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Wet-Process Phosphoric Acid Interaction with High Grade Phosphate Sediments: Statistical Modeling.

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Abstract: The most important factors affecting the preparation of triple superphosphate fertilizer (TSP) in terms of P_2O_5., %conversion efficiency were studied using both changing one factor at a time (OFAT) and the multivariate 24 full factorial methodologies. The obtained results were statistically analyzed using analysis of variances (ANOVA) to measure the adequacy of the fitted model. The first order regression model was built to approximate the preparation of triple superphosphate fertilizer based on the design of experiments (DOE). It was noticed that a low H_3PO_4 acid concentration with a relatively long reaction time was more favorable for improving both water soluble phosphate (W/S) and P_2O_5 conversion efficiency during the preparation of triple superphosphate (TSP). The (DOE) methodology has also been shown to be more effective due to its economic feasibility and reduced time; additionally, the model built for P_2O_5 % conversion efficiency to produce (TSP) when low concentrated phosphoric acid was utilized was judged accurate and reliable. 95 % (-100) mesh, 20% H_3PO_4 solution, 1:4 S/L ratio, and a 20-minute reaction period were the optimal conditions for W/S and P_2O_5 conversion efficiency. Under these ideal conditions, a P_2O_5 conversion of 86.61% was effectively accomplished during the preparation of triple superphosphate fertilizer. These results backed up the model's experimental validity and the presence of ideal conditions. This verified that the developed model for P_2O_5., % conversion was accurate and trustworthy.

Key words: Phosphate Rock, Triple Superphosphate, one Factor at Time (OFAT), Design of Experiment (DOE), Statistical analysis.

1. Introduction.

Phosphate, nitrogen, and potash fertilizers are essential and crucial foods for the soil, and they have a significant impact on agricultural production. These elements may not be available in an absorbable state on agricultural land, or may not be present in sufficient quantities in the soil to nourish plants and produce crops profitably. Phosphate fertilizers consume about 90% of the world's phosphate rock, which is ground and treated with strong acid (concentrated sulfuric acid), with a mixing ratio of about (680 kg phosphate) acidulated by (320 kg concentrated sulfuric acid 70%) to produce single superphosphate (SSP) fertilizer, which contains (14-18% water soluble P_2O_5). Triple superphosphate (TSP) is more concentrated; it contains about (52 % water soluble P_2O_5).

According to the fertilizer manual (IFDC,1997). This is due to the use of phosphoric acid instead of sulfuric acid with a mixing ratio of (1650 kg ton phosphate: 52 % concentrated phosphoric acid). When using phosphate fertilizers, it is important to investigate the proportions of radioactive and toxic elements like uranium, thorium, and cadmium, which can have a negative impact on agricultural product quality and human health. The following Equation [1] represents the main reaction of (TSP) preparation:

$$Ca_{10} (PO_4)_6F_2 + 14 H_3 PO_4 + 10H_2O \longrightarrow 10 Ca (H_2PO_4)_2 H_2O + 2HF \quad (1).$$

A number of side reactions will occur which can have significant effects on both the stoichiometry of the system, and the product quality as shown in the following equations:

$$Fe_2O_3 + 2H_3PO_4 \longrightarrow 2FePO_4.H_2O + H_2O \quad (2)$$

$$Al_2O_3 + 2H_3PO_4 \longrightarrow 2AlPO_4.H_2O + H_2O \quad (3)$$

$$CaCO_3 + 2H_3PO_4 \longrightarrow Ca (H_2PO_4)_2 H2O + CO_2 \quad (4)$$

$$Ca_3 (PO_4)_2 + 2H_2SO_4 + H_2O \longrightarrow Ca (H_2 PO_4)_2 H_2O + 2CaSO_4 \quad (5)$$

$$4 HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \quad (6)$$

$$3 SiF_4 + 4H_2O \longrightarrow Si (OH)_4 + 2H_2SiF_6 \quad (7)$$

The availability of Phosphorus from phosphate rock residue to plants is critical in the long run. In reality, triple super phosphate (TSP) produced the same or better agronomic response than superphosphate in seasonal crops (Rajan and Marwaha., 1993, Thibaud *et al*., 2013, Hagin and Katz, 1985), indicating that the contribution from residual phosphorus can be significant also in the short term. When measured by solubility in chemical extractants such as 2 % citric acid or formic acid, the residual phosphate rocks remaining after extraction of partially acidulated phosphate rocks with water, 2 % citric acid, or neutral or alkaline ammonium citrate are less reactive than the original material (Sylvia *et al*., 2019., Fayiga and Obigbesan, 2017., Sylvia *et al*., 2016., Peter *et al*.,2019) The design of experiments (DOE) technique has not been used in the synthesis of triple superphosphate, although several studies have worked on the production of triple superphosphate (Jibing Xiong *et al.,* 2008., Derqaoui *et al.,* 2022., Abouzeid, 2008). The design of experiments technique has been widely employed to fulfill a variety of research goals in various scientific domains.

This study employed the Design of Experiments (DOE) method to look into partially acidulating high-grade phosphate ore with phosphoric acid. Using statistical design and experiment analysis, the main impacts and interactions of phosphate ore particle size %, phosphoric acid concentration, solid-to-liquid ratio, and denning time on the maximum P_2O_5 conversion efficiency required for TSP manufacture were determined. As a result, the hydrometallurgical system was investigated using 16 runs and 4 replications of the center points.

2. Methodology

2.1 Sourcing of materials and preparation of samples.

The preparation experiments were studied upon bench scale on an East Sebaiya phosphate ore sample from Southern phosphate belt of Egypt. A jaw crusher was used to crush the ore sample until it passed through a 150 µm sieve. The sample was then completely mixed and dried for 24 hrs. in an electric oven at 100-120 °C, before being cooled and stored for future use. A local phosphoric acid was used in the acidification process of the phosphate ore sample under investigation.

2.2 characterization of raw ore sample.

Table1 shows the chemical composition of the ore sample. The results demonstrate that the phosphate sample has a high P_2O_5 content (32.77%) and a high CaO content (41.15%), indicating the existence of other calcium-bearing minerals such as calcite and gypsum in addition to apatite. As can be observed, the weight ratio of CaO/P_2O_5 was found to be appropriate for industrial requirements (P_2O_5 30%, MgO 1%, CaO/P_2O_5 ratio1.6%), with acceptable trace amounts of U and rare earth elements.

Table 1. Chemical components of the experimental ore sample.

Component	Content
P_2O_5	32.77 %
CaO	41.15 %
SiO_2	7.93 %
Al_2O_3	0.5 %
Fe_2O_3	1.45 %
K_2O	1.61 %
Na_2O	0.2 %
MgO	0.33 %
SO_4^{--}	2.3 %
Cl	<0.01%
F	2.78 %
L.O.I	8.98 %
U	93 ppm
ΣREEs	350 ppm

The ASTM "Philips" X-ray diffractometer (PW 1730) was used to determine the mineralogical composition of the phosphate experimental sample on a cobalt radiation target with a Fe filter at 30 kV and 20 mA. The scanning was confined to a range of 2=1 to 2=80 degrees.). **Figure.1** shows the X-ray diffraction pattern of the investigated sample, which shows that the mineral composition includes the apatite mineral fluorapatite as the primary component, as well as calcium hydrogen phosphate hydrate $CaHPO_4(H_2O)_2$, quartz, SiO_2, and calcite, $CaCO_3$.

2.3 Apparatus.

A cylindrical 1 L reactor with a 10 cm diameter was used for the reaction. It was placed in a thermostatically regulated water bath with a Teflon-coated stirrer with a diameter of 4 cm. Stirring impeller speed was set to 400 rpm. A Buchner funnel with a diameter of 4.6 in. was used for filtration. The filter cloth was made of polypropylene with an 80 mesh aperture. Filtering was done with a vacuum pump.

3. Methods.

Table 2: outlines the factors influencing the preparation of triple superphosphate (TSP). Phosphate rock particle size, phosphoric acid concentration and temperature, denning time, and solid to liquid ratio (S/L) are all factors to consider. In all experiments, phosphoric acid was added to the 50 g of ground phosphate sample in the beaker, and the mixture was vigorously

stirred for 5 minutes, or until the mass set up, while the reaction temperature was measured with a thermometer. The mixture is placed in a 100 °C oven for denning, P_2O_5 content was determined by a colorimetric method (spectrophotometer type Shimadzu UV 1208, ammonium molybdate and ammonium metavanadate were used for P_2O_5 analysis), the remaining solids were dried and weighed. The heavy traces element determined by Atomic Absorption Spectrometer type GBC 932 AA (UK) (Marczenko,1986). According to the fertilizer manual, the main parameters affecting TSP preparation are:

Particle size.

Acid temperature.

Denning time.

Acid concentration.

Acid ratio (acid P_2O_5 / rock P_2O_5) solid/ liquid ratio.

The above parameters were systematically studied.

$$\text{P2O5 Conversion\%} = \frac{\text{Water Soluble}}{\text{Total P2O5}} \times 100$$

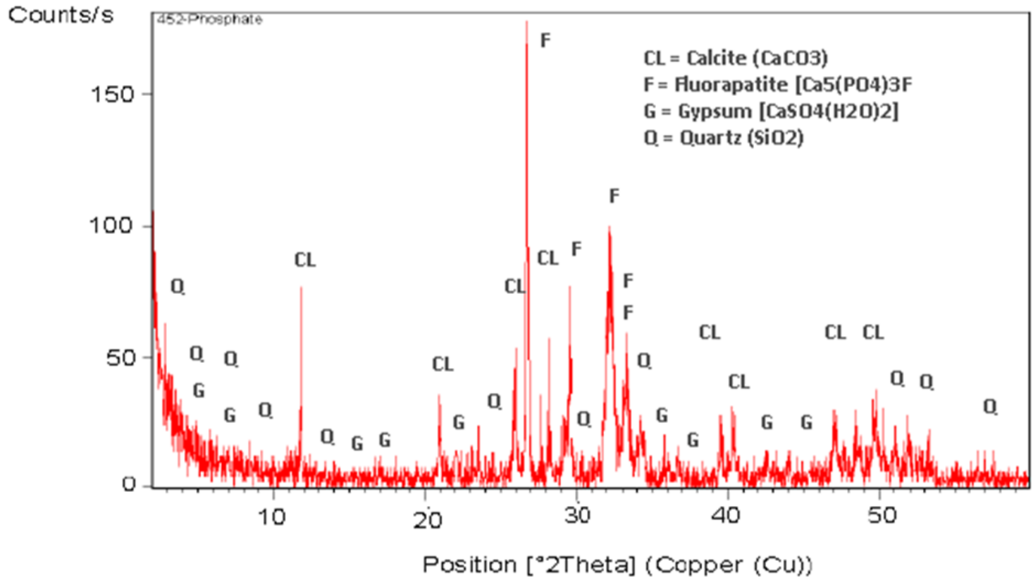

Figure1. XRD pattern of the East Sebaiya phosphate experimental sample.

