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Research Article

Modeling and Optimization of Fluoride and Cadmium Trapping in Phosphogypsum Using Design Methodology

The manufacturing of phosphoric acid from natural calcium phosphate generates a solid residue containing 25–30% humidity. This solid residue (phosphogypsum) generates acidic solution ($\text{pH} \approx 2.5$) containing several toxic ionic species, that coat its grains. Fluorides and heavy metals such as cadmium are considered the most harmful species contained in the released solution from phosphogypsum. The purpose of this work is to study the trapping of fluorides and cadmium in phosphogypsum as well as effluent neutralization before its discharge into natural recipient. Therefore, calcium carbonate finely ground was added and fully mixed with wet phosphogypsum. A four factors central composite design was used to model and to optimize the operating parameters that govern the process. The studied factors were temperature, reaction time, mass, and grains size of CaCO_3 . Considered responses were pH, F^- , and Cd^{2+} concentrations in the released solution after reaction with CaCO_3 . The optimum operating conditions were quite efficient to trap, respectively, 99% Cd^{2+} and 97% of F^- with a final pH of 6.66. So an *original*, easy, simple, and cost effective method to trap some toxic species on phosphogypsum through CaCO_3 addition would likely to be integrated in phosphoric acid manufacturing plant.

Keywords: Cadmium; Calcium carbonate; Central composite design; Fluoride; Neutralization; Phosphogypsum

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1 Introduction

Phosphogypsum is a residue of H_3PO_4 manufacturing industry by the wet process. It's a very fine wet powder containing 25–30% moisture. Phosphogypsum valorization has been studied by several researchers that would help to solve an enormous environmental problem [1, 2].

In fact, phosphoric acid production process leads to the rejection of 1.7 t of phosphogypsum per ton of treated phosphate rock, which corresponds to 5 t of phosphogypsum per produced ton of P_2O_5 [3]. This residue ranks in the category of hazardous and toxic wastes [4]. Even after washing, the residue remains impregnated with an acid solution which pH is between 2 and 3 [5]. Phosphogypsum also contains impurities coming from phosphate rock [2, 6–9] such as cadmium and fluoride. Consequently, there are environmental risks associated with phosphogypsum storage methods. Indeed, during its storage the phosphogypsum liberates a part of its impregnation water. This effluent is highly acidic and contains some ionic entities that may affect the environment (soil and ground water).

Therefore it would be very beneficial to develop a procedure that neutralize the solution and prevent toxic entities to come into

contact with the natural environment. Accordingly, the addition of a reactive alkaline solid into wet phosphogypsum was adopted. This choice was dictated by the results of our earlier work related to the interaction of an industrial effluent (solution released by phosphogypsum) with groundwater [10]. This work highlighted particularly the neutralization of the acidic solution and the formation of a precipitate (CaF_2) able to retain heavy metals, especially cadmium. Consequently, it is foreseeable that an alkaline solid would play the same role as the groundwater (slightly alkaline) and leads to the precipitation of calcium fluoride and trapping of some heavy metals. Indeed preliminary tests showed the neutralization of the phosphogypsum impregnation solution and trapping of heavy metals in the solid matrix. This result easily conceivable could be explained by the formation of CaF_2 after the attack of calcium carbonate by the acidic solution and simultaneous retention of heavy metal by the formed product. Thus, further to these events the phosphogypsum released solution would be neutral and free of toxic ionic entities and hence less harmful to the natural environment.

With regard to the above-mentioned observations, the aim of this work was to determine the optimum conditions for trapping toxic entities (fluoride and cadmium) and neutralization of the released solution through CaCO_3 addition.

Hence a four factors central composite design was chosen. The studied factors were temperature, reaction time, CaCO_3 added mass, and finally the grains size of calcium carbonate. The selected responses are pH, concentrations of fluoride and cadmium ($[\text{F}^-]$

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and $[\text{Cd}^{2+}]$). In fact each response depends on several factors as reported in the literature [11–13].

