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### RESEARCH ARTICLE

#### OBTAINING THE PROTOCOL OF ELIMINATION OF CARBONATES FROM MORROCAN OIL SHALE USING PLACKETT-BURMAN DESIGN

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#### Abstract

This work aimed to implement a screening experiment, to study the effects of different processing and formulation factors on the elimination of carbonates from Moroccan oil shale employing Plackett–Burman screening design. Different factors were proposed for study, such as temperature (°C), concentration (mol/l), ratio (s/l), processing time (h), mean particle size (mm), type of acid (CH<sub>3</sub>COOH, HCl), origin of row material (Tarfaya, Timahdit) and agitation (Yes, No). The quantity of carbonates eliminated was chosen as a response. The results revealed that concentration, ratio, processing time, mean particle size, type of acid and the origin of row material (Tarfaya, Timahdit), showed a significant effect on the quantity of carbonates eliminated, while the temperature and agitation had no effect. The predicted values were in agreement with the experimental values with a coefficient of determination (R<sup>2</sup>) of 0.99. The model has been validated by experiments subsequent to optimized conditions.

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#### Introduction:-

The oil shale is a complex mixture of organic and inorganic components (Qian et al., 2006) and the major mineral constituents in these rocks are: dolomite, calcite, quartz, and feldspars (Zhan et al., 2018; Wang et al., 2018; Chang et al., 2018). According to Caineng Zou (Zou, 2017), Morocco is ranked 7th after the USA, China, Russia, the Democratic Republic of Congo, Brazil and Italy with geologic resources of oil-shale oil total 82\*108t. The largest deposits are divided into several zones, the most important of these are located at Tarfaya (in the south-westernmost part of Morocco) and Timahdit (in the Middle AtlasMountains) (Aboulkas and EL Harfi, 2009; Ichcho et al., 2005).

Oil shale represents a significant potential resource, it is an interesting reserve in energy and their distribution in the world is more homogeneous than oil or gas natural. It is a real source of hydrocarbons, its interest lies in its content of kerogens, capable of turning into oil by increasing temperature and pressure (Qian et al., 2006) during its burial during geological time. Those benefits encourage Moroccan decision-makers to take more interest in its industrial exploitation but the presence of a mineral matrix intimately linked to the organic matters makes its exploitation not easy. This requires a concentration of organic matter by the elimination of carbonates which represent the majority of the raw material.

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Several studies showed that treatment using hydrochloric acid (HCl) have been successfully used to remove carbonates (Aljariri et al., 2019; Amer et al., 2014) and we will also use acetic acid (CH<sub>3</sub>COOH) to make a comparison between them. Among the various groups of designs, the Plackett–Burman designs can be used in screening studies for the detection of influential factors on the experimental response (Abbasi and Habibi, 2016; Garba et al., 2015; Rahimdokht et al., 2016). The objective of the present work was to screening the variables that have an influence on the amount of carbonates removed from oil shale using the Plackett–Burman design (Satya and Hara, 2018; Karlapudiet al., 2018). The eight factors studied are the acid type, the temperature, the concentration, the ratio (l/s), the mean particle size (mm), the processing time, the agitation and the origin of row material.

## Material and Methods:-

### Materials:-

The oil shale used in this work was collected from the R1 layer of Tarfaya and from Y layer of Timahdit, taken from South of Morocco. The shale was grinded (approximately between 0.5 and 1 mm in diameter). The organic matter of the oil shale was chemically linked to the mineral matter essentially formed by calcite, dolomite, silicate and clays. To free the rock from carbonate by dissolution in acids was carried out using HCl and CH<sub>3</sub>COOH. The composition of the 2 samples are given in table 1, it consists essentially of inorganic material with more than 80% in weight (Khouya et al., 2005; Attaoui and Belkbir, 1992).