Table 2. The studied factors impacting the preparation of triple superphosphate using One-Factor-At-a-Time (OFAT) methodology.

Factor	Variable Values	Fixed conditions
Ore particle size %, mish	80,85,90, 93, 96, 100	50°C acid temperature, 50% acid concentration, 1:3 Solid/Liquid ratio and 20 min denning time.
Phosphoric acid temperature, °C	50 °C, 60 °C, 70 °C, 80 °C, and 90 °C.	96% (-100) mesh raw ore particle size, 50% acid concentration, 1:3 Solid/Liquid ratio and 20 min denning time
Denning time, min	15, 18, 22, 25 and 27 min	96% (-100) mesh raw ore particle size, 50% acid concentration, 1:3 Solid/Liquid ratio and 50 °C acid temperature
Phosphoric acid concentration, %	40%, 45%, 50% and 55%	96% (-100) mesh raw ore particle size, 1:3 Solid/Liquid ratio and 50 °C acid temperature and 25 min denning time
Solid/liquid ratio	1:1, 1:2, 1:3 and 1:4.	96% (-100) mesh raw ore particle size, 50% acid concentration, 50 °C acid temperature and 25 min denning time.

3.1 Statistical design of experiments.

The statistical design of experiments (DOE) is a time-saving method for reducing the number of tests needed to optimize a system. It was generally utilized to get a better return with the least amount of work, time, and money (Montgomery, 2017). The design identifies factors with substantial effects as well as the interactions between different factors on a response. Three steps are involved in the design of experiments: statistical design, estimation of coefficients using a mathematical model with response prediction, and statistical analysis (Navidi, 2006). In order to optimize the TSP preparation, four independent variables were chosen based on the results of the (OFAT) investigation: particle size, phosphoric acid concentration, soli/liquid ratio, and denning time. The experimental variables were graded on two scales: low (denoted as -1), high (denoted as +1), and mid-level (denoted as 0). The addition of center points to the design allows to determine whether the linearity of the effects is a reasonable assumption or if quadratic terms should be included in the model, furthermore, including center points in the design protects against second-order effects while also allowing for independent error estimation. To avoid systematic errors, the experiments order was randomized, as shown in **Table3**. The results were analyzed using the Design Expert 11.0.0 software to determine the main effects and interactions between factors.

Table 3. The levels of experimental factors for the full factorial design.

Factors	Coded variables	Low level (-)	High level (+)	Mid-level (0)
Particle size, %	D	50	95	72.5
H_3PO_4 Concentration,%	A	20	50	35
Denning time, min	B	5	20	12.5
Solid/Liquid ratio	C	1	4	2.5

3.2 Plots of Effects with Normal Probability.

According to (Sepideh *et al*.,2022). High-order interactions can occur while examining data from factorials, hence normal probability plots are employed to estimate the significant factors. The actual values of the estimated effects are plotted against their cumulative normal probabilities in this graph. Significant impacts will have nonzero means and will not fall along a straight line, whereas minimal effects will have zero means and will tends to fall along a straight line. In statistical designs, effects are calculated by average the responses that apply to each factor's level. The difference between the average responses at each component's two levels indicates how important that factor is in determining the response assessed. The single impacts generated by changes in the input parameters are estimated using the following formula:

$$\text{Effect} = \frac{2}{m}\sum_{i=1}^{m} (\text{Algebric sign of constant} \times \text{R Observed})$$

where m is the number of runs and R is the response.

3.3 Pareto Plots of Effects.

The Pareto chart is a form of bar chart that shows data in descending order. We can notice the descending sequence of effects caused by distinct variables as well as the interactions between them when we evaluate the effects of various factors on the response. It assists us in creating priority levels during the process design. According to the 80-20 rule, 20% of causes result in 80% of effects (Koch,1998).

4. Results and Discussion.

Triple superphosphate was prepared from East Sebaiya phosphate row ore as aforementioned according to **Eqn.1.** The solid/liquid amount of phosphoric acid involved is estimated according to this reaction. The chemical analysis of local wet process phosphoric acid involved in the reaction shown in **Table 4.**

Table 4: Phosphoric acid chemical assay involved in preparation of triple superphosphate(TSP) fertilizer.

Content	(W/W%)
P_2O_5	50.24
Fe_2O_3	3.06
Al_2O_3	0.76
MgO	0.84
SO_3	3.65
CaO	0.13
Na_2O	0.03
K_2O	0.005
F	0.84
Cl	0.002

4.2 Product yield

The results of triple superphosphate preparation using One-Factor-At-a-Time (OFAT) methodology are given in **Table 5.**

Table: 5 P_2O_5 conversion and P_2O_5 content after investigated the full operational parameters.

Parameters	**Water soluble (W/S), %**	**Citrate soluble (C/S), %**	**Total P_2O_5,%**	**P_2O_5 conversion, % (TSP).**
Particle size %.,				
80	27.35	43.12	39.82	68.73
85	29.56	43.44	41.27	71.62
90	31.68	43.88	42.23	75
93	34.65	44.25	44.45	77.95
96	36.42	44.51	46.55	78.24
100	36.42	44.53	46.55	78.24
H_3PO_4 Temp., °C				
50	36.44	44.37	46.57	78.24
60	36.47	44.45	46.72	78.06
70	36.6	44.73	46.79	78.20
80	37.01	44.81	46.91	78.89
90	37.01	44.92	46.91	78.89
Denning time., min				
15	36.33	45.15	46.5	78.12
18	36.34	45.2	46.49	78.16
22	36.37	45.20	46.53	78.17
25	36.41	45.31	46.56	78.2
27	36.41	45.37	46.56	78.2
Solid/Liquid ratio				
1:1	30.84	45.2	42.83	72
1:2	31.88	45.26	43	74.14
1:3	33.39	45.26	44	75.88
1:4	34.37	45.37	44.38	77.45
H_3PO_4 Conc, %				
40	29.52	45	39.16	75.38
45	30.72	45.13	41.73	73.62
50	33.2	45.5	46.19	71.87
55	33.55	45.67	47.58	70.52

Based on the foregoing information, the maximum operating conditions for TSP preparation from East Sebaiya raw ore are as follows:

- Particle size : 96 % (-100) mesh
- Phosphoric acid temperature : 80 °C
- Denning time : 25 minutes
- Acid ratio (S/L) ratio = 1:2 at which dry TSP product with reasonable free acid content is obtained.
- Phosphoric acid concentration : 55 % P_2O_5 w/w.

The total P_2O_5, W/S, and C/S % in the various solubility categories at the different degrees of acidulation of the rock phosphate were described in **Table 5** and **Figure 2** after an extended study on selecting the ideal parameters value of the triple super phosphate fertilizer production. In the prepared T.S.P, **Table 6**, the yield was dried for 25 minutes at 70-100°C, and another sample was taken to measure the proportion of heavy metals **(Table 7).**

Table 6. Water-soluble.,%, citrate-soluble.,%, total P_2O_5.,% and P_2O_5 conversion., % expressed as percentage of the fertilizer material.

Acidulation Degree.,%	Moisture.,%	W/S.,%	C/S.,%	Total P_2O_5.,%	P_2O_5 conversion., %
40	16.1	33.5	45.11	42	79.76
45	14.96	35.64	45.75	46.54	76.57
50	11.34	36.58	45.96	50.28	72.75
55	8.63	36.8	46.53	51.75	71.11

Table 7. Heavy trace element distribution in prepared triple super phosphate.

Element	As	Cd	Pb	Ni	Cu	Hg	Cr
Trace/ppm	4.25	7.65	11.18	25.61	14.69	0.42	24.09

The available P_2O_5 conversion %, increased as the acidulation degree decreased, reaching a maximum of 79.76 % at 40 % acidulated phosphate rock. This is due to the high possibility of apatite-acid interaction, which results in TSP with low water soluble P_2O_5 and available P_2O_5 content, as well as the high moisture content, which necessitates more energy for drying.

However, when the acidulation degree increases, the available P_2O_5 conversion decreases, reaching a minimum of 71.11% at 55% acidulated material. This is owing to a water deficiency in the system to complete the reactions, as well as an increase in phosphoric acid viscosity.
In terms of the physical state of the yields, decreasing acidulation degree resulted in muddy Ex-Den due to excess water in the system, whereas increasing acidulation degree resulted in sticky Ex-Den due to the high viscosity of the acid and significant concentrations of acid impurities in the system.

The results reveal that the optimum acidulation degree in the range of (45-50 % P_2O_5). But 50 % acidulation degree is preferred to avoid much water in the system, and to get, more acidulated yield, which gives 72.75% water soluble P_2O_5 conversion %, 36.58% water soluble P_2O_5 content, and 50.28% total P_2O_5 content, this is much closer to the Egyptian National Standards.

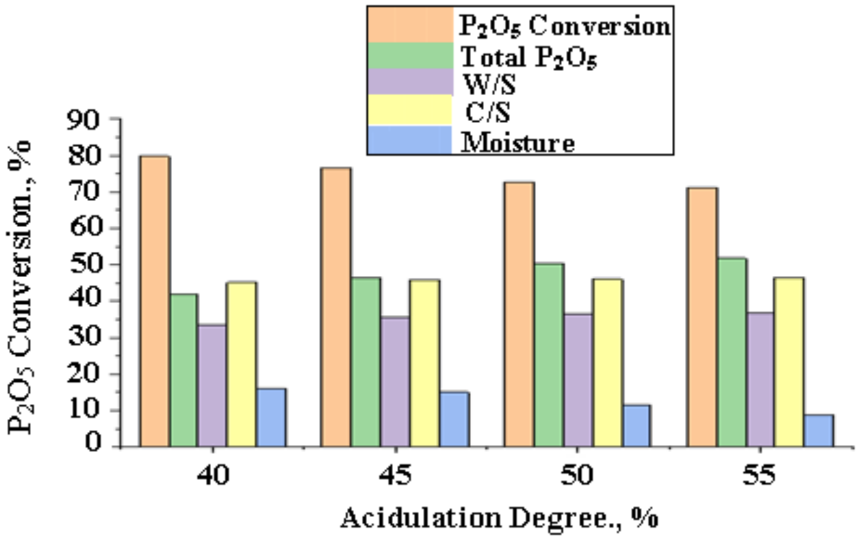

Figure 2. Effect of acidulation degree on Water-soluble.,%, citrate-soluble.,%, total P_2O_5.,% and P_2O_5 conversion., % expressed as percentage of the triple superphosphate fertilizer material.

4.3 Statistical design of experiment methodology (DOE).

4.3.1 The Significant Parameters.

It is expected that the response is linear over the range of factor levels in 2^n factorial designs. In practice, however, the linearity assumption is frequently violated. In this instance, one or more runs with all components set to their center point must be included. The addition of center points to the design assisted to see if the linearity of the effects is a realistic assumption or if quadratic terms should be included in the model. **Table 8** shows the experiment matrix for this design's (TSP) preparation efficiency. The findings revealed that all variables are changed at the same time. A total of 16 runs and four replications of the center points have been designed according to the experimental plan. According to trials **No**(**15&16**), the ideal P_2O_5 conversion efficiency to (TSP) was 86.61% and 84.13 % under the conditions of 20% and 50% H_3PO_4 concentrations, 1:4 S/L ratio, 95 percent (-100) mesh particle size, and 20 min denning duration time. **Experiment 5** represents the lowest P_2O_5 conversion efficiency (46.81%) under conditions of: 20% H_3PO_4 concentration, 1: 4 S/L ratio, 50% (-100) mesh particle size, and 5 minute denning duration.

