Experimental Design Methodology Applied to Boron Removal from brine by adsorption onto in-situ precipitated magnesium hydroxide

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Abstract: The objective of the present study is to investigate the elimination of boron from brine (saline water), by adsorption using Mg $(OH)_2$ precipitate in-situ as adsorbent. To optimize the experimental condition of boron removal and to evaluate statistically the important significant factors, an experimental methodology design was implemented using 2^3 full factorial design. The selected parameters were temperature (25°C and 70°C), molar ratio (10 and 30), stirring speed (200 and 600rpm) and reaction time (15 min and 60 min), while Y_1 (the % of boron removal) and Y_2 (the % of magnesium precipitate) are chosen as the responses variables. The results were analyzed statistically using the analysis of variance, F-test and the student's t-test to check the significance of the variables effects. The model function equation for boron removal and magnesium precipitate was obtained. The obtained results showed that temperature, molar ratio, stirring speed and time affected boron removal. The optimum operating conditions were found as temperature: 25 °C, molar ratio Mg/B: 30, stirring speed: 600 rpm and time: 15 min. These optimum experimental conditions were used to eliminate 92% of boron initially present in brine in the form of $Mg_2B_2O_5$.

Keywords: Adsorption; Boron removal; Experimental Design; Full Factorial Design; Hydroxide magnesium.

INTRODUCTION

Chotts and sebkhas are an important natural source of salts in industrial and agricultural uses, however, the presence of certain impurities in traces amounts, could constitute a major obstacle to the extraction of compound such as MgO. To remedy this difficulty, pretreatment is necessary before obtaining products with desirable characteristics.

Among these impurities, boron is distinguished. It is present as a boric acid or as a water-soluble borate in mixture with others salts [1]. Boron and boron compounds are widely used in industrial applications [2]. The amount of boron in brine changes from one source to another, however the presence of this element remains constantly undesirable for the implementation of certain extractive processes.

Indeed in the case of the treatment of magnesium brines for the production of magnesium oxide or magnesium metal, boron is adsorbed on the magnesium compounds [**3**], so that almost all of the initial boron is found in the finished product. It is therefore advantageous to purify the brine by eliminating the boron before any extraction operation.

A variety of methods and physic- chemical processes have been developed to remove boron from water. As an example, we cite the use of the selective ion exchange resins to boron [4,5], reverse osmosis [6], precipitation [7, 8], electro-coagulation [9], electrodialysis [10], sorption-membrane filtration [11], and solvent extraction after complexation [12] and adsorption [13,14].

Boron removal by these treatments is not always easy to apply in situ, due to their performance, and their cost. Adsorption is an alternative method in the treatment of waters based on the property of different materials to bind and concentrate the boron from aqueous solutions.

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Table I: Experimental operating parameters

Rf power	1.30 KW
Plasma gas flow rate	15.0 L/min
Auxilary gas flow rate	6 L/min
Nebulizer gas flow rate	0.50 L/min
Sample uptake rate	1.5 mL/min
Argon gas (high purity)	99.99 %
Troch type	High solids Axiel (1.8 mm; quartz)
Nebulizer type	Glass concentric; Cyclonic spraychamber
Replicates	3
Wavelength	249.677 nm

In this study, we take advantage of the strong affinity that magnesium hydroxide has for borate ions, to remove them from the brine. So held account of the above, our objective is to precipitate a sufficient fraction of magnesium ions to remove boron. The various factors influencing the adsorption were studied according to the experimental design methodology using two synthetic solution of boric acid in different concentration 20 and 100 ppm.

Design of experiments is useful for scientific research and industrial studies. It was used to optimize the organization of experimental tests to obtain maximum of information with the minimum of experience and the best possible precision on the responses calculated from a model [15].

MATERIAL AND EXPERIMENTAL PROCEDURE

1. Materials

Chemical reagents used for analysis and the preparation of synthetic solutions were boric acid (Fluka), magnesium chloride hexahydrate Extra Pure (lobachimie), sodium hydroxide (Novachim). The dilution water is ultra pure Milli-Q (C= 0.055 µS.cm^{-1}) was prepared using a Millipore apparatus (Simlicity).

2. Preparation of synthetic solutions

The experiments were effected using two synthetic samples. The first with a high concentration of boron 100 ppm and the second with a low concentration of boron 20 ppm. Boron and magnesium solutions were prepared by dissolving the appropriate amounts of boric acid and magnesium chloride hexahydrate in ultra pure water.

In a thermostatic cell, at temperature T, we introduce 50 mL of the sample under speed agitation V. The selective precipitation of magnesium according to the previously selected molar ratio Mg/B, is carried out by adding a defined volume of sodium hydroxide solution (1M).
The equation for this reaction is as follows:

$$\mathbf{2\,NaOH + Mg^{2+} \leftrightarrow Mg(OH)_2 + 2\,Na^{+}}$$

The sample was equilibrated (adsorption/ precipitation) during a pre-determined time, then the solution was filtred using filter paper (Whatman, 0.45 µm).

3. Measurements

The obtained residues are dried, crushed and identified by X-Ray powder diffractometer (XRD PHILIPS) using Cu Kα radiation (λ Kα = 1.54Å). Also the solid phases were characterized by scanning electron microscope (SEM). The residual magnesium was determined by flame atomic absorption spectrometer (AAS Vario 6). The boron measurement were made using a various (sequential ICP-AES) inductively coupled plasma atomic emission with a glass concentric (cyclonic spraychambre) nebulizer [16]. The operating parameters are mentioned in Table **I**.