2 Materials and Methods

2.1 Experimental Protocol

A predetermined mass of CaCO_3 finely crushed was added to each sample of wet phosphogypsum. The resulting mixture was kept at a defined constant temperature for a specified period of time.

The experimental protocol is as follows:

- (1) Weight 200 g of phosphogypsum.
- (2) Add the necessary mass of CaCO_3 .
- (3) Mix well the previous reagents for 10 min.
- (4) Immerse the mixture in a water bath at a specified constant temperature and for a preset time.
- (5) Filter the mixture under pressure of 7 bar to retrieve the liquid phase.
- (6) Analyze chemically the filtrate for cadmium and fluoride ions and determine the pH of the liquid phase.

2.2 Analysis Techniques

A pH meter (691-pH Meter, Metrohm), with a combined glass electrode was used to measure the pH (± 0.01). The ion meter (781-pH/Ion Meter, Metrohm) equipped with a crystalline membrane electrode 6.0502.150 was used to determine fluoride ion concentrations and the error is less than 1%. A potentiometer (TITRINO DMS 716 of Metrohm) was used to determine chloride. The sulfate ions were determined by the gravimetric method. Cl^- and SO_4^{2-} ions concentrations were determined with an error ranging from 0.1 to 0.2%. Flame atomic absorption spectrometer (AAS Vario 6) was used for Cd, Ca, Mg, Co, Zn, Al, Fe, and Cr determinations. A flame photometer was used for K and Na determinations. Finally the spectroscopy UV–VIS was used for the determination of phosphate ions, Perkin-Elmer UV–VIS Lambda 20 spectrometer was employed. All the above ions were determined with an error less than 1%. Further more additional method was adopted to analyze Cd^{2+} ions.

3 Results and Discussion

3.1 Properties of Phosphogypsum

The phosphogypsum impregnating solution (moisture 25–30%) was separated from the solid matrix by filtration under 7 bar pressure and then analyzed. The analytical results are listed in Tab. 1.

The composition, of phosphogypsum free solution, shown in Tab. 1 is not a mean composition but it is timely one, since it varies slightly depending on the plant progress. The above values remain within the same order of magnitude of those yearly measured. Table 1 shows without doubt that the solution is highly acidic and contains several chemical entities including heavy metals; thus the toxic character of this solution and its harm to the natural environment are quite noticed (Tunisian standard N.T.106.002: $6.5 < \text{pH} < 8.5$, $\text{F}^- \leq 3.00 \text{ mg L}^{-1}$, $\text{Cd}^{2+} \leq 0.005 \text{ mg L}^{-1}$).

Phosphogypsum has been characterized by X-ray diffraction and examined under a binocular microscope (20 times). Figures 1 and 2 represent the obtained results.

The diffractogram shows essentially synthetic gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) containing fluorapatite traces ($\text{Ca}_5(\text{PO}_4)_3\text{F}$).

Table 1. Composition of phosphogypsum free solution.

Element	Free solution concentrations
pH	2.35
Conductance (mS)	15.170
Density	1.018
Dry residue (g L^{-1})	19.981
Cl^- (g L^{-1})	5.663
F^- (g L^{-1})	0.685
SO_4^{2-} (g L^{-1})	3.723
PO_4^{3-} (g L^{-1})	3.310
K^+ (g L^{-1})	0.147
Na^+ (g L^{-1})	5.551
Ca^{2+} (g L^{-1})	1.643
Mg^{2+} (g L^{-1})	0.49
Cd^{2+} (mg L^{-1})	1.770
Co (mg L^{-1})	0.219
Zn (mg L^{-1})	1.789
Al (mg L^{-1})	0.147
Fe (mg L^{-1})	0.277
Cr (mg L^{-1})	1.048

Figure 2 illustrates the image of a phosphogypsum sample examined under a binocular microscope. This image shows a mass of gypsum containing unattacked apatite grains. This is in agreement with the above X-ray analysis.