Table 9 summarize the effects of the experimental parameters and their interactions on P_2O_5 conversion percent. Positive values of these impacts indicate that increasing these parameters improved P_2O_5 conversion percent efficiency, while negative values indicate that the response was decreased. In another way, The negative indications in several of the variables in the prediction model equation imply that these factors must be kept at low levels to maximize P_2O_5 conversion efficiency. Positive indicators indicate that the factors should be retained at high levels. With a contribution rate of 47.8236%, Ore particle size had the major effect on P_2O_5 conversion percent, followed by 11.71% (H_3PO_4., %−Time., min−Particle Size) interaction contribution rate, 11.23%. Time., min contribution rate, 4% interaction contribution rate of (Time., min−S/L ratio−Particle Size), and finally 3.4% interaction contribution rate of (H_3PO_4., %−Time., min−S/L ratio−Particle Size). (H_3PO_4., %−Time., min& H_3PO_4., %−S/L ratio−Particle Size& H_3PO_4., %−S/L ratio) interactions, on the other hand, reduce P_2O_5 conversion efficiency by 7.7%, 4.4 %, and 1%, respectively.

Table 8. Triple superphosphate preparation results for the 2^4 full factorial design matrix.

Run #	Conc H_3PO_4 %	Time/ min	S/L Ratio	particle size., %	W/S., %	Total P_2O_5,%	P_2O_5., conversion %
1	20	5	1:1	50	10.12	18.01	56.19
2	50	5	1:1	50	6.7	11.34	59.08
3	**20**	**20**	**1:1**	**50**	**13.15**	**17**	**77.35**
4	50	20	1:1	50	10.12	15.83	63.92
5	20	5	1:4	50	5.74	12.26	46.81
6	50	5	1:4	50	7.51	11.1	67.65
7	20	20	1:4	50	11.38	15.26	74.57
8	50	20	1:4	50	6.98	13.03	53.56
9	20	5	1:1	95	11.71	15.9	73.64
10	**50**	**5**	**1:1**	**95**	**16.94**	**20.48**	**82.71**
11	20	20	1:1	95	11.29	15.28	73.88
12	**50**	**20**	**1:1**	**95**	**16**	**19.64**	**81.46**
13	20	5	1:4	95	13.25	16.93	78.26
14	50	5	1:4	95	11	16.12	68.23
15	**20**	**20**	**1:4**	**95**	**15.87**	**18.31**	**86.61**
16	**50**	**20**	**1:4**	**95**	**14.8**	**17.59**	**84.13**
17	35	12.5	2.5	72.5	13	17.3	75.14
18	**35**	**12.5**	**2.5**	**72.5**	**13.28**	**16.75**	**79.28**
19	35	12.5	1:2.5	72.5	11.73	16.52	71
20	35	12.5	1:2.5	72.5	13.13	17.49	75

Table 9. Estimated effects and coefficients for P_2O_5 conversion; %.

	Term	Standardized Effect	Sum of Squares	Contribution, %
	Intercept			
Model	A- H_3PO_4., %	-0.82125	2.69781	0.122544
Model	B- Time., min	**7.86375**	247.354	11.2357
Model	C- Ratio., ml/ gm	-1.05125	4.42051	0.200794
Model	D – Particle Size	**16.2237**	1052.84	47.8236
Model	AB	-6.51375	169.716	7.70907
Model	AC	-2.34875	22.0665	1.00234
Model	AD	1.85625	13.7827	0.626055
Model	BC	1.61625	10.4491	0.474632
Model	BD	-2.05375	16.8716	0.766363
Model	CD	2.43625	23.7413	1.07841
Model	ABC	-2. 06125	16.995	0.771971
Model	ABD	8.02875	257.843	11.7121
Model	ACD	-4.94125	97.6638	4.43622
Model	BCD	4.69875	88.313	4.01148
Model	ABCD	4.32125	74.6928	3.3928
	Curvature	4.11604	67.7672	3.07822
Error	Lack of fit		0	0
Error	Pure Error		34.2939	1.55775
	Lenth's ME	6.96441		0
	Lenth's SME	12.3979		0

When comparing the conversion efficiency of a One-Factor- at-time, it is apparent that phosphoric acid's high acidulation degree has the first favorable effect in the conversion process and the yield of triple super phosphate. The use of a full factorial design, on the other hand, revealed that a low acidulation degree is more beneficial and has a positive impact on P_2O_5 Conversion efficiency. This is because the water cntent in the system has increased, promoting the completion of the reaction and lowering the viscosity of phosphoric acid.

The findings indicate the 2^n factorial design's key advantage over the One-factor-at-a-time strategy, which demonstrates the effects of main variables as well as the effects of variable interactions and economic feasibility.

4.4 Model fitting and statistical experimental data analysis.

4.4.1 The analysis of varianve (ANOVA).

The difference between the average response at the factor high level and the average response at the factor low level could be used to calculate the effect of the factors. In this regard, the effect of phosphoric acid concentration (factor A) on the P_2O_5 conversion percent process could be calculated as follows: A high average response obtained by averaging the results of experiments 2, 4, 6, 8, 10, 12, 14, and 16. The average response at A low was calculated by averaging the results of experiments 1, 3, 5, 7, 9, 11, 13, and 15.

Average response of P_2O_5 conversion at H_3PO_4 high

(59.08+63.92+67.65+53.56+82.71+81.46+68.23+84.13) / 8 = 70.0925

Average response at H_3PO_4 low

(56.19+77.35+46.81+74.57+73.64+ 73.88+78.26+86.61) / 8 = 70.91375

Difference = 70.0925 – 70.91375= - 0.82125

Hence, Effect of H_3PO_4 factor = - 0.82125.

The same formula is used to determine the effect of all response factors.

Following the experiments, analysis, and model fit to the experimental data, a first-order normal model (linear regression fitted model) between the essential factors and the response was constructed to clarify the response's dependence on the important factors and to obtain the best P_2O_5 conversion efficiency. The model is written as follows:

$$Y=b_0+b_1A+b_2B+b_3C+b_4D+b_{12}AB+b_{13}AC+b_{14}AD+b_{23}BC+b_{24}BD+b_{34}CD+b_{123}ABC+b_{124}ABD+b_{234}BCD+b_{1234}ABCD. \quad (7)$$

Where Y represents the percentage of P_2O_5 conversion efficiency, b represents the estimated coefficients of all main and interaction components in the regression model showed in **Table10**, and A, B, C, and D represent dimensionless coded ore particle size, phosphoric acid concentration, denning duration, and S/L ratio, respectively. **Table 11** shows the statistical analysis of the proposed model, which was developed using Design-Expert software. For each factor, the levels should be indicated in the original units. Because the coefficients are scaled to fit the units of each factor and the intercept is not at the center of the design space, this equation should not be used to evaluate the relative impact of each factor. The model is important since the F-value is 12.24. Due to noise, there is only a 3.10 percent chance that a "Model F-Value" will be this large. Model terms are significant when "Prob > F" is less than 0.0500. Significant model terms include B, D, AB, and ABD. The model terms are not important if the value is larger than 0.1000.

Table 10. Coefficients in Terms of Coded Factors.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	70.50	1	0.8453	67.81	73.19	
A-H_3PO_4 Conc.	-0.4106	1	0.8453	-3.10	2.28	1.0000
B-Time	3.93	1	0.8453	1.24	6.62	1.0000
C-S/L ratio	-0.5256	1	0.8453	-3.22	2.16	1.0000
D-Particle size	8.11	1	0.8453	5.42	10.80	1.0000
AB	-3.26	1	0.8453	-5.95	-0.5669	1.0000
AC	-1.17	1	0.8453	-3.86	1.52	1.0000
AD	0.9281	1	0.8453	-1.76	3.62	1.0000
BC	0.8081	1	0.8453	-1.88	3.50	1.0000
BD	-1.03	1	0.8453	-3.72	1.66	1.0000
CD	1.22	1	0.8453	-1.47	3.91	1.0000
ABC	-1.03	1	0.8453	-3.72	1.66	1.0000
ABD	4.01	1	0.8453	1.32	6.70	1.0000
ACD	-2.47	1	0.8453	-5.16	0.2194	1.0000
BCD	2.35	1	0.8453	-0.3406	5.04	1.0000
ABCD	2.16	1	0.8453	-0.5294	4.85	1.0000
Ctr Pt1	4.60	1	1.89			

Table 11. Analysis of variance (ANOVA) for P_2O_5 conversion (%).

Response	Recovery					
ANOVA for Response Surface Reduced Cubic Model Analysis of variance table [Partial sum of squares - Type III].						
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2099.45	15	139.96	12.24	0.0310	Significant
A-H_3PO_4 Conc.	2.70	1	2.70	0.2360	0.6604	
B-Time	247.35	1	247.35	21.64	0.0187	Significant
C-S/L ratio	4.42	1	4.42	0.3867	0.5781	
D-Particle size	1052.84	1	1052.84	92.10	0.0024	Significant
AB	169.72	1	169.72	14.85	0.0309	Significant
AC	22.07	1	22.07	1.93	0.2589	
AD	13.78	1	13.78	1.21	0.3524	
BC	10.45	1	10.45	0.9141	0.4096	
BD	16.87	1	16.87	1.48	0.3113	
CD	23.74	1	23.74	2.08	0.2452	
ABC	17.00	1	17.00	1.49	0.3099	
ABD	257.84	1	257.84	22.56	0.0177	significant
ACD	97.66	1	97.66	8.54	0.0614	
BCD	88.31	1	88.31	7.73	0.0690	
ABCD	74.69	1	74.69	6.53	0.0835	
Curvature	67.77	1	67.77	5.93	0.0929	
Pure Error	34.29	3	11.43			
Cor Total	2201.51	19				

The final equation of coefficients in terms of coded factors, according to a statistical analysis of the experimental data (**Table 10**), is as follows:

$$YP_2O_5conversion = +70.50-0.4106A+3.93B-0.5256C+8.11D-3.26AB-1.17AC+0.9281AD+0.8081BC-1.03BD+1.22CD-1.03ABC+4.01ABD-2.47ACD+2.35BCD+2.16ABCD. \quad (8)$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

The main and interaction effects, as presented in **Figure3**, were estimated using the data from **Table 8**. The probability plots were used to determine the significant impacts. B (Time), D (Particle size), and interactions (AD, CD, BC, ABD, BCD, and ABCD) are normally distributed with mean non-zero mean, variance σ^2, and are placed far away from the straight line when the impacts of individual factors were investigated using the factorial design. The remaining factors A (H_3PO_4 Conc), C (S/L ratio), and interactions (AB, AC, BD, ABC, and ACD) were statistically unimportant since they did not deviate significantly from the normal distribution (zero-mean) and tended to fall along a straight line.