4. Statistical design of experiments

Design of experiments methodology was developed at the beginning of the century, in the 1920 [17], as part an agronomic study. They are applicable to all disciplines and in all industries from the time when we research the link between a variable of interest (Y) and variables (X_i) may change the value of Y [17]. The great novelty of this methodology is that it proposes a factorial experiment whose all factors vary simultaneously [18].

The experiments design are used to optimize the organization of experimental tests to obtain the maximum of information with the minimum of experience and the best possible precision on the responses calculated from a model.

The total number of experiments (N) needed to understand all the effects is given by N= a^n=2^n where "a" is the number of levels and "n" is number of a factors. This type of matrix allows to calculate the average effect b_0, the main effects b_i and their interactions 2 to 2, 3 to 3,………, until the interaction between n factors.

5. Calculation

Experimental designs setup and treatments of results were analyzed by NemrodW software [21].

RESULTS AND DISCUSSION

1. Studied Factors and Experimental Matrix

The aim of this study is to identify the influence of the different operating variable on boron adsorption process on magnesium hydroxide. The bibliographic research indicates that the process is strongly influenced by the following parameters: quantity of precipitate magnesium hydroxide, contact time, stirring speed and reaction temperature [8].

To study the influence of selected factors on the measured responses and the possible interactions, we choose to run a full factorial matrix 2^4. The studied variables and their levels are given in Table **II**.

In this study, we choose to follow as variables responses the percentage of boron removal and the precipitate magnesium percentage. They were defined as below:

$$Y_1 = \frac{C_0 - C_f}{C_0} \times 100 \qquad Y_2 = \frac{C_0' - C_f'}{C_0'} \times 100$$

With :

C_0 and C_0' are the initial concentrations respectively in boron and magnesium.

C_f and $C_{f'}$ are the residual concentrations respectively in boron and magnesium.

The total number of experiments (N) required for understanding all effects given by:

$N= 2^n= 2^4=16$ with five experiments at the central (in the middle of interval of each factors). The experimental matrix is present in Table **III**.

The experimental response associated to the full 2^4 factorial designs is represented by a model equation of first order. This equation is given by the following expression [22,23].

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j \qquad (1)$$

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{14}X_1X_4 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b_{1234}X_1X_2X_3X_4 \qquad (2)$$

Y is the experimental response.

b_0 represents the average value of the result.

b_i represents the coefficients of effects.

b_{ij} represents the interaction effect of a two-factor interaction X_iX_j.

Taking account that the interaction effects between three or more factors are negligible, the interaction coefficient is computed [17] according to [21] :

$$b_0 = \frac{\sum \pm Y_i}{N} \qquad b_j = \frac{\sum \pm X_{ji} Y_i}{N} \qquad b_{nj} = \frac{\sum \pm (X_{ni} * X_{ji}) Y_i}{N}$$

To study the influence of selected factors on the measured response and the possible interactions, we executed a full factorial design 2^4. The experiments were carried out using two synthetic samples. The first sample with a high boron concentration 100 mg/L and the second with a low boron concentration 20 mg/L.

2. Study of a solution at 100 ppm of boron

a) Identification of significant factors

To minimize block effect, experiments were carried out at random (randomized) as shown in Table **IV**, which summarizes the experimental plan executed and measured responses. Table **V** summarizes the results of experiences to center that served to determine the experimental error.

To determine the significant factors, we performed the student test. Table **VI** summarizes the estimation of the factors effects for the 2

Table II: Factors and levels used in factorial design

Coded variable	Factors	Unites	levels -1	levels 0	levels +1	Steps
X_1	Temperature (T)	°C	25	47.5	70	22.5
X_2	Molar ratio Mg/B	…….	10	20	30	10
X_3	Stirring speed	tr/min	200	400	600	200
X_4	Reaction time	min	15	37.5	60	22.5

Table III: Experimental matrix

Number of experience	Factors				Responses (%)	
	X1	X2	X3	X4	$Y1_i$	$Y2_i$
1	-	-	-	-	$Y1_1$	$Y2_1$
2	+	-	-	-	$Y1_2$	$Y2_2$
3	-	+	-	-	$Y1_3$	$Y2_3$
4	+	+	-	-	$Y1_4$	$Y2_4$
5	-	-	+	-	$Y1_5$	$Y2_5$
6	+	-	+	-	$Y1_6$	$Y2_6$
7	-	+	+	-	$Y1_7$	$Y2_7$
8	+	+	+	-	$Y1_8$	$Y2_8$
9	-	-	-	+	$Y1_9$	$Y2_9$
10	+	-	-	+	$Y1_{10}$	$Y2_{10}$
11	-	+	-	+	$Y1_{11}$	$Y2_{11}$
12	+	+	-	+	$Y1_{12}$	$Y2_{12}$
13	-	-	+	+	$Y1_{13}$	$Y2_{13}$
14	+	-	+	+	$Y1_{14}$	$Y2_{14}$
15	-	+	+	+	$Y1_{15}$	$Y2_{15}$
16	+	+	+	+	$Y1_{16}$	$Y2_{16}$

responses: percentage of boron removal (Y1) and the precipitate magnesium percentage (Y2).

