

PROCESSING OF WADI QENA KAOLINITIC WHITE SANDS BY SELECTIVE DISPERSION AND LEACHING FOR INDUSTRIAL USES

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ملخص:

تم الحصول على كمية كبيرة من الكاولين (- 25 ميكرون) بعد النخل الرطب لخام الرمال البيضاء الكاولينية بمنطقة وادي قنا وذلك بعد معالجتها عن طريق عملية الغسيل الاحتكاكي ويعتبر هذا المنتج هو تطبيق اقتصادي كبير في العديد من الصناعات. في هذه الدراسة، تمت معالجة هذا المنتج (- 25 ميكرون) لإزالة المعادن الملونة (أكاسيد الحديد والتيتانيوم) وتشمل هذه المعالجة خطوتين: أولاً، يتم تشتيت جزيئات الكاولين، وفي الوقت نفسه يتم تجميع جزيئات المعادن الملونة. تمت دراسة العوامل الأكثر تأثيراً في عملية التشتيت / التجميع لتحديد قيمها المثلى، وهي جرعة المجمع ودرجة الحموضة. وقد تم تقليل أكسيد الحديد من 0.623% إلى 0.542% وأكسيد التيتانيوم من 1.669% إلى 0.924% عند الظروف المثلى لجرعة المجمع ودرجة الحموضة. ثانياً، تم خفض نسبة أكاسيد الحديد / التيتانيوم من (-25 ميكرون) عن طريق الإذابة الحمضية، بواسطة حمض الأكساليك وحمض الكبريتيك. وقد تم دراسة العوامل الأكثر تأثيراً على عملية الإذابة وهي تركيز حمض الكبريتيك، حمض الأكساليك ووقت الإذابة وذلك من خلال الإستعانة بأحد برامج تصميم التجارب وتحليل البيانات احصائياً لإختيار الظروف المثلى للإذابة ومعرفة مدى إرتباط القيم بعضها البعض. وقد تم الحصول على أفضل الظروف لتركيز حمض الكبريتيك، تركيز حمض الأكساليك ووقت الإذابة وهي 4.99 مولار، 10.1 غرام / لتر و 2.28 ساعة على التوالي. وقد تم تقليل محتوى أكسيد الحديد إلى 0.2% ومحتوى أكسيد التيتانيوم إلى 0.18% في منتج الكاولين النهائي. مما يضمن إمكانية استخدام هذا المنتج في التطبيقات الصناعية المختلفة.

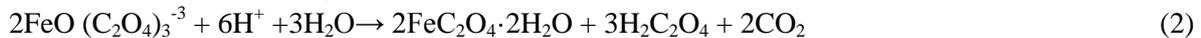
ABSTRACT

A considerable amount of -25 μm kaolin was obtained during the processing of wadi-Qena kaolinitic white sands by attrition scrubbing. This kaolin product is obtained by desliming the kaolinitic white sand. Such product is of a great economic application in many industries. In this study, this product (-25 μm kaolin) was treated or beneficiated to remove colored minerals, (iron / Titanium oxides). The treatment includes two steps. **First**, the kaolin particles are dispersed and at the same time the colored mineral particles are flocculated. The most affecting parameters in dispersion/flocculation process, flocculant dosage and pH are investigated to select its optimum values. In this step and under optimum conditions of flocculant dosage and pH, it was possible to decrease iron oxide from 0.623% to 0.542% and titanium oxide from 1.669% to 0.924%. **Second**, it was attempted to further decrease iron/titanium oxides of -25 μm kaolin by acidic leaching, oxalic acid followed by sulfuric acid. The most affecting parameters which include sulfuric acid concentration, oxalic acid concentration and leaching time. The response surface methodology (RSM) coupled with Box- Behnken design (BBD) and analyses of variance (ANOVA) were performed to optimize the leaching process and determine the main and interaction effects. The response factors were taken as iron oxide content and titanium oxide content. In this context, it was found that the second order polynomial regression model is satisfactory as the predicted responses showed a good agreement with the experimental data. The optimum conditions for sulfuric acid concentration, oxalic acid concentration and leaching time were found as 4.99 molar, 10.1 g/l and 2.28 hr. respectively. Under these experimental conditions, the iron oxide content and titanium oxide content in kaolin product approached 0.2 % and 0.18 % respectively. Which assures the possibility of using such product in different industrial applications.