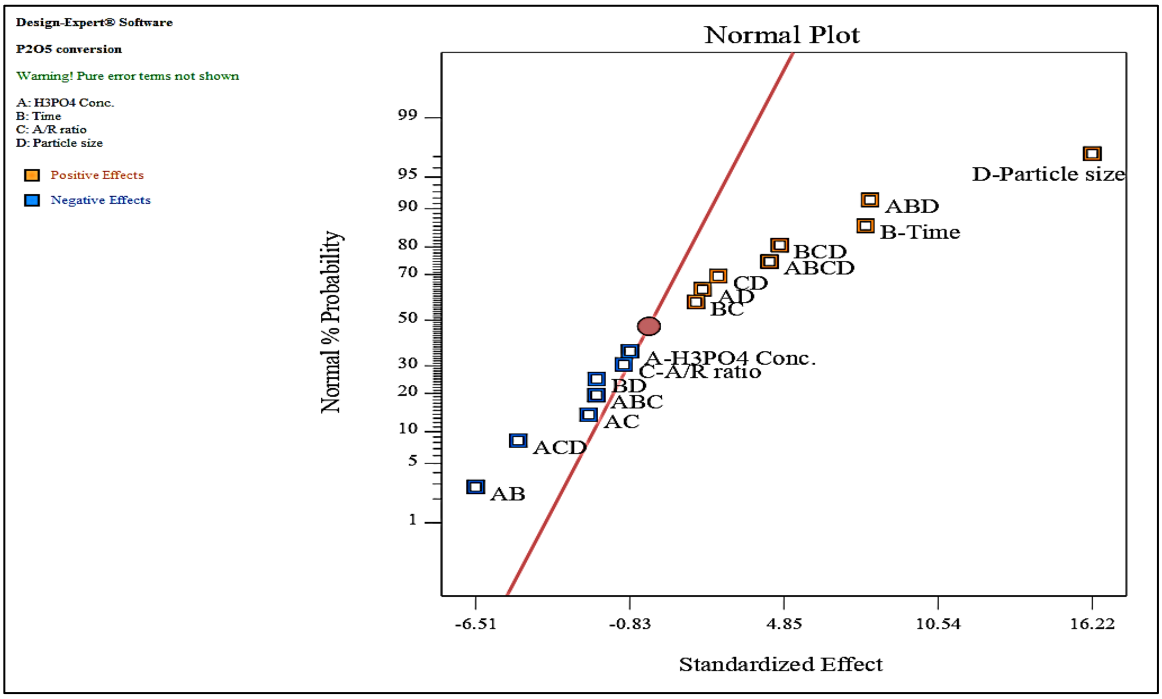

Figure 3. Normal probability plot of the standardized effects of P_2O_5 conversion efficiency.

The obtained results show that, the effect of the major factor particle size has the greatest positive effect on P_2O_5 conversion., % through TSP preparation process (4.895). So that, the effect of raw ore particle size became more and more significant by decreasing the particle size. Time also has a positive effect on P_2O_5 conversion., % through the preparation process (7.86375). However, both of the other main effects, phosphoric acid concentration and S/L ratio, have a negative effect on P_2O_5 conversion efficiency (-0.82125) for phosphoric acid concentration effect, and (-1.05125), for S/L ratio effect. This means that, the increase in the S/L ratio factor level leads to enhance effectiveness the TSP preparation efficiency. However, the increase in phosphoric acid concentration and time will decrease effecting the TSP preparation process efficiency.

The analysis of variance of the conversion P_2O_5 (%)., indicate that the main factor (D) and the interaction between acid concentration-particle size (AD), the interaction between time - S/L ratio (BC), S/L ratio-particle size (CD), the interaction between acid concentration-time-particle size (ABD), time - S/L-Particle size (BCD) and the interaction between acid concentration-time - S/L ratio-Particle size (ABCD) have strongly favorable effect on the TSP

preparation efficiency (1.85625, 1.61625, 2.43625, 8.02875, 4.6987 and 4.32125) respectively. Vice versa, the rest of interactions between acid concentration-time (AB), the interaction between acid concentration - S/L ratio (AC), time-particle size(BD), the interaction between acid concentration-time - S/L ratio(ABC) and the interaction between acid concentration - S/L ratio-particle size (ACD) have strongly unfavorable effect on the TSP preparation efficiency (-6.51375, -2.34875, -2.05375, -2.06125 and -4.94125) respectively.

These results were verified by the Pareto chart represented in **Figure 4**, where the Bonferroni limit is the threshold above which the effects that emerge are significant (very important), while the effect terms below the threshold of the t-limit are insignificant factors. Effects emerging above the t-limit but below Bonferroni limit may possibly be significant (moderately important) (Jue Liang *et al*., 2015).

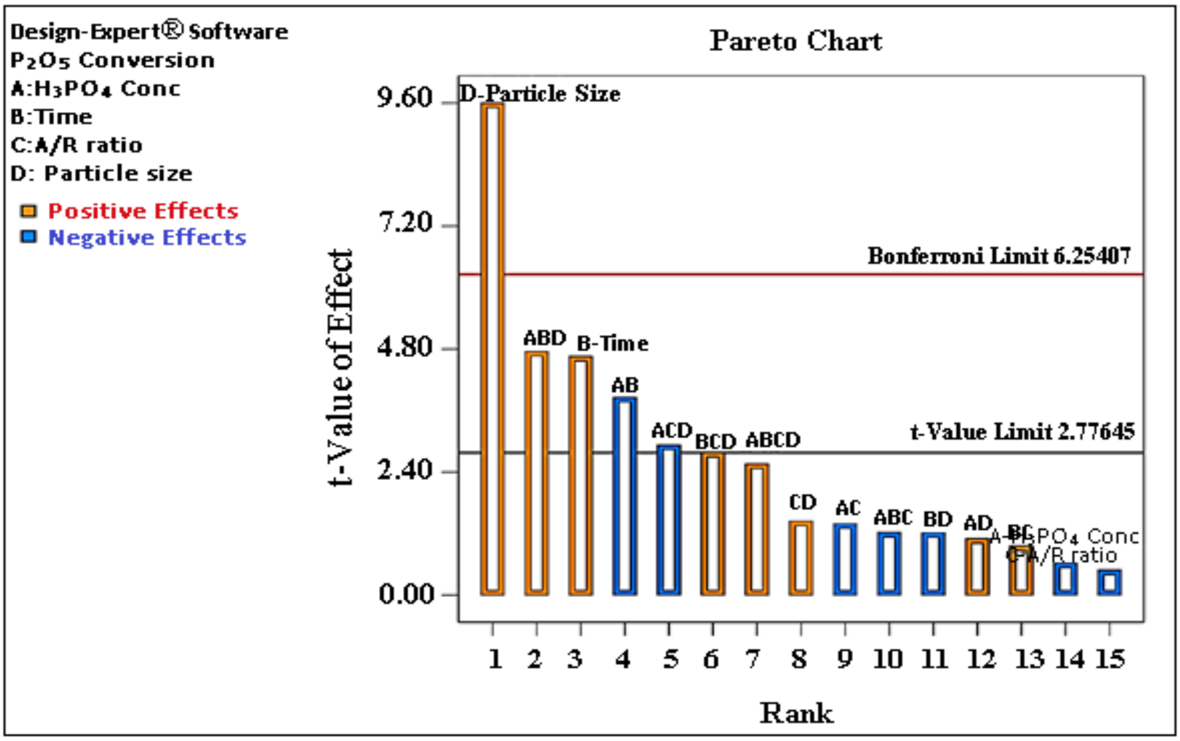

Figure 4. Pareto chart of the main factors and interaction effects on P_2O_5 conversion efficiency.

From the chart, for the conversion efficiency of P_2O_5, the factor effects of the very important main factors and their interactions are found, the most important factor effect the conversion efficiency is the raw material particle size factor D, (above the Bonferroni limit), while the factor time B and the interactions ABD, BCD, AB and ACD which dropped in between Bonferroni and T-value limit could be considered as moderately effect. The interaction ABCD has a very small effect compared to other interaction because it is below the T-value limit.

4.5 Influence of Main Factors on P_2O_5., % Conversion Efficiency Process.

4.5.1 Effect of Phosphoric acid concentration.

The effect of H_3PO_4 concentration on phosphorus pentoxide conversion is presented in **Figure 5.1**. The Figure shows the conversion of P_2O_5 to TSP using H_3PO_4 concentration of 20 % and 50 % which are low and high levels respectively. The other parameters were kept at S/ L ratio equal 1:3, denning time of 25 min, and temperature factor will be ignored because the reaction is exothermic in nature. Higher P_2O_5 conversion was attained at the higher H_3PO_4 concentration of 50 % than at the lower concentration of 20 %. These results are similar to the

results obtained form (OFAT) method, where at (OFAT): H_3PO_4 concentration was enhancing phosphorus pentoxide conversion process up to 50 % and further increase in the phosphoric acid concentration has slightly effect on the conversion process.

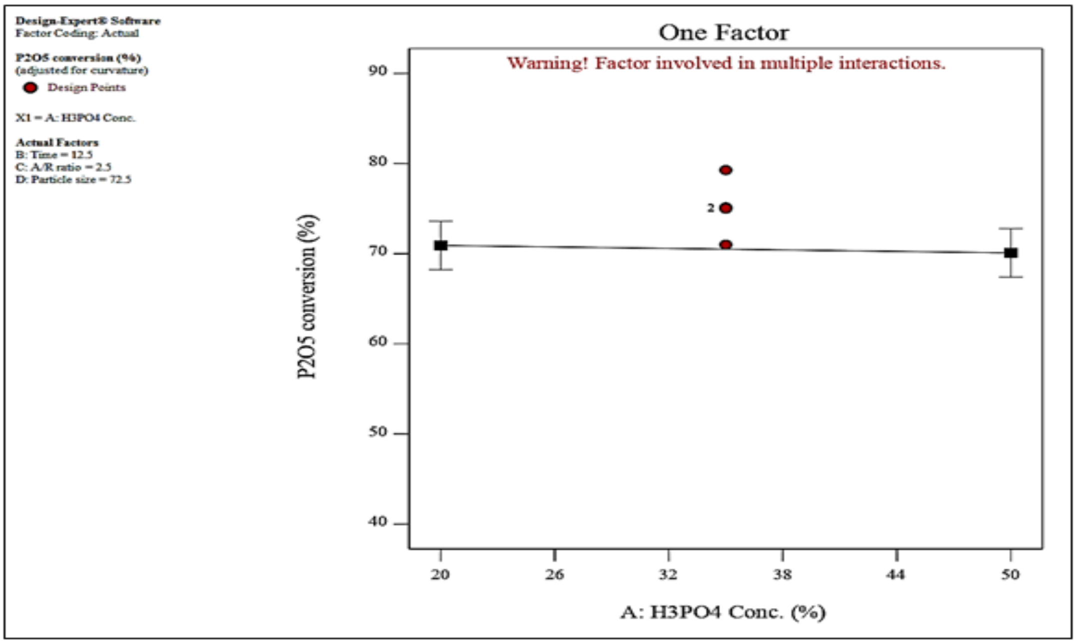

Figure 5.1. Effect of Phosphoric acid concentration (%) on P2O5 conversion (%) efficiency.