According to obtained results, the value of the regression coefficient is incorporated in Eq. (2), which takes the following forms:

Regression equation of boron removal (%) is:

$\mathbf{Y_1}$ = 74,888 – 2,078 X_1 + 15,922 X_2 + 1,761 X_3 - 1,362 X_4 +1,528 X_1X_2 + 0,327 X_1X_3 -1,368 X_2X_3 - 3,348 X_1X_4 + 0,644 X_2X_4 - 0,404 $X_1X_2X_3$ + 2,621 $X_1X_2X_4$ + 1,582 $X_1X_3X_4$ - 0,927 $X_1X_2X_3X_4$

Table IV: 2^4 experimental design matrix for the four independent variables

Number of experience	Execution order	Factors				Responses (%)	
		X_1	X_2	X_3	X_4	Y_1	Y_2
1	7	25	10	200	15	53.60	16.7
2	16	70	10	200	15	61.88	24.63
3	3	25	30	200	15	90.83	37.32
4	15	70	30	200	15	91.87	35.11
5	6	25	10	600	15	63.62	19.35
6	2	70	10	600	15	64.79	12.15
7	11	25	30	600	15	92.65	37.95
8	1	70	30	600	15	90.76	36.37
9	10	25	10	200	60	65.76	19.35
10	14	70	10	200	60	40.13	25.95
11	4	25	30	200	60	91.94	44.57
12	12	70	30	200	60	88.23	21.00
13	13	25	10	600	60	67.31	19.20
14	5	70	10	600	60	54.64	22.00
15	8	25	30	600	60	90.80	42.36
16	9	70	30	600	60	89.40	24.40

Table V: Experiences used to calculate the experimental error.

Number of experience	Factors				Responses (%)	
	X_1	X_2	X_3	X_4	Y_1	Y_2
17	47.5	20	400	37.5	74.26	28.95
18	47.5	20	400	37.5	74.33	26.44
19	47.5	20	400	37.5	73.77	27.07
20	47.5	20	400	37.5	74.54	27.61
21	47.5	20	400	37.5	73.42	26.96
22	47.5	20	400	37.5	74.80	27.88

Regression equation of magnesium precipitate (%) is:

$\mathbf{Y_2} = 27{,}378 - 1{,}867\ X_1 + 7{,}507\ X_2 - 1{,}011\ X_3 - 3{,}088\ X_1 X_2 - 0{,}771\ X_1 X_3 + 0{,}686\ X_2 X_3 - 2{,}194\ X_1 X_4 - 1{,}733\ X_2 X_4 + 0{,}692\ X_3 X_4 + 1{,}551\ X_1 X_2 X_3 - 3{,}233\ X_1 X_2 X_4 + 1{,}042\ X_1 X_3 X_4$

Those results showed that the molar ratio (X_2) has the highest effect. The effect of X_1 is positive, so it appeared that percentage of boron removal (Y_1) increased when X_2 increased. Similar effect was observed with the stirring speed (X_3), it have a positive effect but lower than X_2. The temperature (X_1) and reaction time have a negative effect. The least effect on boron removal was supplied by reaction time (X_4). It was concluded that the significant factors on the first response Y_1 are the temperature (X_1), molar ratio Mg/B (X_2), the

Table VI: Factors signification for the two responses Y_1 and Y_2

Coefficient	**Y_1**				**Y_2**			
	Value	**SD**	**t.exp**	**P**	**Value**	**SD**	**t.exp**	**P**
b_0	*74.888*	*0.127*	*590.12*	*<0.01****	*27.378*	*0.220*	*124.4*	*<0.01****
b_1	*-2.078*	*0.127*	*-16.38*	*<0.01****	*-1.867*	*0.220*	*-8.48*	*0.0375****
b_2	*15.922*	*0.127*	*125.47*	*<0.01****	*7.507*	*0.220*	*34.09*	*<0.01****
b_3	*1.761*	*0.127*	*13.87*	*<0.01****	*-1.011*	*0.220*	*-4.59*	*0.589***
b_4	*-1.362*	*0.127*	*-10.73*	*0.0122****	*-0.069*	*0.220*	*-0.32*	*76.5*
b_{12}	*1.528*	*0.127*	*12.04*	*<0.01****	*-3.088*	*0.220*	*14.02*	*<0.01****
b_{13}	*0.327*	*0.127*	*2.58*	*4.97**	*-0.771*	*0.220*	*-3.50*	*1.73**
b_{23}	*-1.863*	*0.127*	*-14.68*	*<0.01****	*0.686*	*0.220*	*3.11*	*2.64**
b14	*-3.348*	*0.127*	*-26.38*	*<0.01****	*-2.194*	*0.220*	*-9.97*	*0.0174****
b24	*0.644*	*0.127*	*5.08*	*0.384***	*-1.733*	*0.220*	*-7.87*	*0.0532***
b34	*0.251*	*0.127*	*1.97*	*10.5*	*0.692*	*0.220*	*3.14*	*2.56**
b_{123}	*-0.404*	*0.127*	*-3.19*	*2.44**	*1.551*	*0.220*	*7.04*	*0.0892****
b_{124}	*2.621*	*0.127*	*20.65*	*<0.01****	*-3.233*	*0.220*	*14.68*	*<0.01****
b_{134}	*1.582*	*0.127*	*12.47*	*<0.01****	*1.042*	*0.220*	*4.73*	*0.519****
b_{234}	*-0.141*	*0.127*	*-1.11*	*31.8*	*-0.069*	*0.220*	*-0.32*	*76.5*
b_{1234}	*-0.927*	*0.127*	*-7.30*	*0.0753****	*-0.419*	*0.220*	*-1.90*	*11.5*

* Significant at the confidence level 95%. ** Significant at the confidence level 99%. *** Significant at the confidence level 99.9%.

stirring speed (X_3) and the retention time (X_4). Also, the interactions among X_1-X_2, X_1-X_2-X_4 and X_1-X_3-X_4, are significant and have a positive effect on boron removal. On the other hand, the interactions between X_2-X_3, X_1-X_4 and X_1-X_2-X_3-X_4 are significant and have negative effect. This is confirmed by graphical representation which consists to symbolize all the effects studied on a bar graph as shown in (figure 1: (a), (b)) and identify the significant interactions based on student test for an error risk α=5%.