Key words: White sand, kaolin, attrition scrubbing, flotation, Disperse/Flocculation, polyacrylamide, leaching, sulfuric acid, oxalic acid.

1. INTRODUCTION

Kaolin (hydrated aluminum silicate, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), is an industrial clay of important economic benefit. Its fine particle size, platy shape, inertness, non-toxicity, as well as high brightness and whiteness make it a more versatile mineral, with applications in a wide variety of industries. Commercial kaolin resources are found as sedimentary deposits and as weathering or hydrothermal alteration product of rocks containing a high proportion of alumino-silicate minerals [1]. Crude kaolin ore deposits are contained in a variety of Kaolinitic rock types. Primary kaolin generally describes a kaolin ore altered from an igneous or metamorphic rock that was kaolinized in situ by hydrothermal or weathering processes [2]. Kaolin is considered an important industrial mineral because of its excellent firing properties and relatively high melting point. Its major application or use is often extended to include paint, ceramic, rubber and paper industries. In the paint industry, kaolin is used very extensively in water-based paint system as a functional extended pigment with moisture content exceeding 1%. Resistivity test using the conductivity bridge gives an indication of residual soluble salts in paints due to the presence of kaolin. In the rubber industry, kaolin is used because of its reinforcing and stiffening properties. Fine kaolin gives good resistance to abrasion. There are some tests based on properties of kaolin that are to be conducted before using it for the manufacturing of rubber. They include water setting characteristics, oil absorption, stress/strain, tear resistance, abrasion resistance, heat generation, energy rebound, extrusion and plasticity, hardness, aging characteristics, water absorption and free moisture [3]. Kaolin also is chemically inert over a relatively wide pH range, white in color and has good covering power when used as a pigment or extender. It is soft, non-abrasive and has a low conductivity of heat and electricity. Some uses of kaolin, such as in paper coating, or as fillers in paints and plastics require very rigid specifications including particle size, color and brightness and viscosity. There are other kaolin uses require no specifications where the chemical composition is most important such as in cement industry. The paper industry consumes the largest amount of kaolin where it is used both as filler and as a coating material on the paper surface to improve the quality of printing [4]. There are basically two ways for removing titanium impurities by selective dispersion / flocculation: i) disperse kaolin in a water suspension, flocculate the TiO_2 impurities and separate them by sedimentation and ii) disperse kaolin in a water suspension, flocculate the kaolinite, keep impurities in suspension and separate them by sedimentation [5]. The use of organic acids has been very efficient for the whitening of kaolin. The effectiveness of several organic acids (sulfuric acid with oxalic acid or citric acid) to dissolve iron from iron compounds was evaluated. Sulfuric acid with oxalic acid was found the most promising because of its acid strength, good complexing characteristics and high reducing power, compared to other organic acids [6]. Leaching of iron oxides with oxalic acid takes place via the following equations [7, 8].



The present work aims to study the characterization of -25 μm kaolin clay produced from processing of white sands to improve its physical properties. This was carried out by applying selective dispersion of kaolin and flocculation of colored minerals technique. Also, the removal of iron and titanium from -25 μm kaolin clay product in acidic leaching conditions using organic acids was also attempted. In the leaching studies the effect of important parameters was investigated using Mathematical Statistical Factorial Design expert version 9.0 with box-Behnken design technique.

1.1 Location and Geology

Wadi-Qena is one of the largest wadies in the Eastern Desert of Egypt. Glass sands constitute most of the Lower Paleozoic Naqus Formation and are exposed in an area of approximately 450 km^2 at the western margin of the northern part of Wadi-Qena. The quantity of sands available is enormous.

Probable reserves were estimated to be 1 billion metric tons. It consists predominantly of white silica sands and Kaolinitic lenses [9]. Wadi-Qena covers an area of approximately 400 km², represented by the western side of the valley of Qena, which separates the components of the basement rocks (Albraikambria) on the eastern side and the components of sedimentary rocks (Alvaneruszy) on the western side. This area includes white sand an actress created bell’s and white sand covers by Alglala Created which consists of sandstone, shale and limestone containing the fossils. Thickness of this component (Alglala) changes from one area to another [10].