4.5.2 Effect of denning time.

The effect of denning time on P_2O_5 conversion efficiency process is obtained in **Figure 5.2.** The Figure clears the conversion efficiency at different denning time values of low level (5 min) and high level (20 min) respectively. The other parameters were fixed at H_3PO_4 acid of 50%, and 1:3 S/ L ratio. The obtained results indicate that; the conversion efficiency is sharply increased with the increase in denning time. This result is closer to the results obtained by applying (OFAT) methodology for the same investigation, where at (OFAT) procedures the increase in time was enhancing the conversion efficiency of phosphorus pentaoxide.

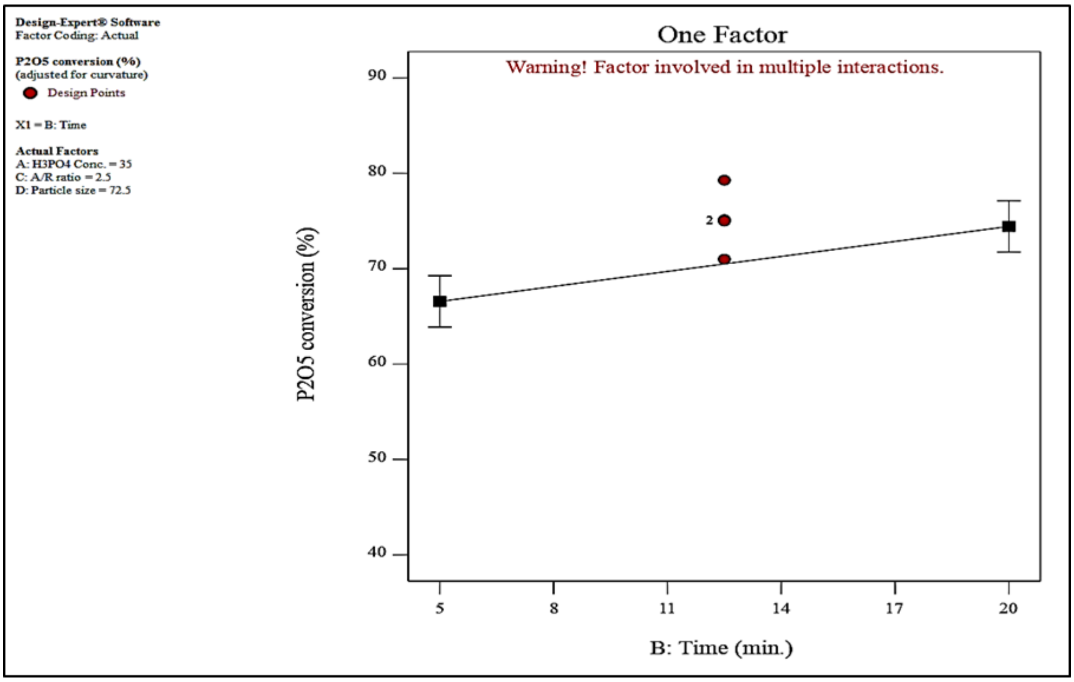

Figure 5.2. Effect of denning time, min on P_2O_5 conversion (%) efficiency.

4.5.3 Effect of solid/ liquid mass ratio.

Figure.5.3 represents the effect of solid/ liquid ratio on P_2O_5 conversion efficiency process. The Figure investigates the conversion efficiency of P_2O_5(%) to triple superphosphate at S/L ratios of 1:1 and 1:4 which are low and high levels respectively, while the other parameters were 50 % phosphoric acid and 20 min denning time. The obtained results show that P_2O_5 conversion efficiency to (TSP) is slightly decreased with increasing S/L ratio from low to high level. This behavior is the completely opposite to the results obtained by applying (OFAT) methodology for P_2O_5 conversion efficiency., %.

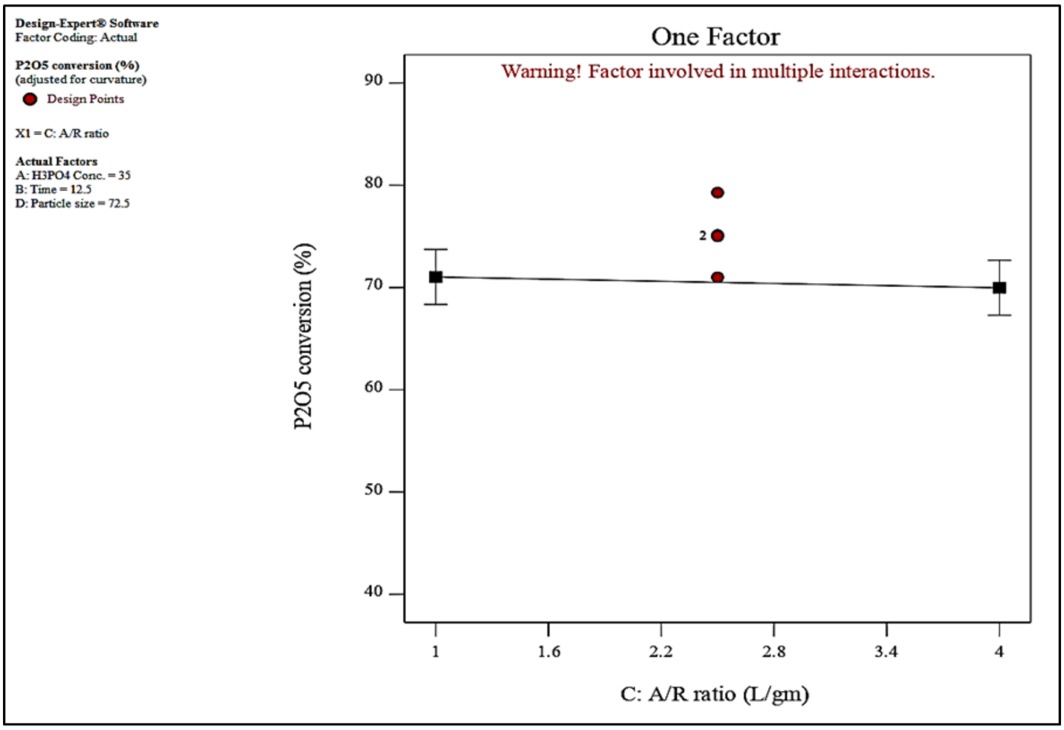

Figure 5.3. Effect of solid/liquid ratio on P_2O_5%, conversion efficiency.

4.5.4 Effect of Ore particle size %, mish.

The experiment was conducted at low and high levels, 50 (-100) mesh and 95(-100) mesh, respectively, to determine the impact of high grade phosphate ore particle size on the P_2O_5% conversion efficiency process shown in **Figure 5.4**. The other parameters were set to 50% H_3PO_4 acid concentration, a 20-min denning time, and a 1:2 S/L ratio. The acquired results demonstrate that P_2O_5., % conversion efficiency to (TSP) is significantly improved and enhanced with an increase in grinding to 95% (-100) mesh; these results are consistent with those obtained using the (OFAT) methodology for the same inquiry.

4.6 Influence of factor Interaction on the preparation of TSP.

The ability to demonstrate the interaction between the various factors under investigation is one of the main benefits of the factorial design procedure. As a result, any two factors' effects on each other should be evaluated. The interaction plots serve this purpose (**Figure 6**) made it possible to thoroughly investigate the potential combined effects of the factors taken into account in the P_2O_5 Conversion. Based on (Xin-jiang *et al*. 2015, Pokhrel., and Viraraghavan, 2008, Antony, 2014): There are no interactions between the two factors if the lines in the plot's cell are parallel. On-parallel lines, on the other hand, indicated a relationship between the two

factors, and a larger angle between two lines in the cell indicated a more substantial relationship. For P_2O_5 conversion's interaction effects, **(Figure5 e, f)** demonstrate that the lines in cells BD (or DB) and CD (or DC) were nearly parallel, indicating that there were few interactions between the two variables in these cells, suggested a slight or no impact on the conversion efficiency. The **(Figure 5a, b, c, and d)** showed that there was a statistically significant interaction between the main effects in the cells AB (or BA), AC (or CA), AD (or DA), and BC (or CB). The fact that the angel between two lines was larger than it was in other cells due to the intersection of the two lines indicated this. According to these findings, the phosphoric acid concentration, contact time, S/L ratio and particle size may all have significant effects on one another.

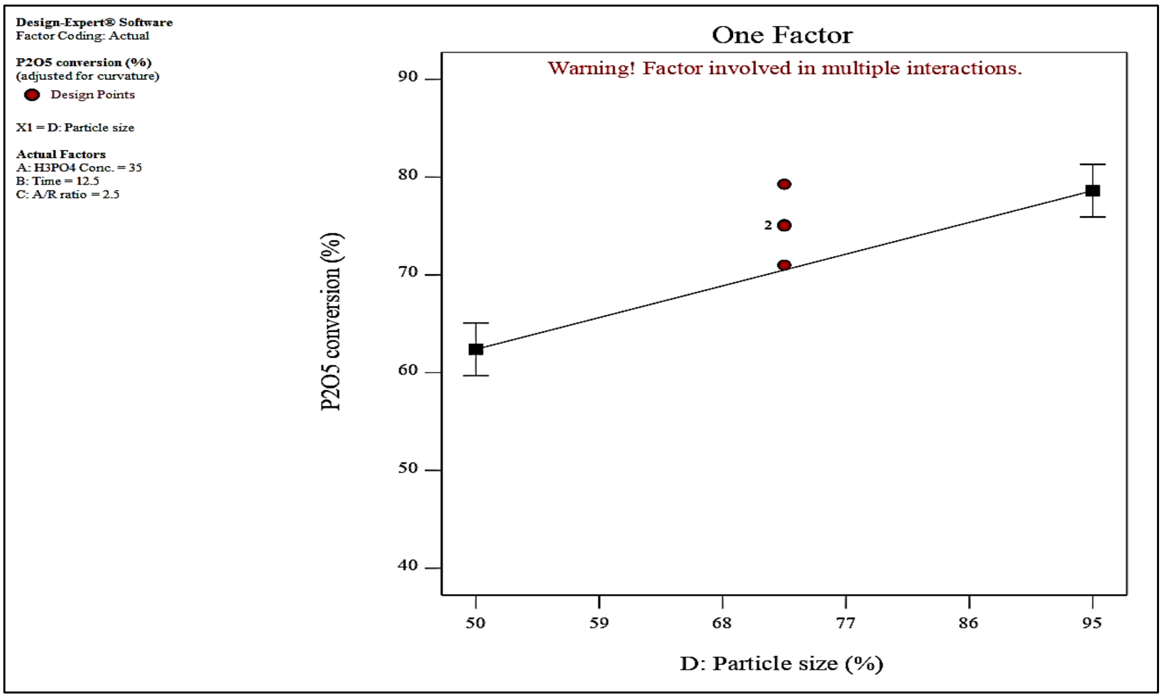

Figure5.4. Effect of phosphate ore particle., mish on P_2O_5% conversion efficiency.