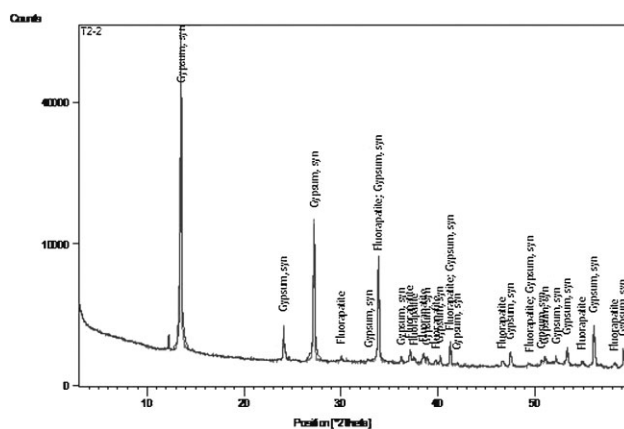


Figure 1. Diffractogram of a phosphogypsum sample.

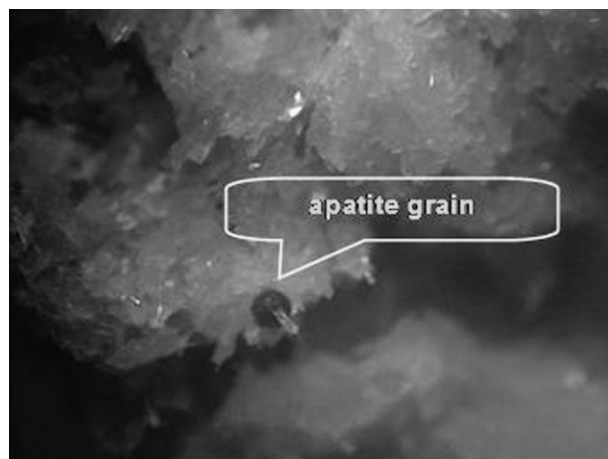


Figure 2. Microscopic image of phosphogypsum (20 times).

3.2 Studied Factors and Experimental Domains

According to a preliminary work, four factors and their fields were adopted in this study. Table 2 illustrates the selected four factors and their fields.

The chosen responses were pH, cadmium and fluoride concentrations, designated by Y_1 (pH), Y_2 (mg L⁻¹), and Y_3 (mg L⁻¹), respectively.

3.3 Experimental Matrix and Models

The purpose of this work is to model and to optimize the selected responses (Y_1 , Y_2 , and Y_3). A central composite matrix is seemed necessary to achieve this goal (Tab. 3). As indicated in this table, the central composite matrix is built on sixteen (four factors: $2^4 = 2^4 = 16$) (from 1 to 16) experiences (levels +1 and -1), eight experiences (from 17 to 24) named star points (levels +2 and -2), and finally eight identical repeated tests performed at the center and named center points (level zero) (from 25 to 32) with the purpose of calculating the experimental variance.

The model equation of second order is given below:

$$Y_i = b_0 + \sum b_j X_j + \sum_{j \neq k} b_{jk} X_j X_k + \sum b_{jj} X_j^2$$

Where Y_i is the chosen response i , b_j the estimation of the significant factor effect j and X_j is its level. Table 4 summarizes the factor effects estimation for the three responses. As it can be seen, the significant factors are: CaCO₃ mass (b_2), Setting time (b_3), two quadratic terms (b_{33} and b_{44}), and an interaction term (b_{23}) to the response pH (Y_1), CaCO₃ mass (b_2), and a quadratic term (b_{22}) to the response cadmium concentration (Y_2) and CaCO₃ mass (b_2), Setting time (b_3), Temperature (b_4), two quadratic terms (b_{11} and b_{22}), and an interaction (b_{34}) to the response fluoride concentration (Y_3).

