

# Modeling and Optimization of Two Clays Acidic Activation for Phosphate Ions Removal in Aqueous Solution by Response Surface Methodology

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## Abstract

This work deals with phosphate ions removal in aqueous solution by adsorption carried out using two clays, both in activated form. One, non-swelling clay, rich in kaolinite, is associated with illite and quartz. The other, swelling, richer in montmorillonite, is associated with kaolinite, illite and quartz. Seven factors including these two clays were taken into account in a series of experimental designs in order to model and optimize the acidic activation process favoring a better phosphate removal. In addition to the choice of clay nature, the study was also interested in the identification of the mineral acid, between hydrochloric acid and sulfuric acid, which would promote this acidic activation. Response Surface Methodology (RSM) was used for this purpose by sequentially applying Plackett and Burman Design and Full Factorial Design (FD) for screening. Then, a central composite design (CCD) was used for modeling the activation process. A mathematical surface model has been successfully established. Thus, the best acidic activation conditions were obtained by activating the montmorillonite clay with a 2N sulfuric acid solution, in an acid/clay mass ratio of 7.5 at 100°C for 16H. The phosphate removal maximum rate obtained was estimated at 89.32% ± 0.86%.

## Keywords

Clay Acidic Activation, Modeling, Optimization, Phosphate Removal, Response

## 1. Introduction

Phosphorus is after nitrogen the fertilizing element that most often limits the development of crops [1]. For this reason, to improve crop yields, fertilization with soil is recommended [2]. In addition, phosphorus is also used for the manufacture of livestock feed as well as for the manufacture of detergents. Phosphorus is absorbed by plants in soil solution and in water as monovalent ( $\text{H}_2\text{PO}_4^-$ ) and divalent orthophosphate ( $\text{HPO}_4^{2-}$ ) anions, each accounting for 50 percent of total phosphorus at neutral pH (pH 6 - 7). At pH 4 - 6,  $\text{HPO}_4^{2-}$  represents about 100 percent of the total phosphorus in solution. At pH 8,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  represent respectively 20 percent and 80 percent of the total phosphorus [3]. The presence of phosphates in water, however, carries risks for aquatic fauna [4] and human health [5]. In fact, the excessive presence of nutrients (phosphate and nitrate) due to human activities disrupts the life cycle of aquatic environments and causes eutrophication [6]. Whether natural or anthropogenic, eutrophication causes several adverse effects on the aquatic ecosystem and human health due to the appearance of algae and cyanobacteria. It also increases the costs of water treatment [7]. According to the United Nations report [8], a part of the world's population lacking access to safe drinking water, continues to drink untreated surface water drawn from streams (river, backwater and lakes). It then becomes imperative to think to a prior treatment of wastewater before any discharge into watercourses or before any consumption. Many treatment techniques already exist in treatment plants.

There are biological treatments [9] and physicochemical processes, based on precipitation operations of calcium, iron or aluminum salts [10] or on coagulation, flocculation of aluminum sulfate [11]. All these techniques are complex and generate secondary sludge. They are so delicate to implement for the popularization of a wastewater treatment method.

In this context, adsorption appears to be an easy, more efficient and, above all, reusable technique by appropriate desorption processes [12]. Adsorption on materials such as clays might be of economic interest because of their abundance and relative ease of access [13]. These phosphate-loaded clays can also be used in agriculture as a phosphate fertilizer [14].

Acidic activation is one of the techniques used to improve the adsorption properties of clays [15]. It consists of replacing inter-foliar cations with protons to increase the adsorbent surface by increasing adsorption sites [16]. The chemical attack is therefore accompanied by a progressive dissolution of the structural cations ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$ ) and  $\text{Si}^{4+}$ , respectively hosted in the octahedral and tetrahedral sites [17]. This dissolution can then lead to dislocation, see the collapse of the crystal lattice and the formation of amorphous silica [18] [19]. These

structural changes depend on several factors, mainly the nature of clay and activation parameters [20].

It turns out that the studies of phosphate ions removal do not focus on optimizing the activation conditions favoring this adsorption. Activation factors are most often fixed, and the study focuses on the optimization of adsorption parameters such as pH, adsorption time, mass of sorbent, the normality of the sorbate [21] [22]. This present study is concerned with the optimization of the activation conditions. Experimental design were used for this purpose given the number of factors selected

Working tool that facilitates decision-making, experimental design is here used to optimize and modeling clays acidic activation. In this study, seven (7) factors that may influence acidic activation process were considered. These are the type and normality of the acid solution, the acid/clay mass ratio, the temperature and activation duration, the nature or the type of the clays as well as their granulometries. This work aims to model this activation process by the establishment of a predictive mathematical model and to determine the optimal conditions that would favor a better phosphate ions removal and investigate the interactions between the different factors.