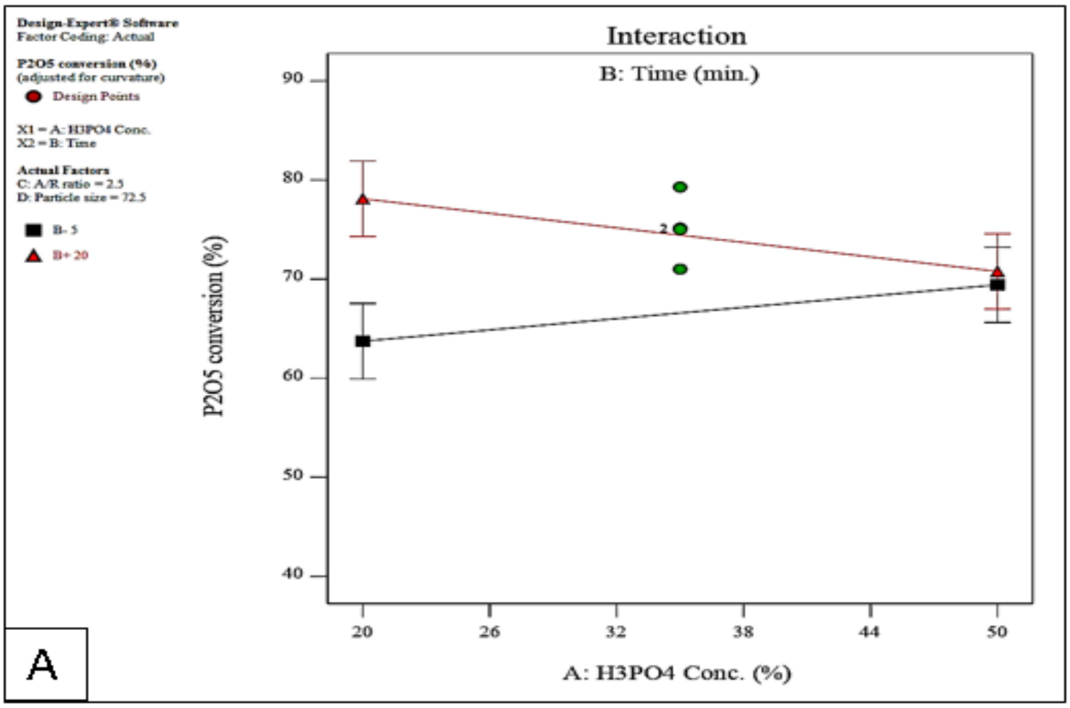

Figure 6.a. Interaction effect plot for A (H_3PO_4 acid concentration) and B (Time).

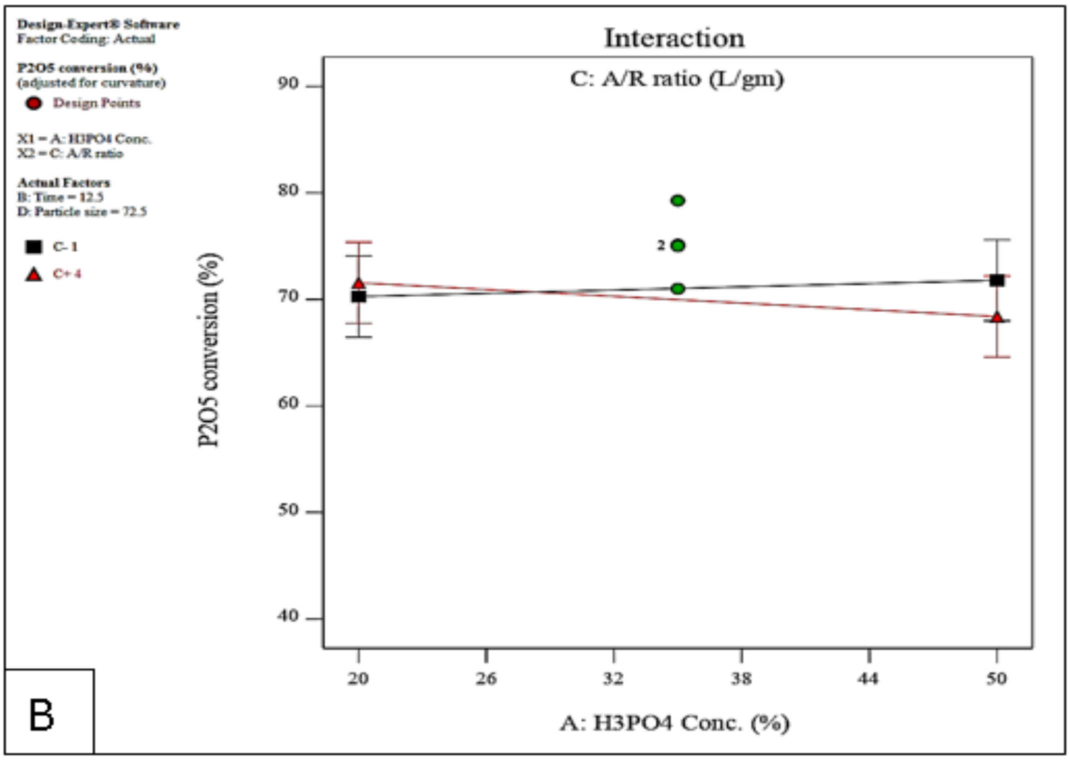

Figure6. b. Interaction effect plot for A (H_3PO_4 acid concentration) and C (S/L) ratio.

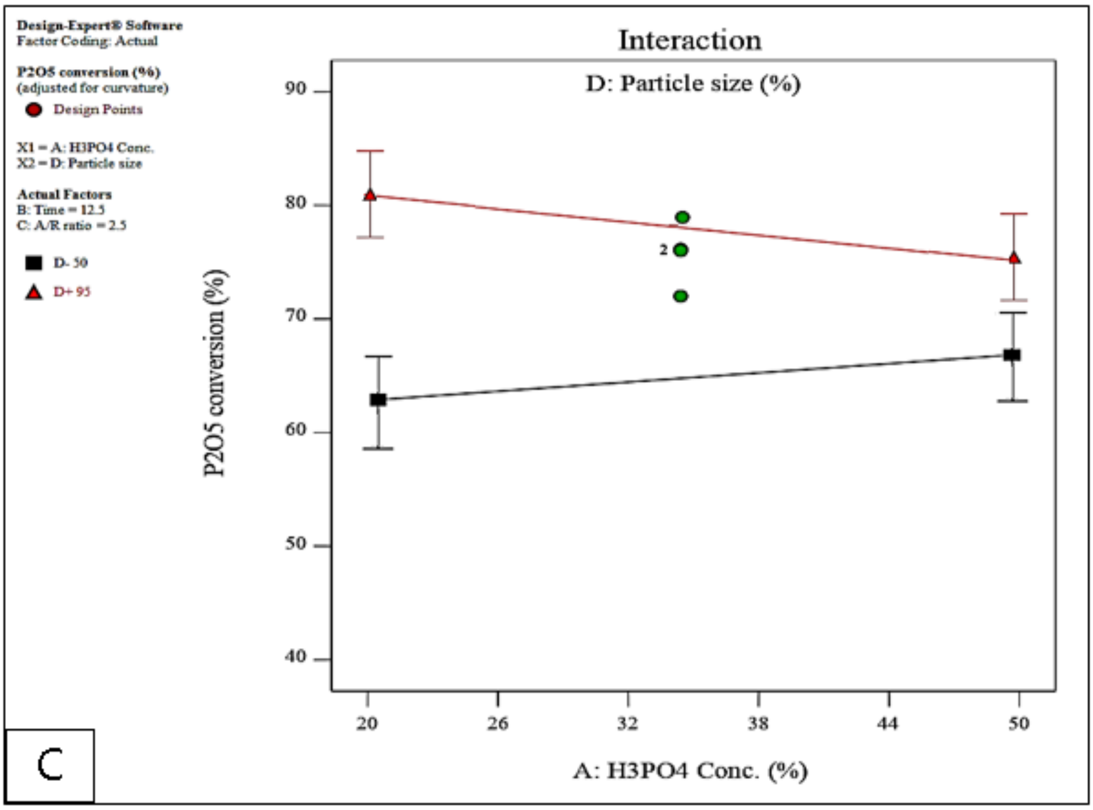

Figure 6.c. Interaction effect plot for A (H_3PO_4 acid concentration) and D (particle size).

Figure 6(a, b, c and d) had strong interaction through P_2O_5 conversion process because the lines in these cells are converging, suggesting a strong impact on the conversion efficiency.

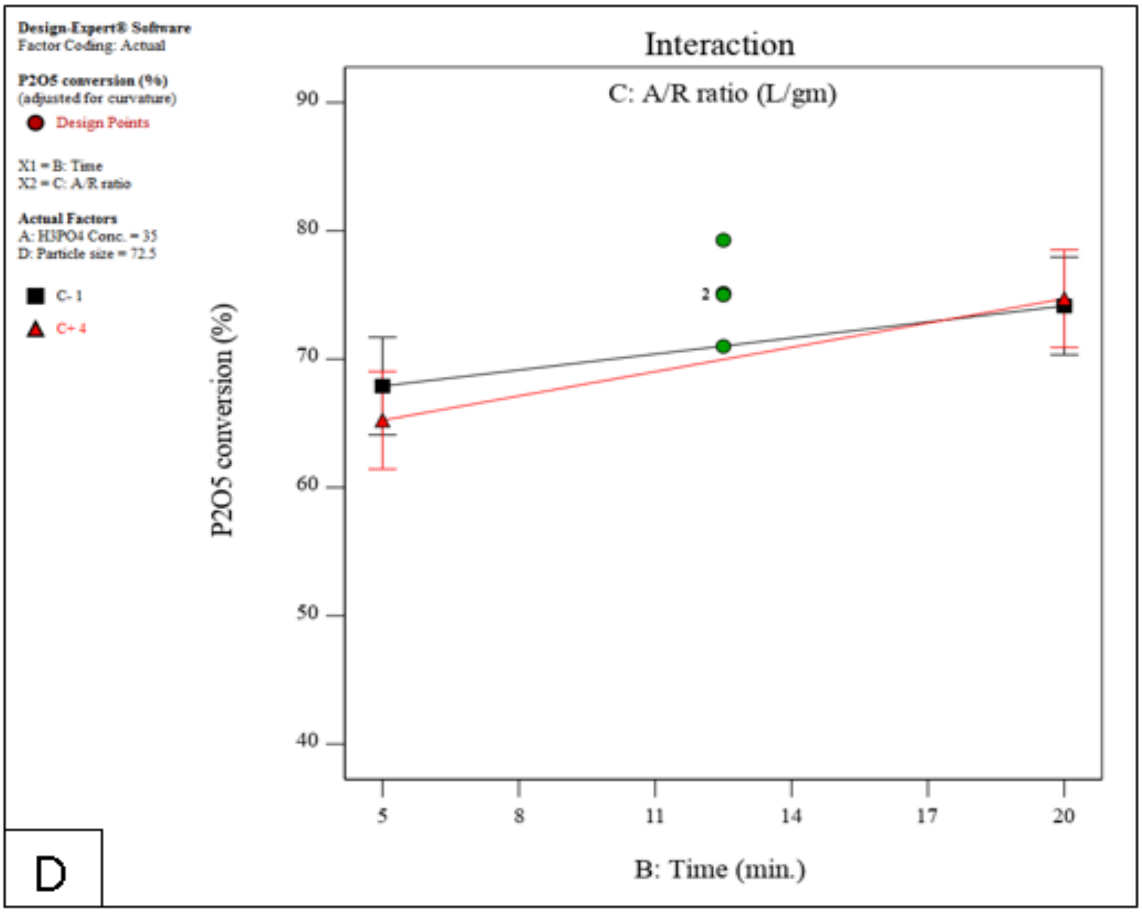

Figure 6. d. Interaction effect plot for B (time) and C (S/L) ratio.