The resulted models are given by the following equations:

(1) pH:

$$Y_1 = b_0 + b_2 X_2 + b_3 X_3 + b_{33} X_3^2 + b_{44} X_4^2 + b_{23} X_2 X_3$$

$$Y_1 = 5.355 + 0.918 X_2 + 0.294 X_3 + 0.178 X_3^2 + 0.275 X_4^2 + 0.395 X_2 X_3$$

Table 2. Studied factors and experimental domains.

Effect	Factors	-2	-1	0	+1	+2	Increment
X_1	Grain diameter of CaCO ₃ (D_G) (μm)	69	106	143	180	217	37
X_2	CaCO ₃ mass (M_G) (g)	2	4	6	8	10	2
X_3	Reaction time (T_r) (h)	3	10	17	24	31	7
X_4	Temperature (T) (°C)	23	26	29	32	35	3

Table 3. Central composite matrix and results.

No of Exp.	D_G (X_1)	M_G (X_2)	T_r (X_3)	T (X_4)	pH (Y_1)	[Cd] (10) (mg L ⁻¹) (Y_2)	[F] (mg L ⁻¹) (Y_3)
1	-1	-1	-1	-1	4.65	3.60	30.80
2	+1	-1	-1	-1	4.71	3.56	37.20
3	-1	+1	-1	-1	6.39	0.15	19.30
4	+1	+1	-1	-1	6.53	0.21	21.60
5	-1	-1	+1	-1	4.84	3.35	28.60
6	+1	-1	+1	-1	4.56	3.11	33.60
7	-1	+1	+1	-1	7.33	0.13	16.90
8	+1	+1	+1	-1	7.41	0.17	22.60
9	-1	-1	-1	+1	5.36	3.25	32.40
10	+1	-1	-1	+1	5.63	3.57	35.80
11	-1	+1	-1	+1	5.82	0.31	20.70
12	+1	+1	-1	+1	6.46	0.46	23.80
13	-1	-1	+1	+1	4.74	3.54	22.10
14	+1	-1	+1	+1	5.09	2.98	24.10
15	-1	+1	+1	+1	7.95	0.11	14.90
16	+1	+1	+1	+1	7.71	0.13	16.60
17	-2	0	0	0	6.45	0.12	26.50
18	+2	0	0	0	5.22	1.56	33.30
19	0	-2	0	0	3.25	9.29	65.50
20	0	+2	0	0	6.25	1.30	32.10
21	0	0	-2	0	5.15	1.25	17.30
22	0	0	+2	0	6.64	0.16	8.90
23	0	0	0	-2	6.15	2.75	16.90
24	0	0	0	+2	6.42	1.10	11.40
25	0	0	0	0	5.55	0.49	14.10
26	0	0	0	0	5.04	0.68	17.90
27	0	0	0	0	5.21	0.74	20.40
28	0	0	0	0	5.62	1.26	15.60
29	0	0	0	0	4.92	0.35	16.30
30	0	0	0	0	4.87	1.47	19.20
31	0	0	0	0	5.68	0.78	15.10
32	0	0	0	0	5.95	1.16	18.50

Table 4. Factors signification for the three responses pH, [Cd] and [F].