Ultimately, what type of clay and mineral acid does the activation process promote? And under what conditions of acid normality, temperature and duration of activation will this be achieved? The interest of this study lies in the methodology used to achieve the expected objective. Response Surface Methodology (RSM) operated through Plackett and Burman Design (PBD), Full Factorial Design (FD) and Central Composite Design (CCD) are used for this purpose. The results obtained, compared with those of the literature on acid activation of montmorillonite and kaolinite, were used to judge the relevance of the methodology used.

The interest of this study lies in the fact that the clays used in this work, one swelling and the other non-swelling, were never used simultaneously for this type of work. The use of experimental designs made it possible to study for the first time the interactions between the factors influencing the acid activation process of clays for phosphate ions removal. Finally, the other element of interest derives from the modeling of this activation process which makes it possible to predict, depending on the nature of the clay and other factors such as the normality of the acid solution, the temperature and the duration of activation, the probability that acidic activation will contribute to promote phosphate ions capture.

## **2. Material and Methods**

### **2.1. Clay Extraction and Purification**

The Clays was collected from two cities of Côte d'Ivoire. One was collected at the northern in the savannah zone, on a site of geographical coordinates 08°08.94'N and 05°05.95'W [23]. This clay, rich in montmorillonite and associated with illite,

kaolinite and quartz has been called MTMO for the following. The other comes from the deposit with coordinates 05° 15'N and 04° 20'W in the south, on the lagoon bank [24]. That one, rich in kaolinite, associated with illite and quartz is designed by KAO for the following. Samples were taken at a depth between 1.5 and 2 m.

Each clay is separated into two granulometric fractions: One less than 50  $\mu\text{m}$  and the other less than 2  $\mu\text{m}$ . The first phase is obtained by wet sieving. The powders are obtained after drying in an oven at 105°C and are denoted MTMO<sub>50</sub> for the clay MTMO and KAO<sub>50</sub> for the KAO clay. The second phase is extracted from the first according to the Holtzapffel protocol [25] based on the action of 50 volumes H<sub>2</sub>O<sub>2</sub> (50%, MERCK) followed by a 0.5 N hydrochloric acid solution (37%, MERCK) treatment. These attacks aim to eliminate organic matter and carbonates respectively. The treatment is followed by washing this sample in a 1 M solution of sodium chloride (PROLABO) for 24 hours, three times and each time the exchange solution (NaCl) was renewed. This treatment aims to facilitate the separation of clay particles from silts and fine sand and to promote homo-ionization. The granulometric phases of 2  $\mu\text{m}$  size noted MTMO<sub>2</sub> and KAO<sub>2</sub>, are obtained in the last step by siphoning and drying the supernatant of the upper 20 cm of a test tube of 2 L, after 24 hours of sedimentation.

## 2.2. Activation Process

The activation was carried out either with hydrochloric acid or with sulfuric acid in a reactor consisting of a three-necked flask of 500 cm<sup>3</sup>, surmounted by a refrigerator. The flask is kept stirring in a heat bath. The clay masses and the amounts of acid are set in various mass acid/clay ratios. The duration time  $t$  of the activation is counted from the moment; the temperature in the flask reaches that fixed for the activation. The activated clay is then centrifuged at 4000 rpm for 15 minutes and then washed with distilled water until acid is removed. Washing is stopped when the supernatant no longer gives any reaction of sulfates with barium chloride for activation with sulfuric acid and, in the case of hydrochloric acid, when silver nitrate test is negative. The activated clay is then dried at 105°C.

## 2.3. Adsorption Test

Activation effectiveness is evaluated from the abatement rate  $Y$  of the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions representing the removal rate of these ions, expressed in percentage; Equation (1).

$$Y = \frac{C_0 - C}{C_0} * 100 \quad (1)$$

$C_0$  and  $C$  in mg·L<sup>-1</sup>, respectively represent the initial and residual mass concentrations of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions.