For the second response Y_2, we note that the temperature and the stirring speed have a negative effect, indicating that the precipitate magnesium amount decrease as the factors X_1 and X_2 changed from its first level to its second level. It was concluded that temperature is the first important factor with a positive effect. The time has a negative effect but is not significant, in fact the coefficient associated has a low negative value (-0.07). The interaction between temperature, stirring speed and time was an important factor affecting magnesium precipitation. The interaction between Molar ration, stirring speed and time was the least important for Y_2.

b) Analysis of residue

Figure 2 shows the distribution of the calculated value versus the experimental value for the two responses. Point are practically aligned suggesting a normal distribution, providing a good agreement between the experimental value and those calculated using the model.

c) Analysis of variance

To further validate this model, an analysis of variance was carried out. Table **VII** summarizes the results of the analysis of variance based on the determination of experimental error by applying new experiments as shown in Table **VII**. These tests were used to estimate the sum of squared deviations, pure error for the measured response.

The obtained results showed that the values of the ratios between the regression mean square and the residual mean square for the two responses Y_1 and Y_2 (1203.7979 and 129.0957) were superior to the tabled $\mathbf{F^{0.05}_{15,6}}$ (same F value [3.84; 4] for the two response). Thus, the significant variables, applied to elaborate the two models, have significant effect on their responses [24, 25]. Therefore, it is possible to confirm the validity of the two elaborated models.

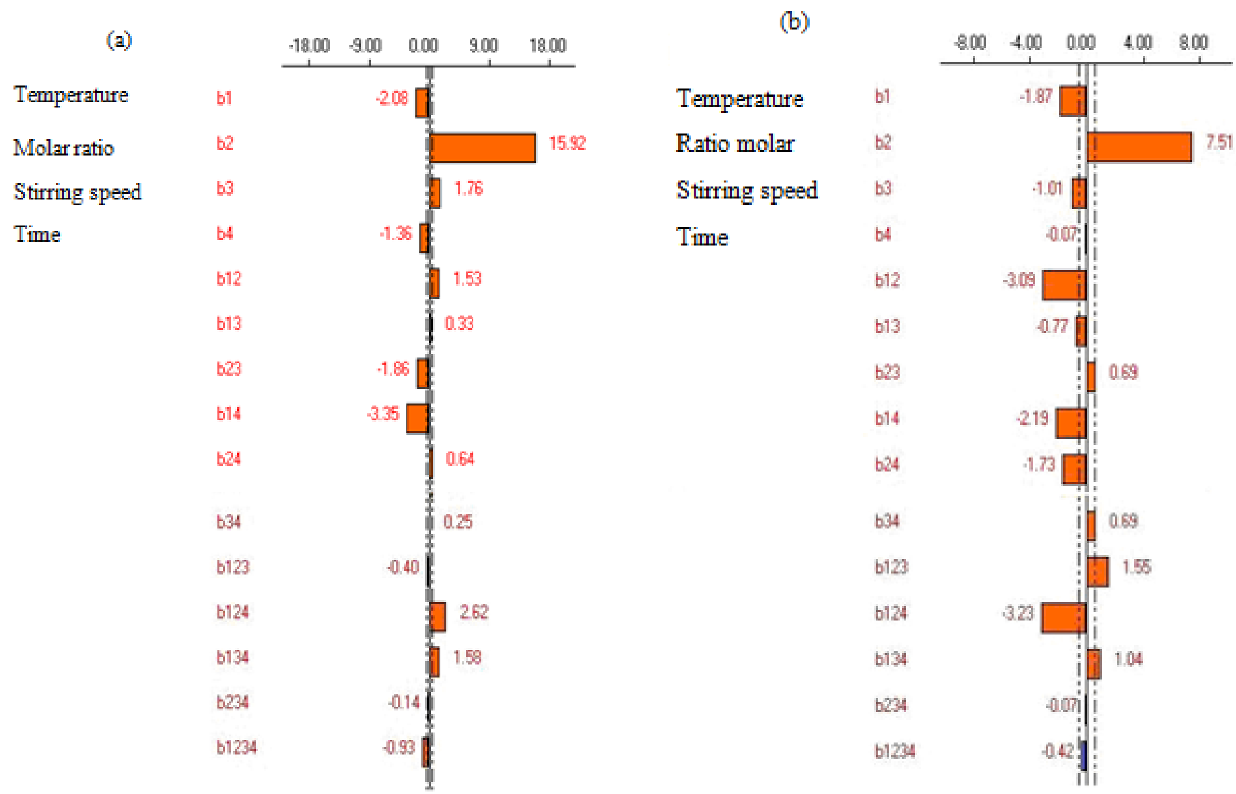

Figure1:Graphic study of effects based on Student test for an error of 5% of the response: (a) for Y_1, (b) for Y_2