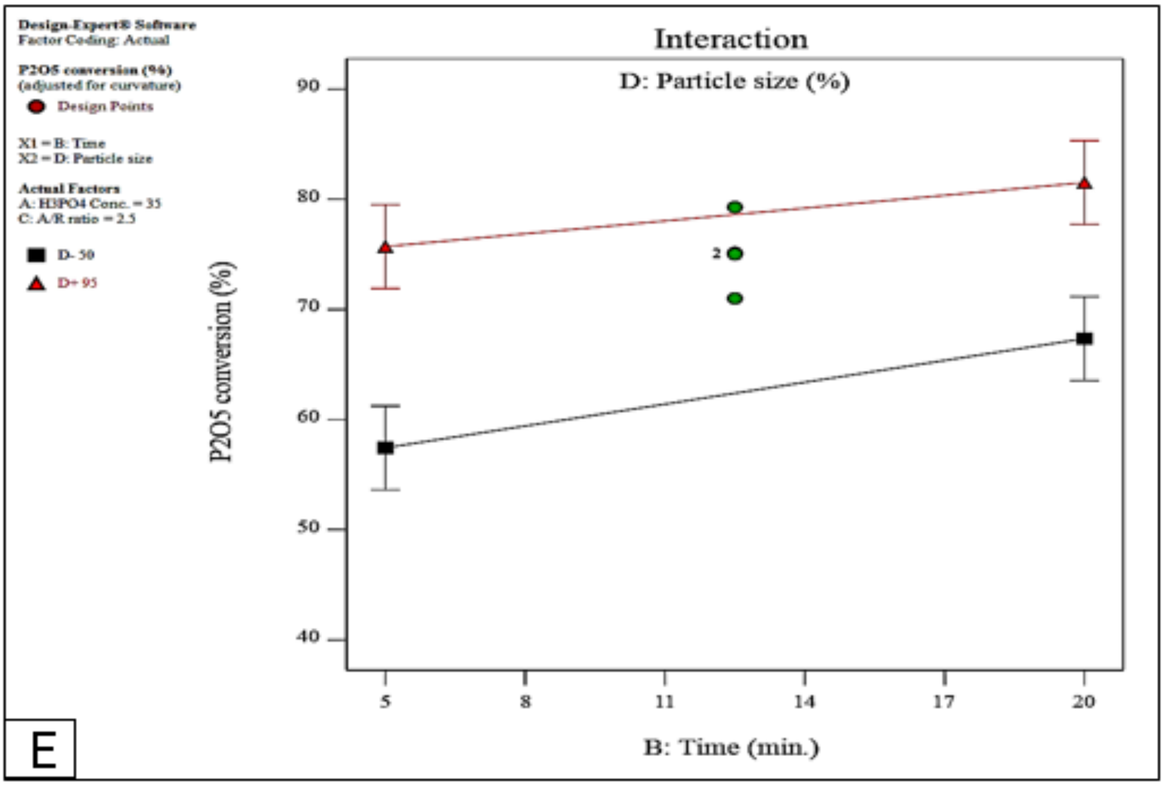

Figure 6.e. Interaction effect plot for B (time) and D (particle size).

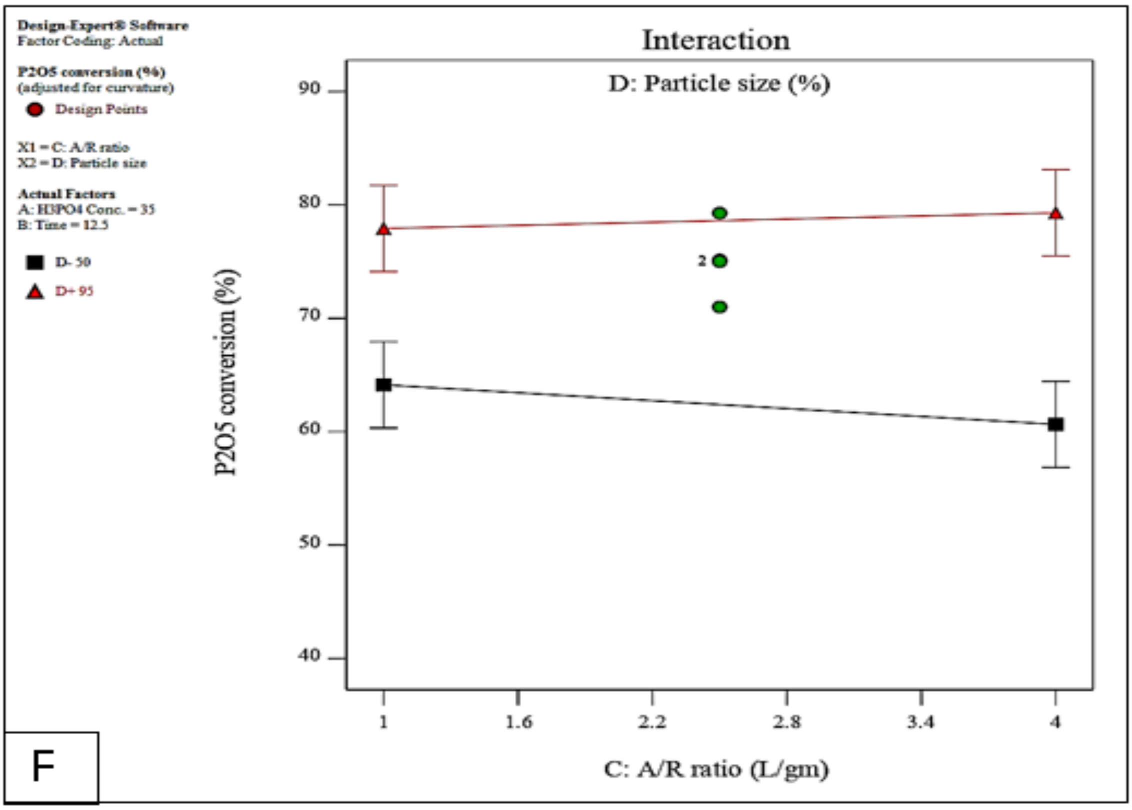

Figure 6. f. Interaction effect plot for C (S/L) ratio and D (particle size).

5. Model's verification.

The modeling validity of the partially acidulated phosphate ore in terms of the overall conversion efficiency percentage for the production of triple superphosphate and the desired results obtained using the recombined fitted - models for each level of the central composite design matrix are determined by the scatter diagram as in **Figure7**. The predicted results are calculated using Equation 8. P_2O_5 conversion efficiency has a linear regression correlation coefficient R^2 of 0.9839.

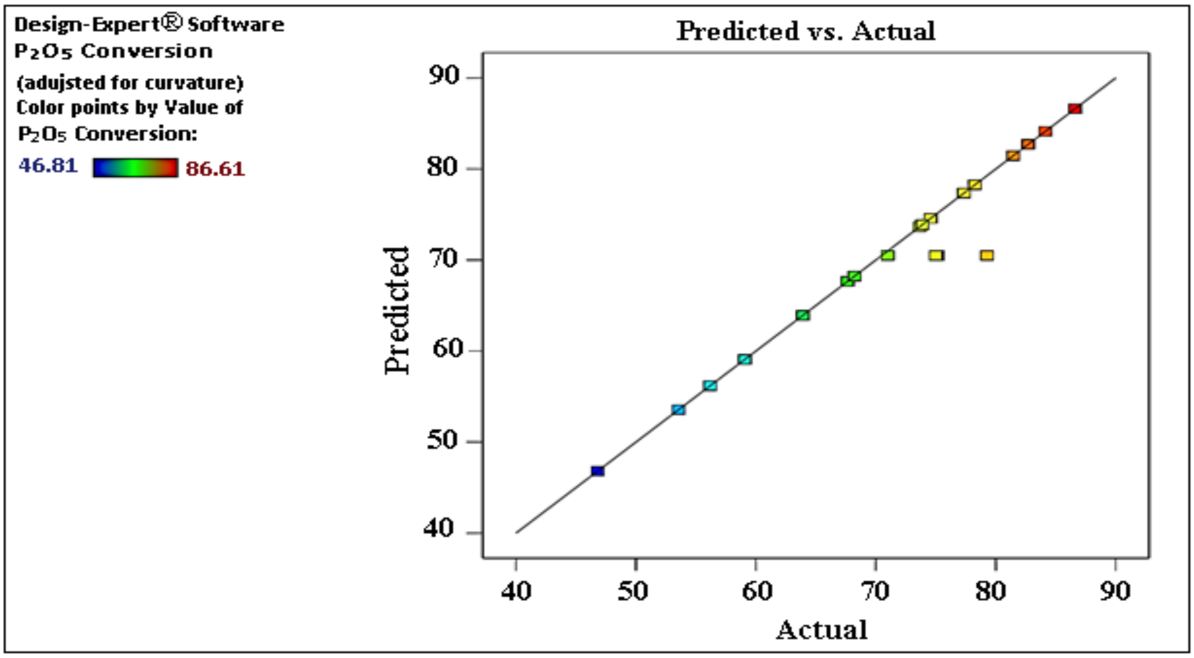

Figure 7. Scatter diagram of experimental values versus predicted values by Equations (8).