2. Material and methods

The used material is -25 µm kaolin product from attrition of Wadi-Qena Kaolinitic white sand. This Kaolinitic white sand was found as consolidated deposits without overburden (Open Pit Quarry). This deposit is situated in the North Eastern Desert, Egypt. It occupies an area of about four hundred square kilometers with coordinates, Latitudes 27° 30', 28° 10' N and longitudes 32° 30', 32° 40' E. Beneficiation processes were conducted on the studied -25 kaolin product to improve their quality to meet the Standard specifications of industrial kaolin. These investigations or processes includes: 1- Laboratory work deals with chemical analysis and mineralogical analysis of feed. 2- Beneficiation processes which include selective dispersion and flocculation. 3- Leaching process with sulfuric and oxalic acids and its Optimization using the Mathematical Statistical Factorial Design.

2.1 Preparation of -25 µm size fraction sample

50 kg of unconsolidated Kaolinitic white sand sample have been collected. It was kindly supplied by the Egyptian geological survey and mining authority. This sample was mixed thoroughly then a representative sample weighing about 1kg was obtained by coning and quartering. Attrition scrubbing experiments were conducted on the representative sample using Denver flotation machine which use attrition kit unit. The attrition scrubbing conducted under the following conditions, Pulp density: 70 solid % by wt., Impeller speed: 2400 rpm, Attrition time: 15 min and Attrition mode: once, twice and triple. To obtain -25 µm fraction, after the sample was wet sieved and deslimed on 0.6, 0.106 and 0.025 mm screens and dried as shown in table (1). The mineralogical analysis of the -25 µm fraction using XRD is shown in table (2) and Fig. (1).

Table (1): indicates Desliming of Wadi-Qena Kaolinitic white sand after attrition scrubbing.

size fraction, µm	Wt., %	Cum. Ret., %
+ 600	1.35	1.35
- 600 + 106	84.25	85.5
- 106 + 25	4.7	90.2
-25	9.8	100
Total	100	

Table (2): Mineralogical composition of -25 µm fraction

Major constituent	Chemical composition
Quartz, low	SiO ₂
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄

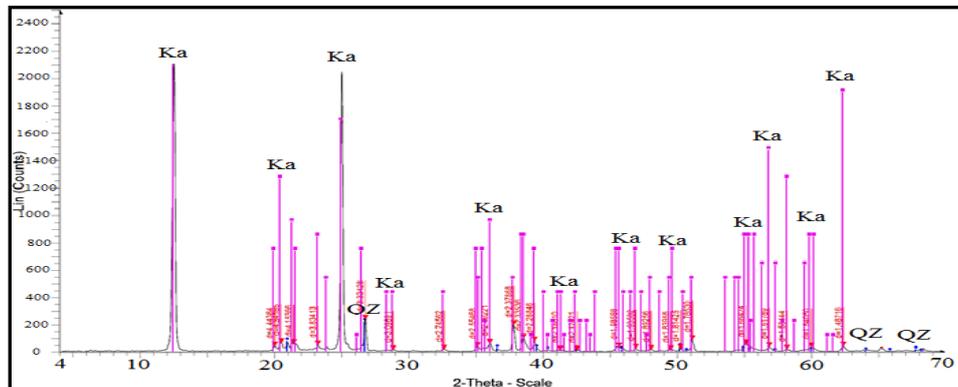


Figure1: pattern of -25 µm fraction

The chemical analysis of the -25 μm sample from attrition and Desliming Kaolinitic white sand ore using (XRF) analysis revealed that the sample composed of various oxides such as SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , TiO_2 , Na_2O , K_2O and P_2O_5 . The major oxides are shown in table (3).

Table (3): Complete chemical analysis of -25 μm fraction.