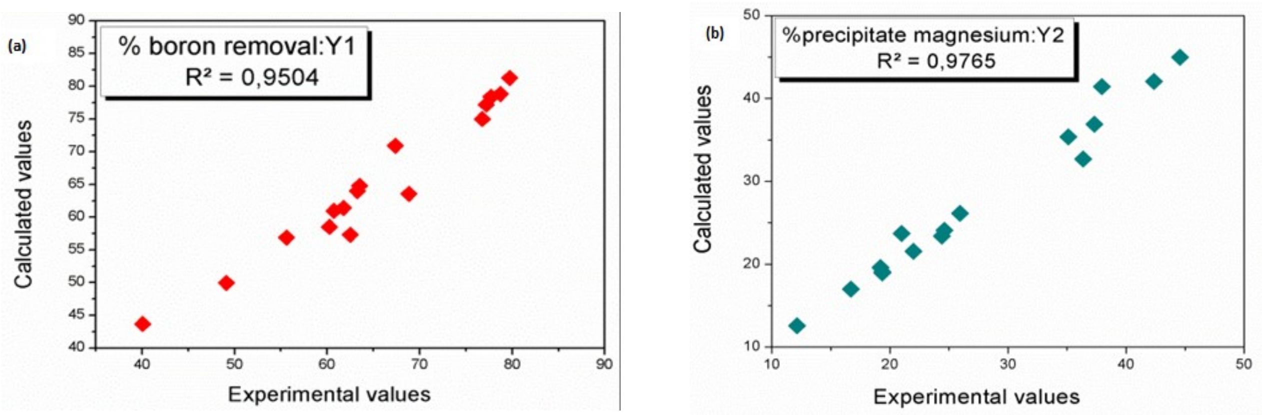

Figure 2: Calculated versus experimental values graph (a) for % boron removal (b) for % precipitate magnesium.

3. Study of a solution at 20 ppm of boron

In this part we carried out the same experiences as before except that boron concen-tration of the solution to be treated is 20 ppm.

a) Identification of significant factors

The experimental design, obtained responses Y1 and Y2 and experiences allowing the calculation of experimental error are listed in Tables **VIII**, **IX**.

Table **IX** summarizes the results of the test at the center. These experiments were performed to calculate the experimental error.

The values of regression coefficient determined for the two responses, the percentage of boron removal (Y_1) and the precipitate magnesium percentage (Y_2) are given in Table **X**.

The values of these were incorporated in Eq. (2) can be shown as:

$\mathbf{Y_1} = 65{,}167 - 4{,}731\ X_1 + 8{,}478\ X_2 - 2{,}688\ X_4 - 1{,}679\ X_1X_3 - 2{,}451\ X_1X_4 + 1{,}459\ X_2X_3X_4$

$\mathbf{Y_2} = 5{,}348 - 0{,}616\ X_1 + 1{,}536\ X_2 - 0{,}209\ X_4 - 0{,}261\ X_1X_2 - 0{,}479\ X_1X_3 - 0{,}183\ X_2X_3 - 0{,}183\ X_1X_4 + 0{,}188\ X_1X_3X_4$

The effects and interactions of the studied factors are represented in **Figure 3.**

From the above figure we can estimate the effect of individual factors and interactional effects. As can be seen from figure 3(a), molar ratio is the first important factor with a positive effect. Temperature and time have a negative effect on the boron removal. The parameter of temperature is the second important factor. Stirring speed has a negative effect but is not significant. Also all the interaction between the factors are not significant and have a negative small values except the interaction among temperature-stirring speed, temperature-time and molar ration- stirring speed-time.

Table VII: The analysis of variance for the first response Y1 and Y2

Source of variation	SS	DF	MS	Ratio	P
			% boron removal Y1		
Regression	4652.69	15	310.179	1203.7979	<0.01***
Residual	1.28833	5	0.257667		
Total	4653.97	20			
			% precipitate magnesium		
Regression	1502.18	15	100.145	129.0957	<0.01***
Residual	3.87873	5	0.775747		
Total	1506.06	20			

*** Significant at the confidence level 99.9%.

Table VIII: 2^4 experimental design matrix for the four independent variables

Number of experience	Execution order	Factors X1	X2	X3	X4	Responses (%) Y_1	Y_2
1	15	25	10	200	15	60.25	3.35
2	3	70	10	200	15	62.49	4.08
3	2	25	30	200	15	77.72	7.42
4	14	70	30	200	15	77.21	7.63
5	12	25	10	600	15	63.50	5.02
6	9	70	10	600	15	55.60	3.50
7	5	25	30	600	15	78.71	7.87
8	10	70	30	600	15	67.36	5.29
9	16	25	10	200	60	60.73	3.76
10	1	70	10	200	60	49.11	3.18
11	4	25	30	200	60	76.77	7.26
12	7	70	30	200	60	63.25	5.81
13	6	25	10	600	60	61.77	4.54
14	8	70	10	600	60	40.06	3.07
15	13	25	30	600	60	79.73	8.19
16	11	70	30	600	60	68.84	5.30

Table IX: Experiences having served for calculating the experimental error.

Number of experience	Factors X1	X2	X3	X4	Responses (%) Y_1	Y_2
17	47.5	20	400	37.5	68.84	5.44
18	47.5	20	400	37.5	64.01	5.17
19	47.5	20	400	37.5	64.84	5.23
20	47.5	20	400	37.5	66.42	5.83
21	47.5	20	400	37.5	66.82	5.67
22	47.5	20	400	37.5	67.65	5.62