Statistically, this means that the independent variables can explain 98.39 % of the sample variation, which means that only about 1.61 % only of the total variation was not explained, this proves the high significant of the model and demonstrates that the first-order polynomial **Eqn (8)** is sufficient for determining the optimum level of the investigated factors in the partially acidulated phosphate ore process, and concluded a good fit to the experimental data. Three-dimensional (3D) graphs were created to acquire a better understanding of the main and interaction effects of P_2O_5 conversion efficiency. The surface plot is a graphical illustration of how two variables might affect the output (conversion efficiency) at the same time. **Figure 8** shows a 3D plot of the effect of adjusting the two parameters for P_2O_5 conversion efficiency: phosphoric acid concentration (A) and reaction time (B). Any factor that was not visible in the plot was preserved at the lowest possible level. The figure demonstrates that using the experimental parameters of run 15, the maximum P_2O_5 conversion efficiency could be attained. According to the experimental conditions of run 15, the curve varied similarly as the concentration of phosphoric acid declined substantially with increasing the time from 5 to 20 min, and then P_2O_5 conversion efficiency reaches its highest value.

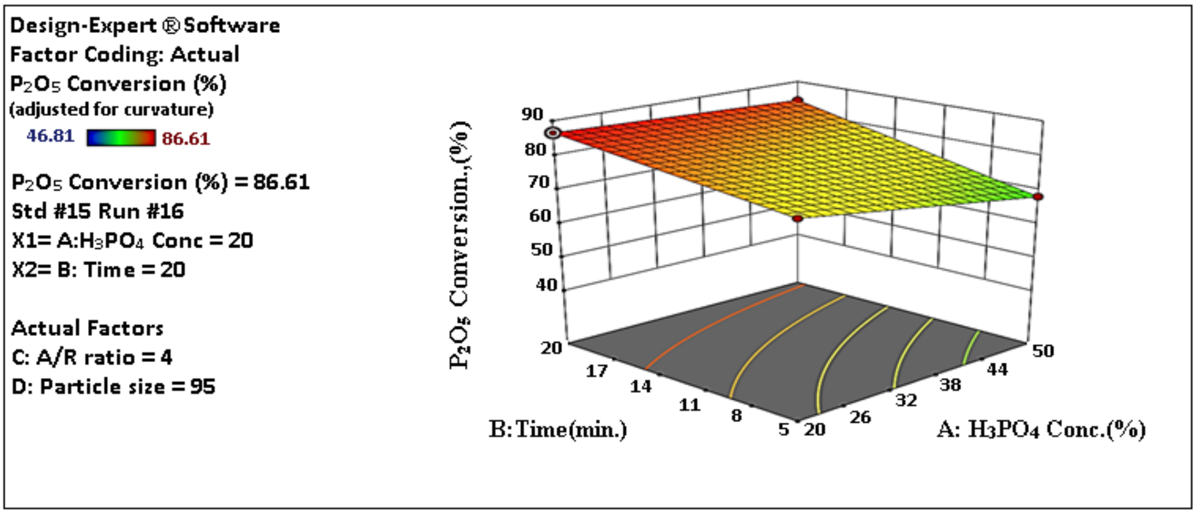

Figure 8. 3D-Surface plots of P_2O_5 conversion (%)efficiency process.

6. Defining the characteristics of the captured triple superphosphate.

Based on the aforementioned investigations, a process for phosphorus pentaoxide conversion to triple superphosphate (TSP) using phosphoric acid was developed under the obtained optimal conditions. The amorphous triple superphosphate generated (TSP) was filtered, rinsed with water and dried at 100 °C. Utilizing XRF, XRD, and FT-IR, the generated TSP's characterization was accomplished. **Table 12** depicts the produced TSP's chemical composition. It is evident from the table that the produced solid was primarily composed of P_2O_5 and calcium carbonate, with traces of some insignificant impurities like; Ni, Cu, Cd, Pb, and As. The TSP also contains a number of impurities, including rare earths and uranium. The X-ray diffraction (XRD) spectrum showed one phase **(Figure 9)**. The identification of the obtained peaks clarify that the obtained solid is mainly composed of phosphorus pentaoxide P_2O_5 and calcium carbonate $CaCO_3$. Other weak peaks are attributed to the existing of impurities, such as unreacted rock, silicate, phosphate and metallic impurities, e.g. Na, Al, and Fe. The FTIR study of the prepared TSP was performed using Frontier FTIR (Bruker Optics). The FTIR spectra as shown in **Figure10**. The obtained spectra showed O–H stretching band for water at 3439 cm^{-1}, P-O (PO_4^{-3}) bands characterized to $10Ca(H_2PO_4)_2$ compound at 1443, 872 and 701 cm^{-1}, P–H band at 2506 cm^{-1}, and Si-O stretching band at 1107 cm^{-1}.

Table 12. Chemical analysis of the produced TSP.

Constituent, %			
Component		**Component**	
Total P_2O_5	43.22	**Unreacted rock**	0.05
CaO	21.37	**Free water**	3.5
SiO_2	1.1	**W/S P_2O_5**	12.35
SO^{--}_4	0.48	**C/S P_2O_5**	17.34
Fe_2O_3	0.09	**Free acid as P_2O_5**	0.45
Na_2O	0.42	**F**	0.01
Al_2O_3	0.08	**Cl**	< 0.01
Constituent, ppm			
U	6.7	**∑ REEs**	105

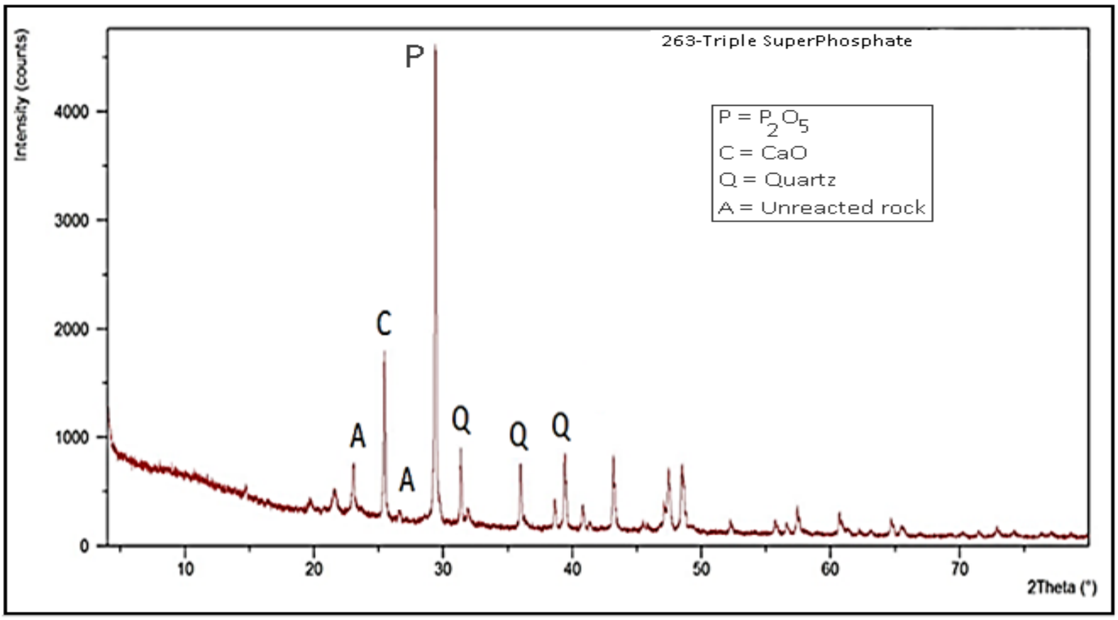

Figure 9. X-ray diffraction pattern of the produced triple superphosphate.

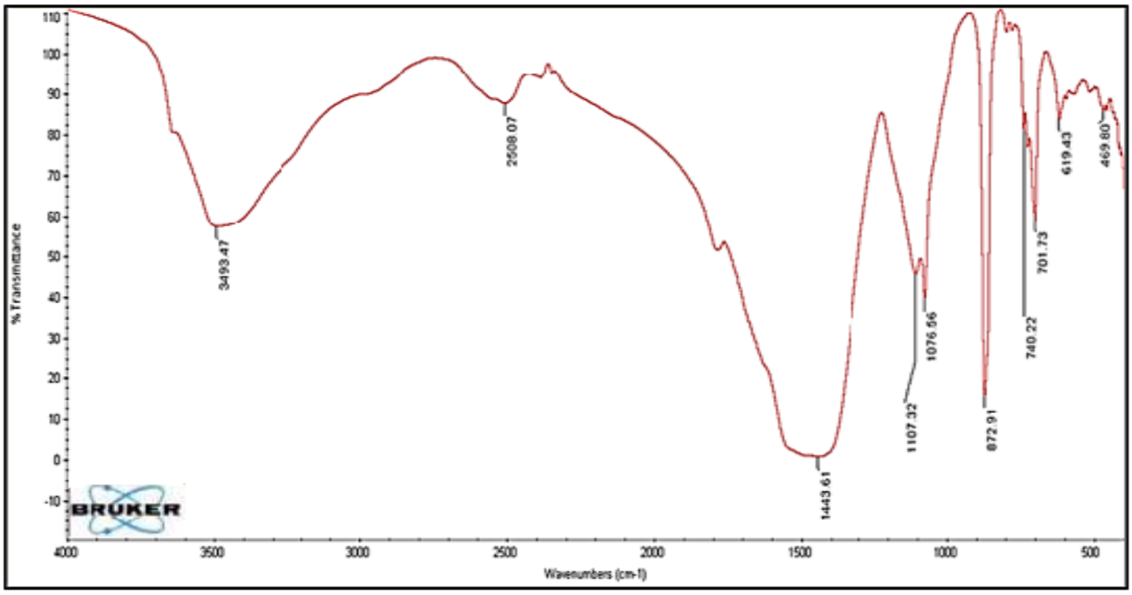

Figure 10. FT-IR spectrum of the produced TSP.

Conclusion

The partially acidulated phosphate ore has been investigated using phosphoric acid solution under various experimental conditions to optimize the preparation efficiency of TSP in terms of P_2O_5 conversion efficiency involving both (OFAT) and (DOE) methodologies. The results obtained by (OFAT) methodology shows and clears only, the effect of main variables, that raw ore particle size and H3PO4 acid concentration, S/L ratio and reaction time have positive effect on the TSP preparation efficiency, while (DOE) methodology clears the effects of main variable and also the effect of variables interactions. In this respect the results obtained from the Design of Experiment methodology(DOE) clear that the most important factor effect the conversion efficiency is the raw material particle size factor (D), while the factor time B and the interactions ABD, BCD, AB and ACD have moderately effect at above 98% confidence interval. According to Design Expert 11.0.0 software's statistical modeling, the best circumstances for P_2O_5 conversion efficiency are 95% (-100) mesh, 20% H_3PO_4 solution, 1:4 S/L ratio, and 20 min denning time. During the preparation of triple superphosphate fertilizer, a P_2O_5 conversion efficiency of 86.61% was effectively obtained under these ideal conditions. These findings supported the model's experimental validity and the presence of ideal conditions. This demonstrated that the model created for P_2O_5 conversion efficiency was accurate and trustworthy. Finally, it is evident that, as an alternative to conventional methods that are time-consuming and polluting in terms of raw materials and the working environment, computational statistical design is a promising and effective in the development and preparation of triple superphosphate through acidification with highly concentrated phosphoric acid.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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(2023) ; https://revues.imist.ma/index.php/morjchem/index