**Table 1:-** Mineralogical composition of Timahdit and Tarfaya oil shale.

Rock type	Carbonates	Clays	Silicate	Organic matter
Tarfaya (layer R1)	67.2%	10%	6.5%	15.9%
Timahdit (layer Y)	37.8%	24%	19.1%	17.7%

### Methods:-

#### Decarbonatation:

Decarbonated oil shale was obtained by dissolution of carbonates using two different acids: hydrochloric acid (H) and acetic acid (A). The choice of acid is based on several tests performed in our laboratory and also according to previous studies. To optimize the decarbonatation conditions, various experiments were performed using different temperatures (20-50 °C), different concentrations (1-3 mol/l), ratios (L/S), mean particle size (0.5-1 mm), different processing times (4-24 h), agitation and origin of row material (R1-Y). 10 g of powdered rock (R1-Y) (mean particle size between 0.5 and 1mm) were prepared respecting the matrix of experiments in Table 3. After filtration, the solid residues were washed carefully with distilled water, dried at 70 °C and stocked in sealed plastic bags for future use. The used equation to calculate the amount of carbonates eliminated is given as follows.

$$Q_m = \frac{m_i - m_f}{m_i}$$

where,  $Q_m$  is the maximum quantity of carbonates eliminated,  $m_i$  is the initial mass of oil shale used and  $m_f$  is the final mass of oil shale obtained.

#### Plackett–Burman Design:

The Plackett Burman Design (PBD) is an efficient screening method to identify the important factors among large number of factors that influences a process. PBD was used to select the significant factors out of eight factors considered in this study that influences the quantity of carbonates removed. For mathematical modeling, the following first-order polynomial model was used:

$$Y = \beta_0 + \sum \beta_i X_i$$

where, Y is the predicted response,  $\beta_0$  is the model intercept and  $\beta_i$  is the linear coefficient and  $X_i$  is the level of the independent variable.

Eight factors (5 continuous variables and 3 independent variables): temperature (°C) (A), concentration (mol/l) (B), ratio (s/l) (C), mean particle size (mm) (D), processing time (h) (E), origin of row material (F), type of acid (G), Agitation (H), has been studied to identify the significant decarbonatation factors of Tarfaya and Timahdit oil shales from morocco and the response (Y) is the amount of carbonates eliminated.

#### Statistical and data analysis:

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). Analysis includes Fisher test (F-test), its associated probability P (F) and the coefficient of determination ( $R^2$ ) which

measure the goodness of fit of the regression model (Mohammadzadeh et al., 2016; Rhazi et al., 2015). JMP 7 software was used for designing experiments as well as for regression analysis of the experimental data obtained (Dayana Priyadarshini and Bakthavatsalam, 2016).

## Results and Discussion:-

### Matric of experience:

In this study, a 12-trial Plackett-Burman Design (PBD) was used to evaluate the eight factors. Each variable was evaluated at two levels: -1 for the low level and +1 for the high level. Table 2 represents the eight factors tested in Plackett-Burman Design and their levels. The experimental design of PBD (factors and tested range) is shown in Table 3.

**Table 2:-** Levels of the factors tested in Plackett-Burman Design.

Factors	Experimental value	
	Low (-1)	High (+1)
Temperature (°C)	20	50
Concentration (mol/l)	1	3
Ratio (s/l)	5	20
Mean particle size (mm)	0.5	1
Processing time (h)	4	24
Origin of row material	R	Y
Type of acid	H	A
Agitation	YES	NO

**Table 3:-** Plackett–Burman Design of factors (in coded levels) with the maximum amount of carbonates removed as response.

Run order	A	B	C	D	E	F	G	H	Q <sub>m</sub>
1	+	-	-	-	+	-	+	+	28
2	+	+	+	+	+	-	+	+	65.6
3	-	+	-	+	-	-	-	+	60.1
4	-	-	+	-	-	+	+	+	31.5
5	-	+	+	-	+	+	-	+	44.9
6	+	-	-	+	-	+	-	+	34.4
7	-	-	+	+	-	-	+	-	60.8
8	+	+	+	-	-	-	-	-	70.6
9	-	-	-	-	+	-	-	-	28.6
10	+	+	-	-	-	+	+	-	31.9
11	-	+	-	+	+	+	+	-	29.6
12	+	-	+	+	+	+	-	-	41.1

Temperature (A) ; Concentration (B) ; Ratio (s/l) (C) ; Mean particule size (D) ; Processing time (E); Origin of row material (F) ; Type of Acid (G) ; Agitation (H)

### Evaluation of the quality of the model:

The linear regression analysis shown in the graph (figure 1) is established by JMP 7 software. The figure 1 presents a projection of the observed values of the maximum quantity of carbonates eliminates as a function of the predicted values.