Table X: Factors signification for the two responses Y_1 and Y_2

Coefficient	**Y_1**				**Y_2**			
	Value	**SD**	**t.exp**	**P**	**Value**	**SD**	**t.exp**	**P**
b_0	65.167	0.445	146.48	<0.01**	5.348	0.065	82.36	<0.01***
b_1	-4.731	0.445	-10.63	0.0127**	-0.616	0.065	-9.48	0.0221***
b_2	8.478	0.445	19.06	<0.01**	1.536	0.065	23.65	<0.01***
b_3	-0.899	0.445	-2.02	9.9	0.037	0.065	0.57	59.5
b_4	-2.688	0.445	-6.04	0.179**	-0.209	0.065	-3.22	2.34*
b_{12}	0.143	0.445	0.32	76.1	-0.261	0.065	-4.01	1.02*
b_{13}	-1.679	0.445	-3.77	1.30*	-0.479	0.065	-7.38	0.0717*
b_{23}	0.557	0.445	1.25	26.6	-0.183	0.065	-2.82	3.71*
b14	-2.541	0.445	-5.71	0.230**	-0.183	0.065	-2.82	3.71*
b24	1.083	0.445	2.43	5.9	-0.034	0.065	-0.53	61.9
b34	0.913	0.445	2.05	9.5	0.099	0.065	1.53	18.6
b_{123}	0.849	0.445	1.91	11.4	-0.087	0.065	-1.34	23.9
b_{124}	0.918	0.445	2.06	9.4	-0.026	0.065	-0.39	70.9
b_{134}	0.693	0.445	1.56	18	0.188	0.065	2.90	3.39*
b_{234}	1.459	0.445	3.28	2.19*	0.152	0.065	2.34	6.6
b_{1234}	0.687	0.445	1.54	18.3	0.018	0.065	0.28	79.1

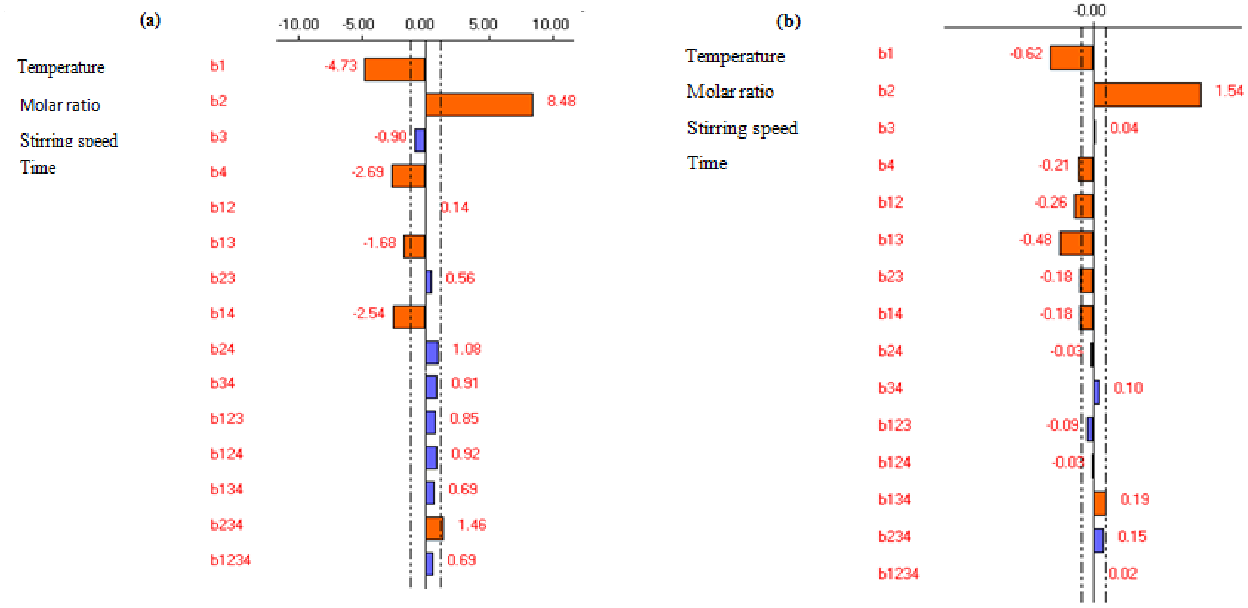

Figure 3: Graphic study of effects based on student test for an error risk of 5%
a: response Y_1, b: response Y_2

b) Analysis of residue

The obtained results for the two answers are outlined on the following figure.

These figure show that the points are distributed throughout a linear right which explains a good concordance between the calculated value and those experimental. The validity of the model can be proven by the analysis of variance.

c) Analysis of variance

To confirm the validity of Y_1 and Y_2 we realized the analysis of variance.

Table **XI** regroups the results of the variance analysis based on the determination of the experimental error. These tests allowed the estimation of the sum of square, the pure error for the measured responses. The obtained results show that the regression mean square and the residual mean square for the two responses (39.9334 and 50.9659) are superior to $\mathbf{F_{15,6}^{0.05}}$ (same F value [3.84; 4] for the two responses). Thus the significant variables used to elaborate the two models, have a large significant effect on their responses [24, 25]. Therefore the models can be considered valid.

4. Discussion

Examining the results reported in Table IV (solution 100 ppm), we notice that the boron removal efficiencies (Y_1) and those of magnesium