Constituent	Wt.%
SiO_2	47.724
Al_2O_3	36.054
Fe_2O_3	0.623
TiO_2	1.669
CaO	0.319
MgO	0.158
Na_2O	0.082
K_2O	0.039
P_2O_5	0.209
Cl	0.038
SO_3	0.086
ZnO	0.012
ZrO_2	0.053
L.O.I	12.8
Total	100 %

2.2 Beneficiation studies

To obtain the specifications of applications of kaolin, upgrading techniques including selective dispersion of kaolin / flocculation of colored minerals of - 25 μm fraction and leaching of colored mineral oxide of - 25 μm fraction are applied. To optimize the leaching process, Mathematical Statistical Factorial Design version 9.0 was applied.

2.2.1 Selective dispersion of kaolin and flocculation of colored minerals.

Aqueous suspensions of kaolin with 40% solids content were prepared. Sodium silicate (2 kg/ton) followed by Sodium hexametaphosphate (4kg/ton) were added to kaolin clay suspension as dispersants. Sodium hydroxide was added to adjust pH. The suspension was plunged at 1000 rpm for 45 min period. In a second step, kaolin clay suspension was diluted to 12%. The suspension was conditioned at 1000 rpm for 15 min, with different dosage (5, 10, 15 and 20 g/t) of polyacrylamide as surfactant or flocculant for iron oxides. To study the influence of pH on selective flocculation, the pH of suspension was adjusted to 7, 8, 9, 10 and 11. These samples were poured into graduated (250 mL) cylinder, stirred for 2 min and submitted to sedimentation for 30 min. Thereafter the overflow and underflow was separated.

2.2.2 Optimization of the leaching process of -25 μm fraction using Mathematical Statistical Factorial Design

All leaching tests were conducted in a 250 ml conical flask placed over a hot plate magnetic stirrer. 20 g of sample (-25 μm) was added in 100 ml of an acid solutions of different concentrations for different times and constant temperature of 90°C under continuous stirring of 200 rpm. The content was then filtered, repeatedly washed with distilled water to remove any unspent acid, and dried at 120 °C for 2 h. The filter cake was examined by ICP-MS (Inductive coupled plasma mass spectrophotometry) in order to measure its content of Fe and Ti. While acid concentration (sulfuric acid concentration), reducing agent concentration (oxalic concentration) and leaching time were variable parameters, stirring rate and temperature were kept constant during leaching process. The main purpose of the design of the experiment is to find out the common relationship between the multiple process variables in order to determine the optimum operating conditions for the system. It is essential that the design methodology should be economical as well as it should also reduce

experimental time to save both material and personnel cost [11, 12]. This combined process (leaching process) was modeled and optimized using a Box–Behnken design (BBD) with response surface methodology (RSM). The effects of sulfuric acid concentration, oxalic acid concentration and time were investigated. RSM is an empirical optimization technique for evaluating the relationship between experimental outputs (or responses) and factors called X1, X2, X3, etc. This method (RSM) is usually used in combination with factorial design methods such as Box–Behnken designs and central-composite designs. Adopting Box–Behnken designs (BBD) can sharply reduce the number of experimental sets without decreasing the accuracy of the optimization compared with traditional factorial design methods. The minimum and maximum ranges for the three factors are illustrated in terms of coded and uncoded symbols in table (4). In order to evaluate the significance of regression model and effect of the factors and their interactions analysis of variance (ANOVA) was performed. ANOVA is a statistical technique that subdivides the total variation in asset of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [13, 14]. To evaluate the interaction effects of sulfuric acid concentration, Oxalic acid concentration, and time in the formulations; 3-factor, 3-level Box Behnken design was used. A total of 15 experimental runs were generated by design expert software, for which nonlinear computer generated quadratic model is shown below [15, 16].

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_{12} + \beta_{22} X_{22} + \beta_{33} X_{32} \quad (4)$$

Table (4): Minimum and maximum levels of the three studied factors in terms of coded and uncoded symbols.