Tests were carried out at 30°C in an oscillating water bath of JULABO SW1 type. Each time, 1 g of activated clays is introduced into a 100 mL flask containing

25 mL of a 40 mg/L synthetic  $\text{KH}_2\text{PO}_4$  (MERCK) solution. The pH was adjusted at 4.7 using 1N sulfuric acid solution or 1 M sodium hydroxide solution according to previous works [26]. The adsorption time was set at 24 hours. Eventually, the mixture is centrifuged at 4000 rpm for 15 minutes and then filtered (0.45 microns). Residual phosphate ions determination in the filtrate is carried out by spectrophotometry at 880 nm with a JASCO-type spectrophotometer, after the formation of the blue-colored phosphor-molybdic complex [27].

## 2.4. Modeling and Optimization

The optimization was carried out through Response Surface Methodology (RSM). This technique aims to quantitatively determine the response function variation represented in this study by the abatement rate  $Y$ , with respect to the factors having a significant influence [28] [29]. These influencing factors are first identified from a screening study. RSM and screening are the two main uses of design of experiments (DOE). DOE consist of offering few experiments while varying all the factors simultaneously in order to obtain as much information as possible [30]. This approach is diametrically opposed to the unitary method also called “one factor at a time” which consists in varying each factors, one after the other, by affecting all the possible values [30]. Since the response function is defined, the implementation of DOE begins with factors presentation, experimental domain definition, matrix design elaboration, essays execution in a random and ends with factors effects determination. The experimental domain is a range of variations allowed for the factor in which it will be possible to carry out the experiments. This range is delimited in a two-level experimental design, by the low level (-1) and the high level (+1). These levels are numbers in the case of a quantitative factor, and a state for a qualitative factor. The screening was carried out in this study after two experimental designs application, namely Plackett and Burmann Design (PBD) and the Full Factorial Design (FD). The development of the first is based on the seven-factor of Hadamard matrix. **Table 1** shows the coded ( $X_i$ ) and non-coded ( $U_i$ ) values of the seven variables examined as well as

**Table 1.** Factors and Experimental Domain of Plackett and Burmann design.

Coded variables ( $X_i$ )	Factors ( $U_i$ )	Experimental Domain	
		Low level (-1)	High level (+1)
$X_1$	$U_1$ : Temperature ( $^{\circ}\text{C}$ )	35	80
$X_2$	$U_2$ : Acid type	$\text{H}_2\text{SO}_4$	HCl
$X_3$	$U_3$ : Acid normality (N)	1	5
$X_4$	$U_4$ : Activation duration (H)	3	10
$X_5$	$U_5$ : Clay granulometry ( $\mu\text{m}$ )	2	50
$X_6$	$U_6$ : Mass ratio	3.5	7.5
$X_7$	$U_7$ : Clay nature	montmorillonite	kaolinite

\*The low (-1) and high (+1) levels represent limits of possible values or states of the factors.

the experimental domain used for this design.

The matrix is obtained by right circular permutation of the basic pattern about seven factors: ++++--- [31]. The last line is made up of signs -. The factors effects determination allowed establishing a relationship between the explained variable  $Y$  response function and the explanatory variables representing the  $X_i$  factors. This relationship is presented in the form of a 1<sup>st</sup> degree model where all interactions between factors are neglected [32]. For seven (7) factors, the model is written as indicated by Equation (2):

$$Y = b_0 + \sum_{i=1}^7 b_i X_i \quad (2)$$

where,  $b_0$  represents the constants (or average effect) of the model and  $b_i$  the factors effects determined by the least square method or by software. The factors coefficients obtained at the end of this screening have helped to show the relevance of factors. The coefficient  $b_i$  is statistically different from zero and the factor  $X_i$  is considered for the following of the study if the absolute value of its  $b_i$  coefficient is greater than two times the experimental standard deviation  $\sigma_e$  [32]. The  $\sigma_e$  value is given by Equation (3).

$$\sigma_e = \frac{\sigma}{\sqrt{n}} \quad (3)$$

$\sigma$  is the standard deviation of the repetitions average performed under the conditions of one of the tests if there is a qualitative factor or, from the test at the center if there are only quantitative factors [32].

The second experimental design used is the Full Factorial Design (FD;  $2^k$ ) with the  $k$  factors considered relevant from the previous design. FD allowed to investigate the possible interactions between these factors, to face modeling of the activation process by a first-degree model taking into account the interactions (Equation (4)), as well as to define the final experimental domain to be used for optimization [28].

$$Y = b_0 + \sum b_i X_i + \sum \sum b_{ij} X_i X_j; \quad i \neq j \quad (4)$$

Here  $b_{ij}$  represent the interaction effects of 2 order. At the end of the data processing, the Pareto diagram gives the effective contribution of each factor. These contributions are calculated with Equation (5):

$$P_i = \frac{b_i^2}{\sum_{i=1}^6 b_i^2} \quad (5)$$

$b_i$  are the main coefficients and interaction coefficients. Experimental results led to a CCD with the  $q$  factors having the highest contributions.