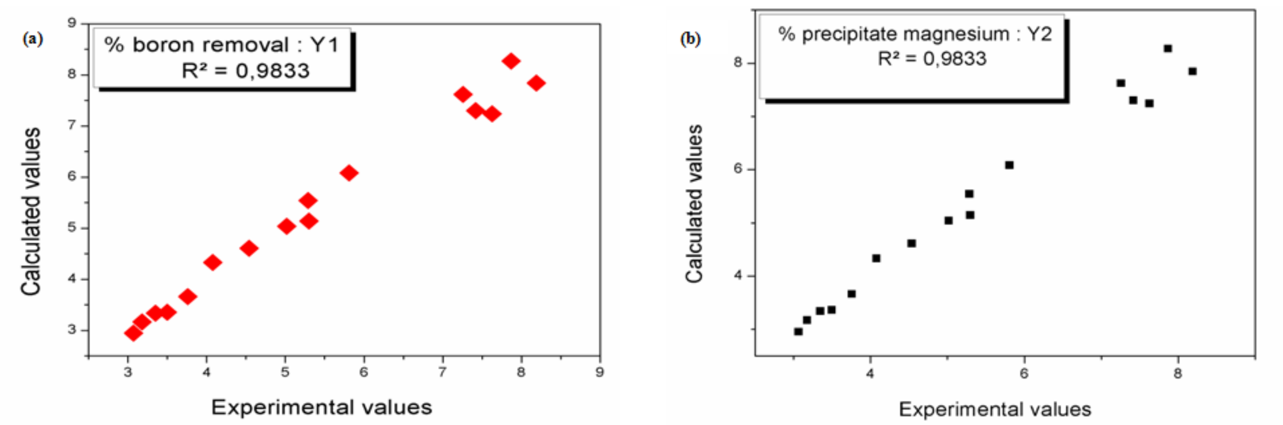

Figure 4: Calculated versus experimental values graph (a) for % boron removal (b) % precipitate magnesium

Table XI: Analysis of variance Y1 and Y2

Source of variation	SS	DF	MS	Ratio	P
		% boron removal Y1			
Regression	1896.82	15	126.454	39.9334	0.035***
Residual	15.8332	5	3.16664		
Total	1912.65	20			
		% precipitate magnesium			
Regression	51.6028	15	3.4402	50.9659	0.0192***
Residual	0.3373	5	0.0675		
Total	51.9402	20			

*** Significant at the confidence level 99.9%.

precipitation vary respectively in the range [40.13 to 92.65 %] and [12.15 to 44.57 %]. However, in paragraph 3 (solution 20 ppm), the variation of Y_1 and Y_2 are less important. They are respectively [40.06 to 79.73%] and for Y_1 [3.07 to 8.19%] for Y_2.

These observations can be explained by the fact that the adsorption phenomena are favored when the solute concentration is elevated [26]. Therefore, passing from a boron solution of 100 ppm to 20 ppm, we noted lower removal efficiencies.

Examination of the coefficients values shows that the boron removal yield is strongly depends on the molar ration Mg/B (X_2). Indeed the maximum values of Y_1 is attained for the level (+1) of factor X_2.

It is mentioned that the temperature is an influencing factor for Y_1. The best yields are reached when X_1 is at level -1. To explain this result, we can say that the constant of dissociation of the boric acid depends on the temperature; it is governed by the following equation:

$$\text{Log } K = A/T + B + CT \text{ (avec } A = -2193\text{ ; } B = 3{,}093\text{ ; } C = -1{,}650 \times 10^{-2}) \text{ [27]}$$

The elimination yields are the highest for factor X_4 at level -1. Thus if the treatment period becomes long and under the stirring effect, it is possible to release the adsorbed boron. We can reduce these phenomena by leaving the solution to stand after stirring to allow the interaction between the solution and the precipitate, or by adding an additive such as H_3PO_4 [7].

5. Optimization

By regarding the values and the signs of the significant effects (factors and interactions effects), we concluded that maximization of the removal of boron from brine is reached for experience number 7 in the two cases. To make sure of this result, experience N7 synthetic sample) was repeated several times. The removal yield remained almost constant (Y_1=92%). The optimal conditions are summarized in Table **XII**.

The treatment of the brine of Sbekha El Maleh in these operating conditions can make possible the elimination of 92% of boron initially present. The XRD diffractograms of the solids obtained from the natural brine and the synthetic solution are schematized on the figure 5 (a and b).

The XRD diffractograms reveal that boron was retained by Mg $(OH)_2$ for the two studied solutions. In the case of synthetic solution, it was retained mainly in form of $Mg_2B_2O_5$ cited in the literature for calcium adsorption which presents the same behavior as magnesium according to the following mechanism [7].

For the solid obtained from the natural brine, it also contains the MgB_2O_5 but it consists essentially of $Na_2(B_4O_6(OH)_2)$. This is probably due to the existence of sodium in the brine (NaCl saturated solution).

Table XII: Optimal conditions

Variable	Coded Value	Factor
X_1	25 °C	temperature
X_2	30	Ratio Mg/B
X_3	600 tr/min	stirring speed (tr/min)
X_4	15 min	Reaction time (min)