Variables	Symbols		Levels		
	Coded	uncoded	-1	0	1
Sulfuric concentration (molar)	x ₁	X ₁	1	3	5
Oxalic concentration (g/l)	x ₂	X ₂	10	30	50
Time (hr)	x ₃	X ₃	1	2	3

The number of experiments (N) required for development of BBD is defined as [17].

$$N = 2k(k - 1) + C_0$$

(5)

The relationship between the coded variables and uncoded variables is described by the following equations:

$$x_1 = (X_1 - 3) / 2 \quad (6)$$

$$x_2 = (X_2 - 30) / 20 \quad (7)$$

$$x_3 = (X_3 - 2) / 1 \quad (8)$$

Where X₁, X₂ and X₃ are the uncoded variables and x₁, x₂, and x₃ are the coded variables. Obviously, all three uncoded factors have their own units. By introducing coded variables, we make the factors dimensionless [18]. Box-Behnken response surface experimental design does not only help in determining the accurate values of experimental parameters but also provides the possibility to evaluate the interaction between variables with a reduced number of experiments. Table (5) shows Box–Behnken design for development and optimization of the leaching process of (-25 μm) kaolin fraction using the Mathematical Statistical Factorial Design by Design version.9 Expert Software [19].

Table (5): Box–Behnken design for development of the leaching process for (-25 µm) fraction.

No	Dependent variables		
	Sulfuric concentration (molar)	Oxalic concentration (g/l)	Time (min)
1	5	50	2
2	3	30	2
3	1	30	1
4	3	50	1
5	5	30	3
6	1	30	3
7	5	10	2
8	3	10	1
9	1	10	2
10	3	30	2
11	5	30	1
12	3	50	3
13	3	30	2
14	3	10	3
15	1	50	2

3. RESULTS AND DISCUSSION

3.1 Selective dispersion of kaolin.

3.1.1 Effect of polymer dosage on the physical properties of -25 µm Kaolin.

The effect of flocculant concentration on the flocculation of colored minerals from kaolin was investigated by using different polymer dosages 5, 10, 15, and 20 g/ton. The experiments were carried out at 40% Pulp density during conditioning; 12% Pulp density during separation, 2 kg/t. Sodium silicate, followed by 4 kg/t Sodium hexametaphosphate as a dispersant, pH. 9.5 during conditioning and pH. 9 during separation. It can be seen that the best performance in terms of physical properties of the overflow kaolin product was achieved at polymer dosage of 15 g/ton as shown in Figures (2) and (3). The brightness of dispersed kaolin increased from 76.45 to 81.32, Iso-brightness increased from 84.15 to 86.85, whiteness increased from 91.73 to 93.18, redness decreased from 0.22 to 0.17 and yellowness decreased from 5.84 to 3.96.

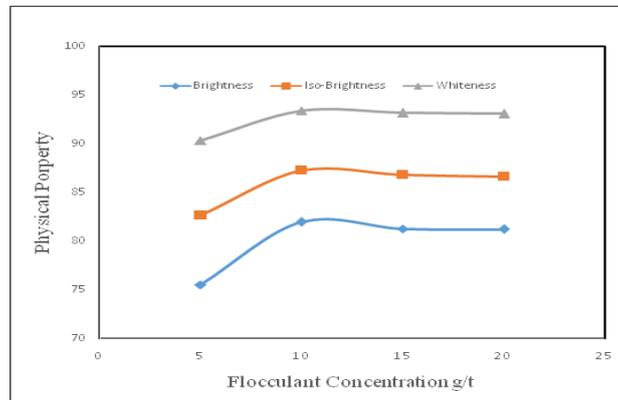


Figure 2. Brightness, Iso-Brightness and whiteness of the kaolin product, after sedimentation step at different flocculant concentrations.

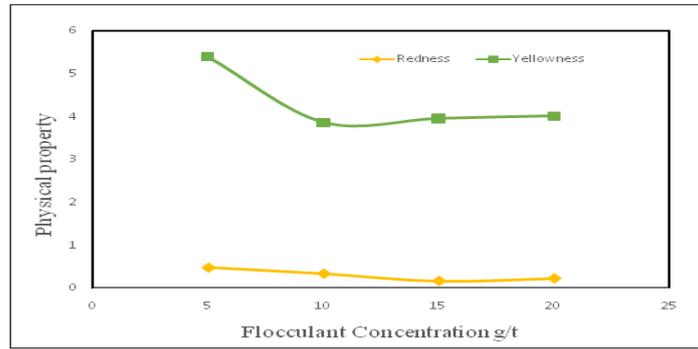


Figure 3. Redness and Yellowness of the kaolin product, after sedimentation step at different flocculant concentrations.