The CCD experiment matrix has been built using three sets of essays, including  $2^q$  in FD,  $2 \times q$  star essays and  $n$  central essays [28] [30].

Tests at the center will be used to estimate the experimental error and to enforce the optimality criteria characterized by the pseudo-orthogonality of the matrix and the isovariance of the response throughout the experimental domain. CCD allowed establishing a second-level model to describe the process being

studied. The corresponding mathematical model is given in the form of Equation (6) below:

$$Y = b_0 + \sum b_i X_i + \sum \sum b_{ij} X_i X_j + \sum b_{ii} X_i^2 + e; \quad i \neq j \quad (6)$$

where  $b_{ii}$  represents the coefficients of the squares and  $e$  is a random error. The optimal conditions for activation are subsequently deduced.

A multiple linear regression program using the NEMROD-W 9901 French version software [33] is used to determine factor coefficients and all statistical estimates. The validation of models has been motivated by determination coefficients interpretation,  $R^2$  and  $R_A^2$  given by NEMROD-W.  $R_A^2$  corresponds to the adjusted value of  $R^2$ .  $R^2$  is defined as the ratio between the explained variance and the total variance [34]. The total variance takes into account the variance explained and that due to the residuals [30] [35].  $R_A^2$  always less than  $R^2$ , allows to consider the number of variables necessary for the theoretical model establishment because a high value of  $R^2$  can sometimes be due to an excess of factors [35] [36]. According to Lambert *et al.* [37] and to Joglekar & May [38], the model could be validated if  $R^2$  is greater than 0.80. But for Baudot [36] and Scibilia [35], adequacy between a theoretical model and experimental results must be accepted considering  $R_A^2$  rather than  $R^2$ ;  $R_A^2$  has to be greater than 0.77.

These conclusions were tested by other statistical analysis tools such as Analysis Of Variance (ANOVA) or coefficient of variation C.V (Equation (7)) from the residuals which represent the difference between the experimental values and the values calculated from the predictive model.

$$C.V = \frac{1}{N} \left[ \sum_{i=1}^N \left| \frac{Y_{\text{exp}} - Y_{\text{calc}}}{Y_{\text{exp}}} \right| \right] \times 100 \quad (7)$$

$N$  is the number of tests. According to these data, the model is accepted if the coefficient of variation is less than 5% [39].

## 3. Results and Discussions

### 3.1. Factors Screening

#### 3.1.1. Plackett and Burman Design

**Table 2** presents Hadamard matrix, experimental design, response values  $Y$  calculated using eq 1, factors coefficients and experimental errors  $2\sigma_e$ . The experimental standard deviation  $\sigma_e$  1.48 was determined with the five-run repeat of the test 1; the values obtained as percentage of abatement being respectively 29.75; 28.25 and 24.75. The analysis of the coefficients suggests that the acid solution normality ( $X_3$ ), the duration of activation ( $X_4$ ) and clay's nature ( $X_7$ ) are the most influential factors. This result would support the idea that the acidic activation would depend on the nature of the clay [40], and that montmorillonite-rich clays would be more prone to acidic activation than those, richer in kaolinite [41].

According to Srasra *et al.* [42], and Christidis *et al.* [43], this is due to the acid activation that causes structural changes in the smectites. These changes, according

**Table 2.** Experimental Hadamard matrix with phosphate removal rate.

n° exp	Factors														Phosphate Removal $Y_{exp}$ (%)
	Coded Variables							Real Variables							
	$X_1$	$X_2$	$X_3$	$X_4$	$X_5$	$X_6$	$X_7$	$U_1$ (°C)	$U_2$	$U_3$ (N)	$U_4$ (H)	$U_5$ (µm)	$U_6$	$U_7$	
1	+1	+1	+1	-1	+1	-1	-1	80	HCl	5N	3	50	3.5	MTMO	<b>28.75</b>
2	-1	+1	+1	+1	-1	+1	-1	35	HCl	5N	10	2	7.5	MTMO	<b>38.75</b>
3	-1	-1	+1	+1	+1	-1	+1	35	H <sub>2</sub> SO <sub>4</sub>	5N	10	50	3.5	KAO	<b>22.5</b>
4	+1	-1	-1	+1	+1	+1	-1	80	H <sub>2</sub> SO <sub>4</sub>	1N	10	50	7.5	MTMO	<b>58.75</b>
5	-1	+1	-1	-1	+1	+1	+1	35	HCl	1N	3	50	7.5	KAO	<b>23.75</b>
6	+1	-1	+1	-1	-1	+1	+1	80	H <sub>2</sub> SO <sub>4</sub>	5N	3	2	7.5	KAO	<b>20</b>
7	+1	+1	-1	+1	-1	-1	+1	80	HCl	1N	10	2	3.5	KAO	<b>38.75</b>
8	-1	-1	-1	-1	-1	-1	-1	35	H <sub>2</sub> SO <sub>4</sub>	1N	3	2	3.5	MTMO	<b>42.5</b>
	Coefficients							$b_1$	$b_2$	$b_3$	$b_4$	$b_5$	$b_6$	$b_7$	$b_0$
	Values							2.35	-1.725	-6.725	5.5	-0.8	1.1	-7.975	34.225
	Experimental error $2\sigma_e$										2.96				