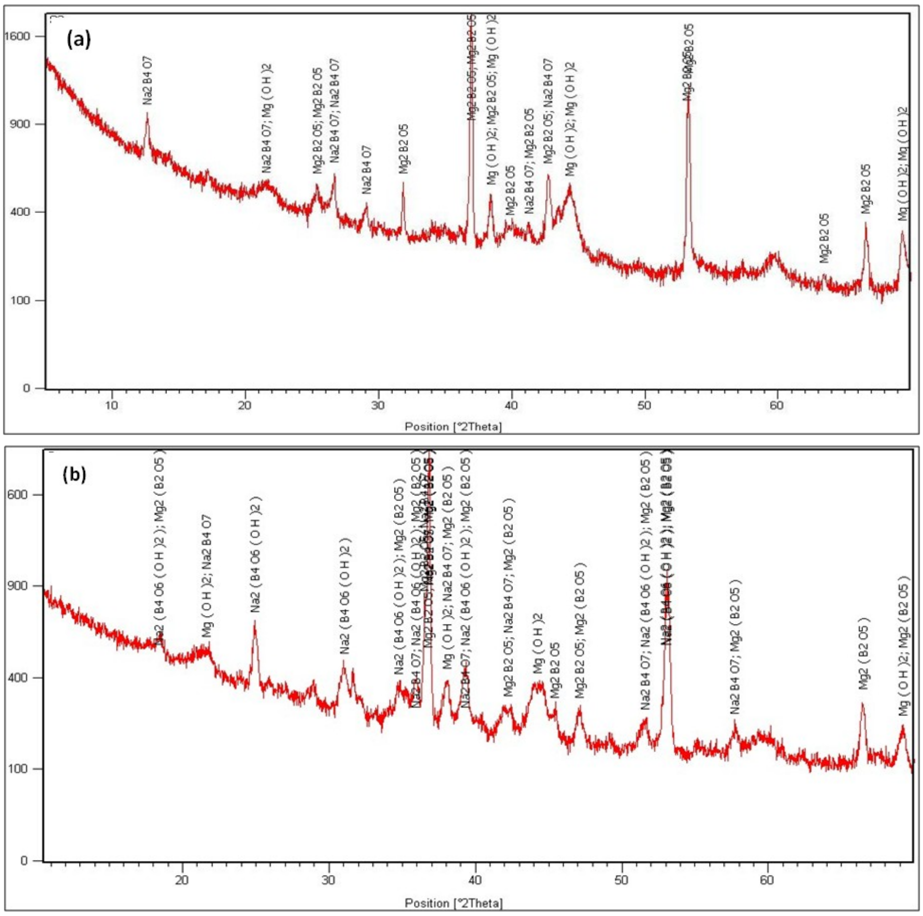

Figure 5: X-ray diffraction diagram of obtained solid. (a) the synthetic solution, (b) natural brine.

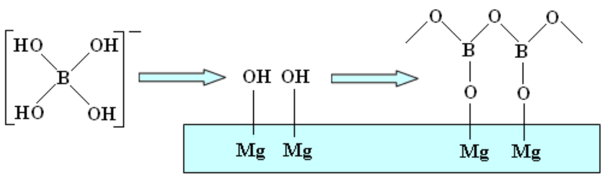

Figure 6: Schematic mechanism on Mg $(OH)_2$ surface [7].

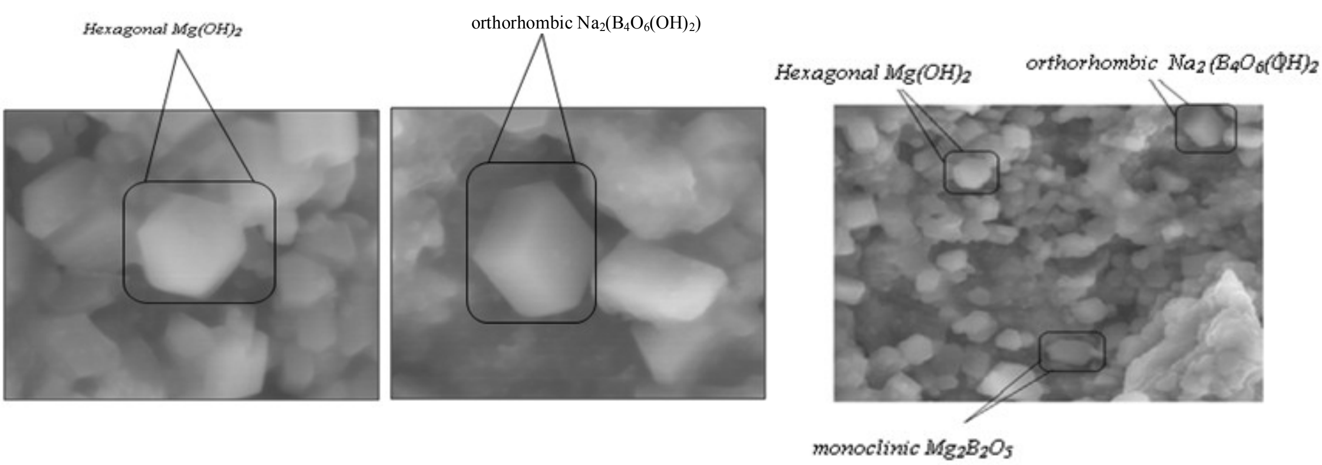

Figure 7: SEM analysis of the obtained precipitate.

The SEM analysis of this solid illustrated in Figure 7, confirms these results by the coexistence of hexagonal crystals corresponding to $Mg(OH)_2$, others with parallelepiped geometry corresponding to $Na_2(B_4O_6(OH)_2)$ of orthorhombic structure and crystals of different geometry may be due to MgB_2O_5 monoclinic structure.

CONCLUSIONS

The application of the adsorption technology of boron on $Mg(OH)_2$ allowed 92 % of elimination of the boron initially present in the brine. This procedure was evaluated using the methodology of experiments design. Indeed, a full factorial design 2^4 was used to model two responses (Y_1: percentage of boron removal, Y_2 percentage of precipitate magnesium).

The obtained results showed that there is an agreement between the experimental values and those calculated from the model developed which confirms its validity. The optimal conditions are temperature (X_1): 25 °C, ratio Mg/B (X_2): 30, stirring speed (X_3): 600 rpm and Reaction time (X_4): 15 min. Finally the optimal operating conditions were applied to treat the natural brine (Sebkha el Maleh de Zarzis).

We succeeded to eliminate the boron present in form of borate of magnesium (Suanite: $Mg_2B_2O_5$). It is a rare boron compound which is used for the production of borax. This result was confirmed by XRD and SEM analysis.

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