3.1.2 Effect of pH during separation on the physical properties of Kaolin -25 μm product during dispersion of Kaolin and flocculating of colored mineral.

The effect of pH during separation on flocculation of colored minerals was investigated by using different pH values of 7, 8, 9, 10 and 11. The typical operating conditions were conducted as follows 15 g/t flocculant concentration during separation. The experiments were carried out at 40% Pulp density during conditioning; 12% Pulp density during separation, 2 kg/t. Sodium silicate, 4 kg/t Sodium hexametaphosphate and pH. 9.5 during conditioning. The results are shown in figures (4) and (5). It can be seen that the best performance in terms of the physical properties of the overflow kaolin product was achieved at pH 9 for flocculant applied in the present study. The brightness increased from 76.45 to 81.32, Iso-brightness increased from 84.15 to 86.85, whiteness increased from 91.73 to 93.18, redness decreased from 0.22 to 0.17 and yellowness decreased from 5.84 to 3.96. The selective adsorption of flocculants is better at pH 9, where negative charges present on the kaolin surfaces help in adsorbing the titaniferrous mineral surfaces by polyacrylamide polymers [20].

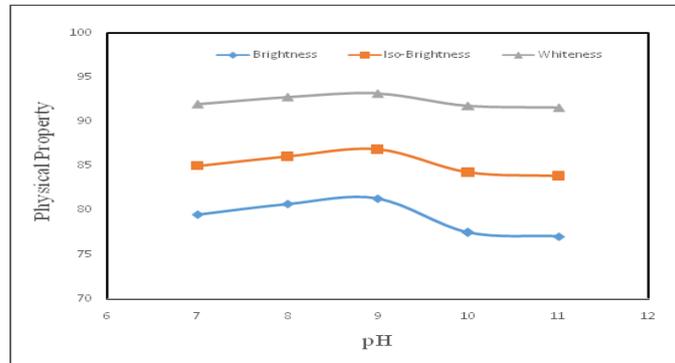


Figure 4. Brightness, Iso-Brightness and whiteness of overflow product (kaolin), after sedimentation step at different pH values.

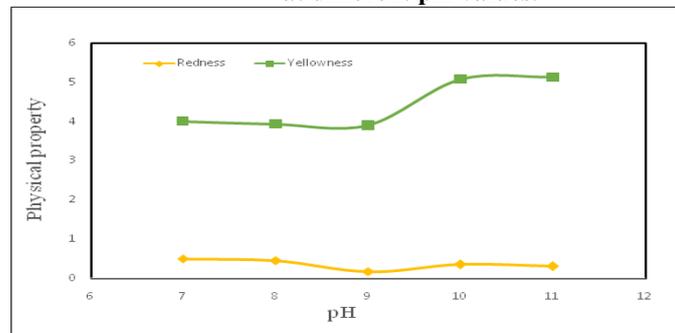


Fig -5: Shows Redness and Yellowness of overflow product (kaolin), after sedimentation step at different pH values.

3.2 Optimization of leaching process of -25 µm kaolin sample with Box-Behnken design method (BBD).

3.2.1 Regression model representation

A 3 factor 3 level Box-Behnken design (BBD) for (Response Surface Method) RSM was used to study the correlation between the combined effect of individual parameters and two responses over three levels. The experimental design matrix and the responses based on experimental runs proposed by BBD are given in Table (6). No transformation was chosen while analyzing both the responses. Among the linear, two-factor interaction (2FI) and quadratic polynomials, the quadratic model was suggested to be the most suitable for this process by the Design-Expert® Software, Version 9.0 (Stat-Ease, Minneapolis, USA). It showed a lower standard deviation along with higher R² values. Final equations in terms of coded factors for responses Y₁ (Fe₂O₃ %) and Y₂ (TiO₂ %) in kaolin residue are obtained as follows,

Table (6): Box–Behnken design for development and optimization of the flotation process for (-25 µm).