to them, induce an increase of their specific surface area and the average pore volume, thereby contributing to improving their adsorption and discoloration capacity. The other sample, consisting only of non-swelling clay (kaolinite and illite), for which the access of protons to their octahedral layers is strongly restricted, does not benefit from the effect of acid activation on adsorption.

However, the nature of the clay being a qualitative factor, it has been fixed for the continuation. From then on, we would have only two factors left. However, the temperature ( $X_1$ ) with a coefficient  $b_1$  of 2.35 close to  $2 \times \sigma_e$  has been considered in the following as a relevant factor for this process. At the end of this screening, three factors were selected: Normality, temperature and duration of activation. This selection of factors is consistent with that of Gannouni *et al.* [18] and Haffane *et al.* [44] who present these three factors as the most relevant to conduct acidic activation of clays.

The normality of the acid solution, for example, influences the kinetics of attack [19] [45]. According to these authors, it is observed that more the acid solution is concentrated, shorter is the activation duration and lower is the temperature. Conversely, if the concentration is low, the activation duration is longer, and the temperature is higher. They often locate the temperature between 30 and 120°C, the acid normality from 0.5N to 20N, the activation duration from 3 to more than 20 hours; and the mass acid/clay ratios between 3 and 8. Later on, the values of the non-influencing factors were fixed according to the experimental design methodology, at their low or high level, by considering the sign of their coefficient  $b_i$ . Thus, the optimization of the activation for this phosphate removal was sought by using the MTMO clay with 2 µm particle size activated by sulfuric acid in an acid/clay mass ratio of 7.5.

The use of sulfuric acid for activation experiments agrees with those of other



studies. In fact, Pushpaletha *et al.* [46] reported that the catalytic properties of their clay are improved when activation is carried out with sulfuric acid rather than with hydrochloric acid. Kara *et al.* [47] observed that the adsorption capacity of their clay increased after activation when they successively used the mineral acids, in the order: nitric acid, hydrochloric acid and sulfuric acid. Regarding particle size, the particle size fraction smaller than 2  $\mu\text{m}$  is better because it would contain more clay minerals than the sieve fraction at 50  $\mu\text{m}$  in which these minerals would remain buried in larger particles [48].

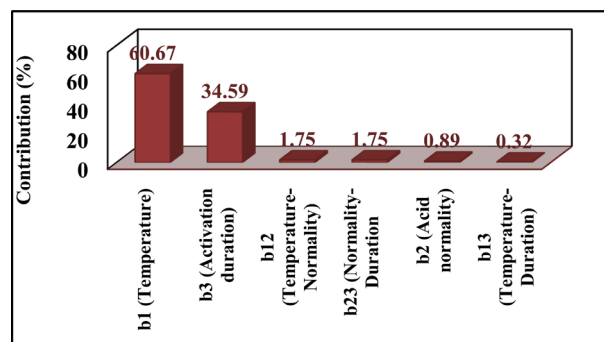
### 3.1.2. Full Factorial Design (FD)

This FD conducted with three factors was interpreted after eight ( $2^3$ ) essays. The experimental area of this design is defined as follows: The temperature factor ( $U_1$ ) with a low level set at 65°C and the high level at 90°C; the normality factor ( $U_2$ ) with the low level 0.5N and the high level 2N, then the activation duration factor ( $U_3$ ) with the low level 8H and the high level 12H. **Table 3** presents the matrix and experimental designs; test results and coefficients of variation.

The data processing with the software, gives the first-degree polynomial (Equation (8)). **Figure 1** depicts the Pareto diagram highlighting the relevance of key factors and interactions.