Coefficient	Value	Standard deviation	t-exp	Signification
pH				
b_0	5.355	0.155	34.47	<0.01***
b_1	-0.060	0.090	-0.67	51.3
b_2	0.918	0.090	10.23	<0.01***
b_3	0.294	0.090	3.28	0.442**
b_4	0.120	0.090	1.34	19.9
b_{11}	0.163	0.081	2.01	6.0
b_{22}	-0.108	0.081	-1.34	19.8
b_{33}	0.178	0.081	2.20	4.19*
b_{44}	0.275	0.081	3.41	0.336**
b_{12}	0.014	0.110	0.13	90.2
b_{13}	-0.075	0.110	-0.68	50.4
b_{23}	0.395	0.110	3.60	0.223**
b_{14}	0.064	0.110	0.58	56.9
b_{24}	-0.111	0.110	-1.01	32.5
b_{34}	0.022	0.110	0.20	84.0
[Cd] (mg L⁻¹)				
b_0	0.866	0.189	4.58	0.0266***
b_1	0.109	0.109	1.00	33.1
b_2	-1.720	0.109	-15.76	<0.01***
b_3	-0.159	0.109	-1.45	16.4
b_4	-0.135	0.109	-1.23	23.4
b_{11}	-0.074	0.098	-0.75	46.4
b_{22}	1.040	0.098	10.57	<0.01***
b_{33}	-0.107	0.098	-1.09	29.2
b_{44}	0.197	0.098	2.01	6.1
b_{12}	0.050	0.134	0.37	71.4
b_{13}	-0.077	0.134	-0.58	57.3
b_{23}	0.025	0.134	0.19	85.2
b_{14}	0.007	0.134	0.05	96.1
b_{24}	0.039	0.134	0.29	77.6
b_{34}	-0.004	0.134	-0.03	97.4
[F] (mg L⁻¹)				
b_0	17.138	0.947	18.09	<0.01***
b_1	0.967	0.547	1.77	9.5
b_2	-6.458	0.547	-11.81	<0.01***
b_3	-2.458	0.547	-4.49	0.0320***
b_4	-1.300	0.547	-2.38	2.95*
b_{11}	1.911	0.493	3.88	0.121**
b_{22}	7.886	0.493	15.99	<0.01***
b_{33}	-1.039	0.493	-2.11	5.0
b_{44}	-0.776	0.493	-1.57	13.4
b_{12}	-0.250	0.670	-0.37	71.4
b_{13}	-0.050	0.670	-0.07	94.1
b_{23}	0.837	0.670	1.25	22.8
b_{14}	-0.575	0.670	-0.86	40.3
b_{24}	0.713	0.670	1.06	30.2
b_{34}	-1.737	0.670	-2.59	1.89*

*, **, *** Represent the signification level.

(2) Cadmium concentration:

$$Y_2 = b_0 + b_2X_2 + b_{22}X_2^2$$

$$Y_2 = 0.866 - 1.720X_2 + 1.040X_2^2$$

(3) Fluoride concentration:

$$Y_3 = b_0 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{34}X_3X_4$$

$$Y_3 = 17.138 - 6.458X_2 - 2.458X_3 - 1.300X_4 + 1.911X_1^2 + 7.886X_2^2 - 1.737X_3X_4$$

3.4 Analysis of Residue

Figure 3 reveals the distribution of the calculated versus experimental values for the three responses (Y_1 , Y_2 , and Y_3). Figures 3a–c show, that the points are almost randomly distributed about the line