According to the graph of the correlation, there is a distribution, the experimental performance is close to the theoretical line; the graph illustrates the good correlation between the values observed and that predicted with a coefficient of determination  $R^2$  of the order of 1 (figure 1).

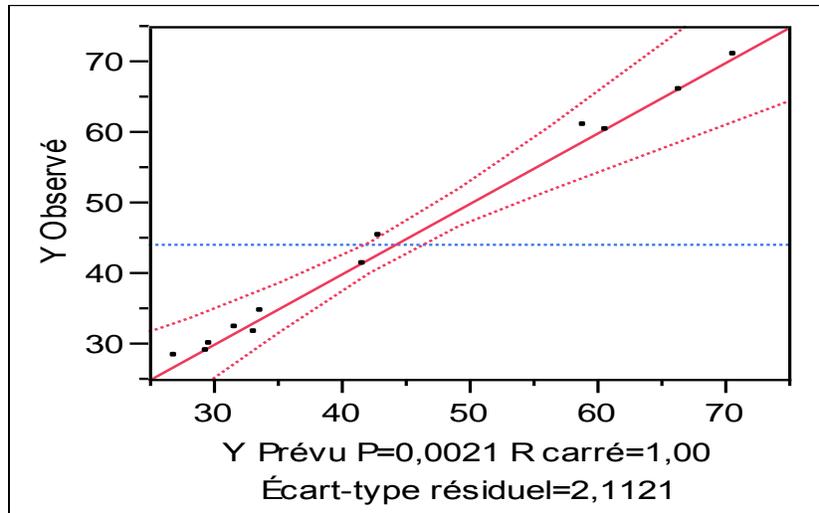


Fig 1:- Graphical representation of observed values as a function of predicted values.

From table 4 it is observed that the value of  $R^2 = 0.99$  and  $R^2$  adjusted = 0.98 are very close. This is reflected in the fact that the observed variation is explained by the direct effects of the factors. This coefficient is very close to 1, so the quality of the adjustment of the Plackett-Burman Design chosen for the screening of the conditions is the best.

Table 4:- Summary of the adjustment.

R squared	0.995255
Adjusted R squared	0.9826
Residual standard deviation	2.112068
Response average	43.925
Observations (or weighted sum)	12

**Test of analysis of variance anova:**

In this analysis (Table 5), it should be noted that, the sum of the squares attributed to the total variation evaluated with 11 degrees of freedom is divided into a sum of two variations: one due to the regression which is estimated with 8 degrees of freedom, the other to the estimated residual variation with 3 degrees of freedom as defined in Table 5.

To assess the quality of the postulated model, Fisher Snedecor's test was used. On the basis of the comparison of the variance in the established model with respect to the variance of the residual, through the Fisher Snedecor test, we can say that for the model to be very significant at 95%, it is necessary that:  $F_{exp} \gg F(\alpha, \text{mod}, v_{res})$ , where  $\alpha = 0.05$  (5%).

The results of the analysis of the variance (Table 5) show that the experimental value of Snedecor ( $F_{exp} = 78.6479$ ), which is the ratio between the square of the model and the mean square of the residue, is well above the value critical distribution ( $F(0.05; 8; 3) = 8.85$ ) at a 95% confidence level at 8 and 3 degrees of freedom. Therefore, the ANOVA results given by the JMP 7 software is very significant with a confidence level of 95% and the model for response Y is considered compliant and of good quality.

Table 5:- Analysis of the variance ANOVA by the JMP software for the Y response.