**Table 3.** Experimental factorial matrix ( $2^3$ ) and phosphate removal rate.

n° exp	Factors						Phosphate removal $Y_{\text{exp}}$ (%)	Theoretical phosphate removal $Y_{\text{calc}}$ (%)	Coefficient of variation (%)
	Coded variables			Real variables					
	$X_1$	$X_2$	$X_3$	$U_1$ (°C)	$U_2$ (N)	$U_3$ (H)			
1	-1	-1	-1	65	0.5	8	31.25	34.22	9.5
2	+1	-1	-1	90	0.5	8	51.25	48.28	5.8
3	-1	+1	-1	65	2	8	38.75	35.78	7.66
4	+1	+1	-1	90	2	8	42.5	45.47	6.99
5	-1	-1	+1	65	0.5	12	43.75	40.78	6.79
6	1	-1	+1	90	0.5	12	53.76	56.72	5.51
7	-1	+1	+1	65	2	12	43.75	46.72	6.79
8	+1	+1	+1	90	2	12	61.25	58.28	4.85



**Figure 1.** Pareto diagram giving factors contributions and their interactions.

$$Y = 45.78 + 6.41X_1 + 0.78X_2 + 4.84X_3 - 1.09X_1X_2 + 0.47X_1X_3 + 1.09X_2X_3 \quad (8)$$

According to **Figure 1**, only the temperature ( $X_1$ ) and the activation duration ( $X_3$ ) have the highest contributions. The interactions between the factors as well as the contribution of normality remain marginal because their effects are statistically null. Temperature and activation duration appear as the most relevant in the activation process for  $\text{H}_2\text{PO}_4^-$  ions removal. Their global contribution is 95.26% corresponding to 60.67% for temperature and 34.59% for the activation duration.

This result agrees with the observations of Khoek et Lim [45] and Tyagi *et al.* [19]. They reported that the temperature and the duration of activation are higher as the concentration of the acid is low. Indeed, the acid solution normality fixed in this FD between 0.5 and 2N, can be considered low compared to extreme values used up to 20N [19] [45]. Under these conditions, the temperature and the duration of activation remain the factors, which control this activation process. Sulfuric acid solution normality was set at 2N, taking into account the positive sign of the coefficient  $b_2$ .

Validation of the first-degree model was examined based on the statistical data provided by the NEMROD software through ANOVA. These include the coefficients of determination  $R^2$  and  $R_A^2$  with respective values of 0.885 and 0.194, the average of the coefficient of variation of 6.73%, the contribution of residues of 11.51% in the total sum of the squares and 58.6% of model significance. These data do not allow to validate this model because although  $R^2$ , lower than 0.80 is acceptable [37] [38], the other indices are not likely to allow this validation. Indeed, the coefficient of variation [39] and the sum of the squares due to residuals [30] are not less than 5%. A CCD was then conducted with the two most influential factors highlighted by the Pareto diagram namely the temperature and the duration of activation. The very low value of  $R_A^2$  less than 0.77, shows that the use of three factors for process modeling was excessive and would confirm the importance of  $R_A^2$  [35] [36].

### 3.2. Modeling and Optimization

With the two factors those are temperature and activation duration ( $q = 2$ ), the CCD consisted of four FD tests, four in-star tests and five central essays [30]. Each factor is ranged between  $-r$  and  $+r$  equal to  $2^{q/4}$  *i.e.* between  $-1.414$  unit and  $+1.414$  unit. These coded values translate into real values  $50^\circ\text{C}$  and  $100^\circ\text{C}$  chosen as the limit of the experimental domain for the temperature ( $U_1$ ); 8 hours and 16 hours for the duration ( $U_2$ ). The explored experimental domain and the levels attributed to each variable are presented in **Table 4** [32].

**Table 4.** Variables and experimental domain of CCD.

	$-r = -1.414$	$-1$	$0$	$+1$	$+r = +1.414$
$X_1$ ( $^\circ\text{C}$ )	50	57	75	93	100
$X_2$ (H)	8	9	12	15	16

Test results, predicted responses, residuals, and percentages of deviation are shown in **Table 5**; the FD tests are shown in tests 1 to 4, star and center tests respectively in tests 5 to 8 and 9 to 13.