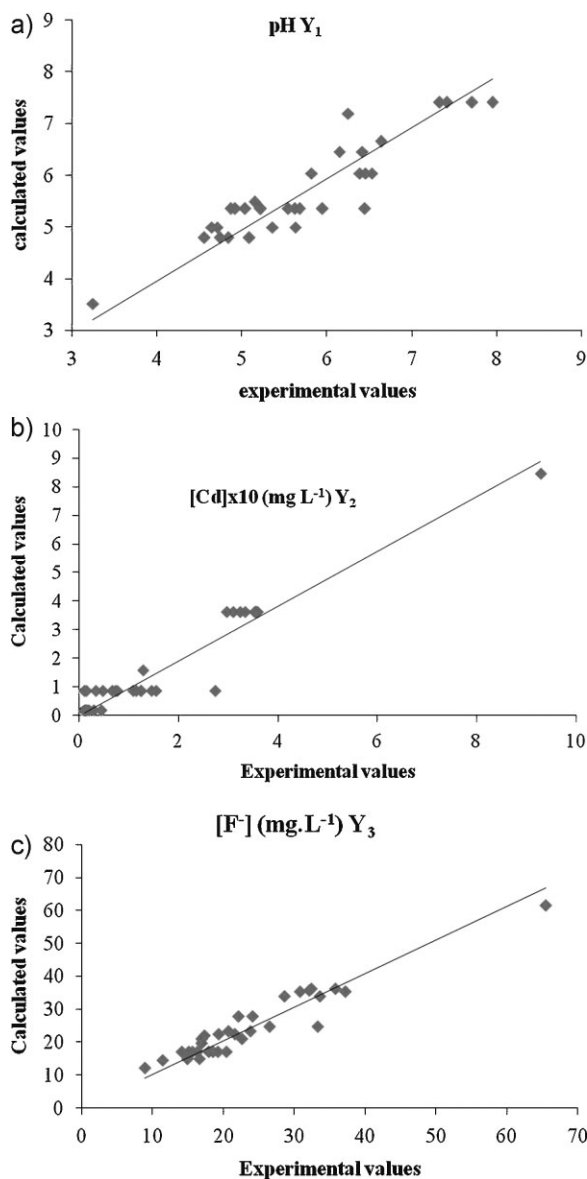


Figure 3. (a) Calculated versus experimental values graph for pH, (b) calculated versus experimental values graph for $[Cd^{2+}]$, and (c) calculated versus experimental values graph for $[F^-]$.

representing exact agreement providing little evidence of lack-of-fit for the three quadratic models. The deviations in the graphs correspond to root mean square errors of 0.409, 0.5049, and 3.299 for the responses Y_1 , Y_2 , and Y_3 , respectively. The maximum value that the standardized residuals take are 1.095 and 1.884 for the responses Y_1 and Y_2 , it means that about 95% of them should fall within ± 2 . However the maximum standardized residuals value of Y_3 response is 5.798 which exceeds the value 2. Hence it is necessary to go through a variance analysis of Y_3 response as it is beneficial to confirm the validity of Y_1 and Y_2 responses.

3.5 Analysis of Variance

Table 5 summarizes the variance analysis of the chosen responses Y_1 , Y_2 , and Y_3 . The main results for Y_1 , Y_2 , and Y_3 are, respectively, 0.211,

Table 5. Variance analysis.

Source of variation	SS	DF	MS	Ratio	Signification
Y₁ pH					
Regression	27.874	5	5.575	28.249	<0.01***
Residual	5.131	26	0.197		
Lack of fit	4.018	19	0.211	1.331	36.700
Pure error	1.113	7	0.159		
Total	33.005	31			
Y₂ (mg L⁻¹)					
Regression	103.455	2	51.728	186.584	<0.01***
Residual	8.040	29	0.277		
Lack of fit	6.963	22	0.317	2.058	16.600
Pure error	1.077	7	0.154		
Total	111.495	31			
Y₃ (mg L⁻¹)					
Regression	3184.885	6	530.814	37.473	<0.01***
Residual	354.130	25	14.165		
Lack of fit	320.351	18	17.797	3.688	4.3*
Pure error	33.779	7	4.826		
Total	3539.015	31			

*, **, *** Signification levels.

SS, sum square; DF, degree of freedom; MS, mean square.

0.317, and 17.797 as lack of fit mean square and 0.159, 0.154, and 4.826 as estimation of experimental variance. Thus, the values of the ratios between the lack of fit mean square and the estimation of experimental variance 1.331 and 2.058 for the responses Y₁ and Y₂ are inferior to tabled $F_{19,7}^{0.05}$ and $F_{22,7}^{0.05}$, respectively. However, the value for the response Y₃ (3.688) is only slightly larger than the tabled $F_{18,7}^{0.05}$. Consequently, it is possible to confirm the validity of the three quadratic elaborated models. In addition, the values of the ratios between the regression mean square and the residual mean square for the three responses Y₁, Y₂, and Y₃ (28.249, 186.584, and 37.473) are superior to the tabled $F_{5,26}^{0.05}$, $F_{2,29}^{0.05}$, and $F_{6,25}^{0.05}$, respectively. Thus, the significant variables, applied to elaborate the three models, have a large significance on their responses.

