluconic ($pK_a = 3.6$) and oxalic acid ($pK_a = 1.06$), which explains the highest extraction degree of P_2O_5. It is known[15] that a process of acid decomposition is limited by the diffusion, which correlates with the liquid viscosity. A relationship between the dissociation constant values, solid-to-liquid ratio, and phosphate solubilization was detected. According to Eqs. (1) and (2), the phosphorite dissolution leads to the formation of CaX_2 (citrate, oxalate, and gluconate), phosphoric acid, and $Ca(H_2PO_4)_2$. Phosphate ions can also form a range of compounds in combination with metals such as Ca, Fe, Al, K, and Na, available in the liquid phase as a result of the solubilization of phosphorite. We assume that as a result of acid dissolution, calcium (citrate, oxalate, and gluconate) can precipitate on the phosphate particles. In this way the process of acid decomposition will be limited by the contact between the liquid and solid phases. This dissolution (precipitation and adsorbtion/desorbtion) equilibrium controls the concentration of phosphate ions in the liquid.[14] As a result of the phosphate solubilization, PO_4^{3-} and Ca^{2+} ions pass to the liquid phase. It can be assumed that the main chemistry of the solubilization of phosphorite by citric, oxalic, and gluconic acids consists in the formation of

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phosphoric acid, Ca phosphates, and chelation of metals involved in the liquid phase, which agrees with results of previous reports.[11,23,24] A complex formation between organic acid anions and metal cations such as Ca, Fe, and Al depends on the number and position of carboxylic (COOH) and hydroxy (OH) functional groups in the organic acids.[25] It is suggested that the position of the hydroxy group in organic acids with respect to the carboxylic group is responsible for the dissociation constant values and the capability of the dissolution. This fact together with the other previously mentioned facts explains the better ability of citric and gluconic acid to dissolve TP.

CONCLUSIONS

It was established that the variation of the factors studied has a different influence on the effective functions: the quantity of the available organic acid in the system (y_1) and the extent of TP solubilization (y_2). On the basis of the results, regression equations of the objective functions were obtained. The mathematical models will allow a better control of the acid processing of TP by the bioconversion with microorganisms producing organic acids, in particular citric, oxalic, and gluconic acid.

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