Equation (9) represents the theoretical response of the abatement rate of phosphate removal.

$$Y = 43.120 + 6.380X_1 + 10.901X_2 + 10.901X_1^2 + 4.775X_2^2 + 3.718X_1X_2 \quad (9)$$

The coefficients of determination associated with this model, given by the NEMROD software are 0.952 for  $R^2$  and 0.917 for  $R_A^2$  all higher than respectively to 0.80 and 0.77 and the average of the deviation percentages 2.67%, which is less than 5%. These statistical results show that the 2-degree polynomial model proposed for modeling the clay activation for  $\text{H}_2\text{PO}_4^-$  ions removal is satisfactory. This conclusion is supported by the analysis of the variance (ANOVA) for the predicted response (Equation (9)) of this process as reported in **Table 6**.

**Table 5.** Experimental design and results of the central composite matrix.

n° exp	Factors				Experimental Phosphate removal $Y_{\text{exp}}$ (%)	Theoretical phosphate removal $Y_{\text{calc}}$ (%)	Residues (%)	Coefficient of variation (%)
	Coded variables		Reals variables					
	$X_1$	$X_2$	$U_1$ (°C)	$U_2$ (H)				
1	-1	-1	58	9	39.97	38.66	1.31	3.28
2	+1	-1	93	9	40.8	42.06	-1.26	3.09
3	-1	+1	58	15	55.51	54.1	1.41	2.54
4	+1	+1	93	15	69.05	72.22	-3.17	4.59
5	-1.414	0	50	12	41.32	42.83	-1.51	3.65
6	+1.414	0	100	12	67.25	64.08	3.17	4.71
7	0	-1.414	75	8	38.75	37.25	1.5	3.87
8	0	+1.414	75	16	69.45	68.08	1.37	1.97
9	0	0	75	12	43.75	43.12	0.63	1.44
10	0	0	75	12	42.97	43.12	-0.15	0.35
11	0	0	75	12	43.38	43.12	0.26	0.60
12	0	0	75	12	41.75	43.12	-1.37	3.28
13	0	0	75	12	43.75	43.12	0.63	1.44

**Table 6.** ANOVA for phosphate removal by adsorption on MTMO activated clay.

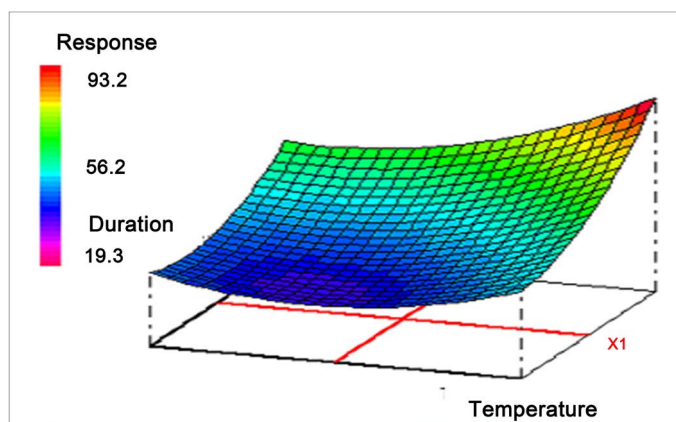
Source of variation	Sum of squares	Freedom degree	Middle square	Ratio	Significance
Regression	1602.76	5	320.553	464.4344	***
Residue	81.3053	7	11.615		
Validity	78.5445	3	26.1815	37.9332	**
Error	2.76	4	0.6902		
total	1684.0653	12			

**Table 6** indicates that the sum of the squares of the residuals that is 81.3053 is smaller than a third of the sum of the squares of the regression equal to 534.25 with a high rate of significance materialized by the three stars (Tinsson, 2010). It also indicates that the sum of the squares due to the error in the residuals is worth *i.e.* only 3.39% or 0.16% of the sum of the squares. Then, it appears that these errors can be neglected. The model expressed by Equation 9 can effectively be used to describe correctly the process studied.

The theoretical response area depicted in **Figure 2** indicates that the maximum rate of abatement that can be achieved is 93.20%

Resolution of Equation (9) indicates that this theoretical maximum is obtained with temperature equal to +1.414 in coded value *i.e.* 100°C in real value and duration of activation of +1.414 *i.e.* 16H. The high duration obtained is related to the low acidic solution concentration. Indeed, Jahouach [49] reported that discoloration of olive oils by activated clays with a 15N concentrated sulfuric acid at 70°C has only needed 3H for the optimization of its process. Besides, Adjia [50] found that the adsorption of heavy metals from wastewater by clay occurs at 30°C with a 0.5N hydrochloric acid solution for 24 hours.