3.6 The Response Surfaces

The use of the NemrodW software [14] enabled us to obtain the response surfaces and it is possible to superpose the curves of the responses Y₂/Y₁ and Y₃/Y₁ which are shown in Figs. 4a and b. This procedure enables the determination of the optimum conditions in order to guarantee maximum retention of cadmium and fluoride.

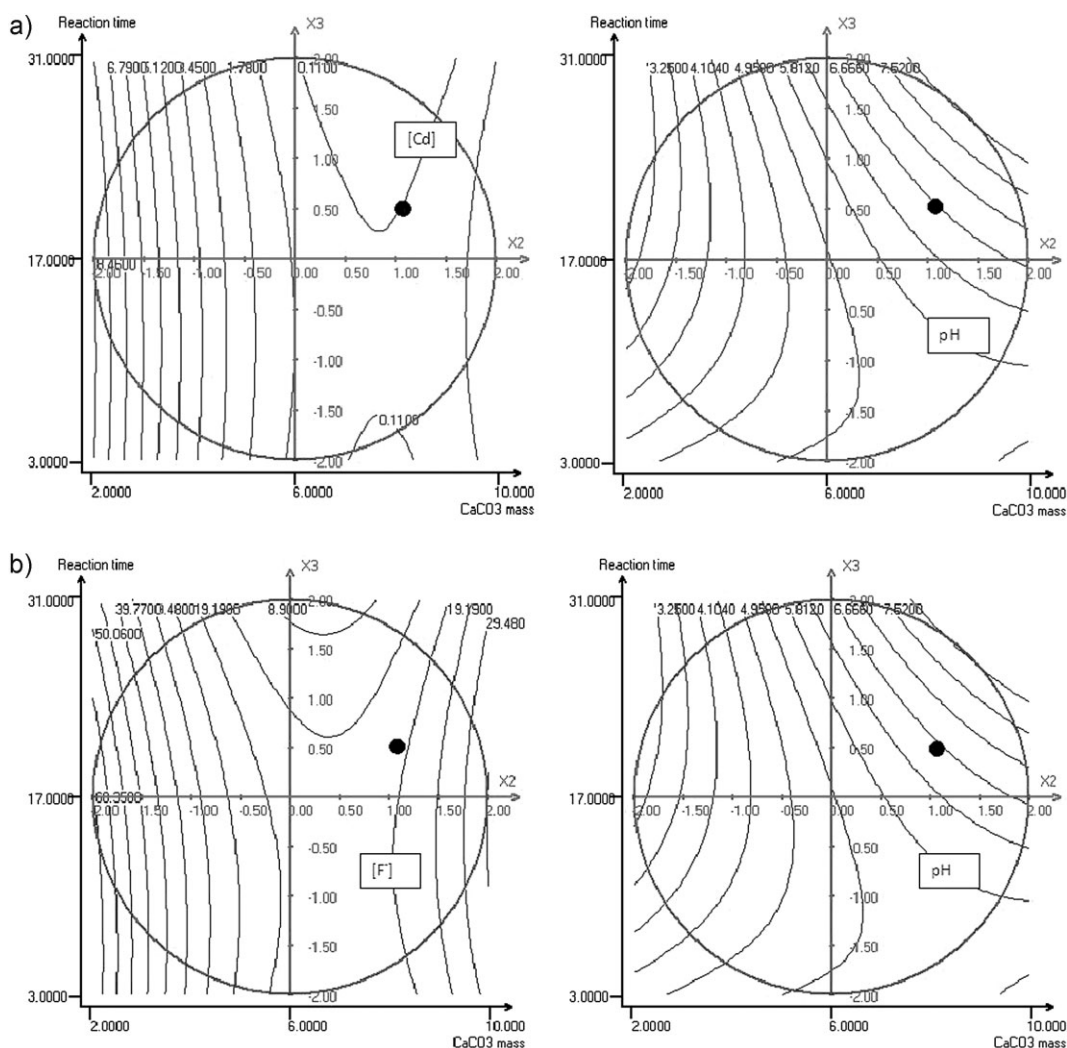
**Figure 4.** Isoresponse curves variation as function of factors grains mass (X₂) and reaction time (X₃): (a) Cadmium-pH and (b) Fluoride-pH.