Source	Degree of freedom	Sum of squares	Average square	Rapport F
Model	8	2806.6800	350.835	78.6479
Residues	3	13.3825	4.461	Prob. > F
Total	11	2820.0625		0.0021

**Pareto diagram:**

The contributions of the factors are ranked in ascending order and then represented as a bar graph (Pareto diagram), shown in Figure 2. The Pareto chart review classifies the influence of different factors in the following order: the ratio (l/s), the type of acid, the concentration, the time, the mean particle size, the type of oil shale, the temperature, and then the agitation.

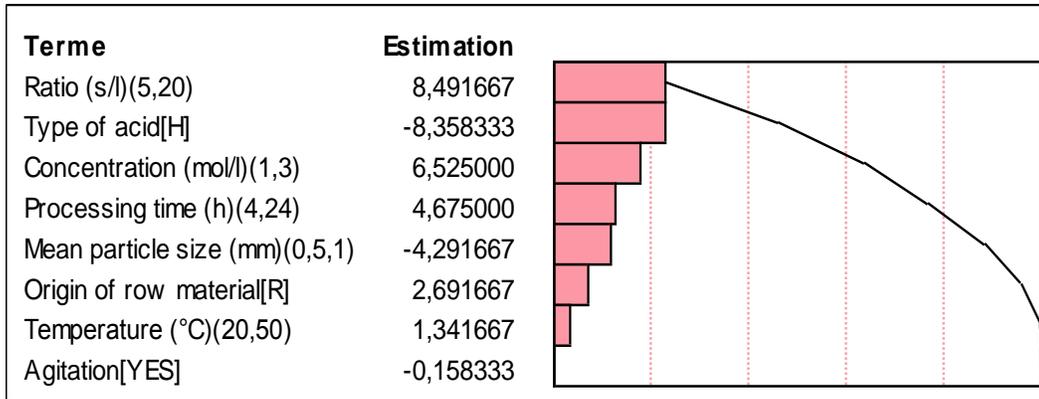


Fig 2:- Pareto diagram.

**Determination of the equation of the model:**

The coefficients of the Plackett-Burman model equation are given by the JMP software and are shown in Table 6. According to this table, we note that the effects of the factors: ratio (s/l), origin of raw material, concentration, granulometry, processing time and acid type are very significant with a value of p value  $0.0001 < P\text{-value} < 0.05$ . The equation of our model after elimination of all factors with a P-value higher than 0.05 is as follows:

$$Y = 43.925 + (8.49 * C) - (8.36 * G) + (6.53 * B) + (4.68 * E) - (4.29 * D) + (2.69 * F)$$

Table 6:- Graph of the effect of different factors.

Terme	Estimation	Écart-type	Rapport t	Rapport t	Prob.> t
Ratio (s/l) (5 ; 20)	8.4916667	0.609702	13.93		0.0008
Type of acid [H]	-8.358333	0.609702	-13.71		0.0008
Concentration (mol/l) (1 ; 3)	6.525	0.609702	10.70		0.0017
Processing time (h) (4 ; 24)	4.675	0.609702	7.67		0.0046
Meanparticle size (mm) (0.5 ; 1)	-4.291667	0.609702	-7.04		0.0059
Origin of row material [R]	2.6916667	0.609702	4.41		0.0216
Temperature (°C) (20 ; 50)	1.3416667	0.609702	2.20		0.1151
Agitation [YES]	-0.158333	0.609702	-0.26		0.8119

**Prediction profiler for the response:**

The prediction profile provided by the diagram below (figure 3) confirms that the factors that seem to be more influential are; concentration (B); ratio (s/l) (C); mean particle size (D); processing time (E); the origin of the row material (F), and the type of acid (G).

The mode of treatment of an analysis of the diagram also makes it possible to conclude that these factors affect the response in the antagonistic way. It is clear that an increase in concentration and ratio (s/l) leads to an increase in the ability to remove the carbonates from the Timahdit and Tarfaya oil shale.



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