For the confirmation of the process studied here, three additional control tests were carried out with the activated montmorillonite clay sample under the conditions defined by the coordinates of the theoretical optimum (**Table 7**). The phosphate captures obtained are 88.65%; 89.03% and 90.30% whose average is 89.32%. The standard deviation of 0.86 and a coefficient of variation representing



**Figure 2.** Response surface for optimization of adsorption of  $\text{H}_2\text{PO}_4^-$ .

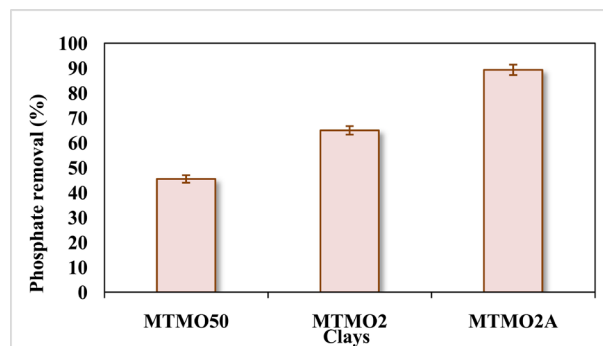
**Table 7.** Determination of optimal condition proposed by Nemrod W Software and validation tests.

n° exp	Factors				Theoretical phosphate removal $Y_{\text{calc}}$ (%)	Experimental Phosphate removal $Y_{\text{exp}}$ (%)	Average Experimental Phosphate removal $Y_{\text{exp}}$ (%)
	Coded variables		Reals variables				
	$X_1$	$X_2$	$U_1$ (°C)	$U_2$ (H)			
14	+1.414	+1.414	100	16	93.30	88.65	
15	+1.414	+1.414	100	16	93.30	89.03	89.32
16	+1.414	+1.414	100	16	93.30	90.30	

4.26% compared to the theoretical maximum of 93.20%, less than 5% validates the conclusions of this optimization although there is a difference between them. This difference taken into account by the model through the ANOVA revealed according to **Table 6** that the sum of the squares due to the error in the residues is worth only 3.39% corresponding to 0.16% of the sum of the square.

### 3.3. Comparison Tests between Activated and Non-Activated Clays

**Figure 3** presents with standard deviations, the  $\text{H}_2\text{PO}_4^-$  ion removal percentage using non-activated clays  $\text{MTMO}_{50}$ ,  $\text{MTMO}_2$  and activated clay  $\text{MTMO}_{2A}$ , obtained under the optimal activation conditions with  $\text{MTMO}_2$ .



**Figure 3.** Phosphate removal percentages with non-activated  $\text{MTMO}_{50}$  and  $\text{MTMO}_2$  and activated  $\text{MTMO}_{2A}$  clay samples.

This Figure shows that lower particle sizes improve phosphate ion removal. Phosphate removal percentage increases from 45.51% ± 0.79% to 65.02% ± 0.81% respectively for  $\text{MTMO}_{50}$  and  $\text{MTMO}_2$ . In fact, clay treatment favors aluminum-silicon chemical binding breaks. So, sites where  $\text{H}_2\text{PO}_4^-$  ions can be adsorbed increases. Due to their lower size,  $\text{MTMO}_2$  clay offers more active sites for phosphate ion adsorption and the phosphate removal increase for this sample. These sites could be the non-satisfied valences (+Al-OH) of broken bindings in layer edges according to Wey [51] and Garcia [52]. Acidic activation which favors bindings breaks increase non-satisfied valences sites [53]. Consequently, more phosphate ions are involved in adsorption reaction. Then, phosphate removal increases up to 89.32% with  $\text{MTMO}_{2A}$ .

## 4. Conclusion

This study aimed to determine the optimal conditions for acidic activation of two clays respectively rich in montmorillonite and kaolinite for dihydrogen phosphate ions removal in aqueous solution through surface response methodology. Seven factors that are acidic solution type and normality; activation duration and temperature; nature and particle size of the clays as well as the acid/clay mass ratio were considered for this purpose. A preliminary screening study showed the interest of working with montmorillonite clay for which acid activation was beneficial as opposed to kaolinite-rich clay. The activation process

was subsequently interpreted using a CCD by a second order polynomial model. Optimal activation conditions are finally summarized in the use of Montmorillonite clay of 2  $\mu\text{m}$  particle size, activated with 2N sulfuric acid, in a mass ratio of 7.5 at 100°C for 16 H. An abatement rate of 89.32% with a standard deviation of 0.86 was achieved under these conditions. This work ultimately determined, depending on the nature of the clay and other acid activation factors, the likelihood that acidic activation of clay would favor phosphate ions removal.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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