Table 6. Tested optimal conditions and optimal conditions verification.

(a) Tested optimal conditions			
Effect	Name	Value	
$X_1 = 0$	Particles size (μm)	143	
$X_2 = 1$	CaCO_3 mass (g)	8	
$X_3 = 0.5$	Reaction time (h)	20.5	
$X_4 = 0.33$	Temperature ($^{\circ}\text{C}$)	30	
(b) Optimal conditions verification			
Parameter	Solution 1	Solution 2	Solution 3
pH	6.64	6.60	6.65
$[\text{F}^-]$ (mg L^{-1})	16.68	17.21	16.58
$[\text{Cd}^{2+}]$ (mg L^{-1})	0.021	0.017	0.018

Those conditions are: $X_1 = 0$: particles size = 143 μm ; $X_2 = 1$: CaCO_3 mass = 8 g; $X_3 = 0.5$: setting time = 20.5 h $X_4 = 0.33$: temperature = 30 $^{\circ}\text{C}$. Under the established conditions the resulted responses are pH 6.66, $[\text{Cd}^{2+}] = 0.018 \text{ mg L}^{-1}$, and $[\text{F}^-] = 16.54 \text{ mg L}^{-1}$ which reveals that 98% of cadmium and 97% of fluoride were extracted. Used calcium carbonate (CaCO_3) mass represents 4% of the total mass of treated phosphogypsum which corresponds to 40 kg of calcium carbonate per ton of treated phosphogypsum. In order to confirm the validity of the established three models, the determined optimal conditions were experienced three times on phosphogypsum and the resulted solutions (solutions 1–3) were analyzed. Table 6a exhibits the experimental conditions and Tab. 6b shows the obtained responses.

It is clear that the experimental results fit well with the calculated ones; the established tree models are therefore in good agreement with the experimental performed work.

4 Concluding Remarks

A four factors central composite design was employed in order to model and optimize the chosen responses (pH, cadmium concentration, and fluoride concentration). According to the four factors fields, three valid models were established.

According to these models, the addition of 40 kg of calcium carbonate per ton of phosphogypsum permits under the established conditions (particles size = 143 μm ; CaCO_3 mass = 8 g, setting time = 20.5 h, temperature = 30 $^{\circ}\text{C}$), to neutralize the released solution (pH 6.66 in accordance with TN 106.002) and to reduce the concentrations of cadmium ($[\text{Cd}^{2+}] = 0.018 \text{ mg L}^{-1}$) and fluoride ($[\text{F}^-] = 16.54 \text{ mg L}^{-1}$). The previous values are not compliant to Tunisian norm ($\text{F}^- \leq 3.00 \text{ mg L}^{-1}$, $\text{Cd}^{2+} \leq 0.005 \text{ mg L}^{-1}$) but they correspond to a retention of 98% cadmium and of 97% fluoride. These

results, despite the fact that they are under the permitted limits, they represent a good achievement, given that currently the total effluent goes into the natural environment. However, we believe that the established process can very probably be improved by studying the effect of new reagents.

Finally this work permits to make available an original, easy, simple, and cost effective method to trap some toxic species on phosphogypsum through CaCO_3 addition. This procedure may be used to prevent natural recipient pollution when phosphogypsum is stored. To implement this procedure in industrial practice, it is conceivable to insert a mixing step (wet phosphogypsum + CaCO_3) before discharge and storage of wet phosphogypsum in natural environment.

The authors have declared no conflict of interest.

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