No	Dependent variables			Responses			
	Sulfuric concentration (molar)	Oxalic concentration (g/l)	Time (min)	Fe ₂ O ₃ %		TiO ₂ %	
				actual	predicted	actual	predicted
1	5	50	2	0.218	0.216375	0.307	0.312
2	3	30	2	0.29	0.28	0.284	0.270667
3	1	30	1	0.245	0.242	0.44	0.456
4	3	50	1	0.232	0.230375	0.415	0.391
5	5	30	3	0.215	0.218	0.324	0.308
6	1	30	3	0.232	0.22875	0.4	0.381
7	5	10	2	0.209	0.204375	0.184	0.176
8	3	10	1	0.222	0.223375	0.374	0.363
9	1	10	2	0.22	0.221625	0.427	0.422
10	3	30	2	0.28	0.28	0.264	0.270667
11	5	30	1	0.222	0.22525	0.329	0.348
12	3	50	3	0.223	0.221625	0.275	0.286
13	3	30	2	0.27	0.28	0.264	0.270667
14	3	10	3	0.21	0.211625	0.329	0.353
15	1	50	2	0.222	0.226625	0.239	0.247

$$Y_1 = + 0.28 - 6.875 \cdot 10^{-3} X_1 + 4.250 \cdot 10^{-3} X_2 - 5.125 \cdot 10^{-3} X_3 + 1.750 \cdot 10^{-3} X_1 X_2 + 1.500 \cdot 10^{-3} X_1 X_3 + 7.500 \cdot 10^{-4} X_2 X_3 - 0.028 X_{12} - 0.035 X_{22} - 0.024 X_{32} \quad (9)$$

$$Y_2 = + 0.27 - 0.045 X_1 - 9.750 \cdot 10^{-3} X_2 - 0.029 X_3 + 0.078 X_1 X_2 + 8.750 \cdot 10^{-3} X_1 X_3 - 0.024 X_2 X_3 + 0.022 X_{12} - 3.208 \cdot 10^{-3} X_{22} + 0.081 X_{32} \quad (10)$$

The predicted values of the responses were determined by the aforementioned equations. The positive sign of the coefficients in regression equation indicated a synergistic effect, while the negative sign represented an antagonistic effect on the response [21]. From Eq. (9), it was evident that the constant 0.28 was independent of any factor or interaction of the factors, the linear terms X₁, X₃ and second-order X₁₂, X₂₂, X₃₂ had a negative effect on the (Fe₂O₃%) response. Hence the response increased as these terms decreased, whereas the terms X₂, X₁X₂, X₁X₃ and X₂X₃ had a positive influence which denoted that there would be a decrease in Fe₂O₃ % with the decrease in the magnitude of these parameters. Similarly, from Eq. (10) it was evident that the constant 0.27 was independent of the

studied parameters. The linear terms X_1, X_2 and X_3 , interaction terms X_2X_3 and second-order term X_{22} had a (-ve) effect with the TiO_2 % response whereas the interaction terms X_1X_2, X_1X_3 , quadratic terms X_{12}, X_{32} had a (+ve) effect on the response (TiO_2 %).

3.2.2 Statistical analysis

A statistical analysis of variance (ANOVA) based on BBD was performed with design-Expert®Software, Version 9.0 (Stat-Ease, Minneapolis, USA) proposed to determine the fitness and significance of the proposed model. ANOVA is an analytical technique that is used to identify the importance of the model and its parameters, using Fisher's *F*-test. It also determines the effects of the individual variables and interactions between them on the responses. The model and model terms are considered to be significant only when the values (Prob > F) are less than 0.0500 and terms with Fisher's statistical test *F*-test (*F* model, mean square regression/mean square residual) value have greater importance to produce an effect on the response [22,23]. The ANOVA assessed the significance of the fitting of the quadratic model for both responses (Y_1 and Y_2). The results for response surface of Y_1 (Fe_2O_3 %) is shown in Table (7).

Table (7): ANOVA for response surface quadratic model of Y_1 (Fe_2O_3 %).

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	8.948*10 ⁻³	9	9.942*10 ⁻⁴	16.78	0.0032	significant
X1-sulfuric acid concentration	3.781*10 ⁻⁴	1	3.781*10 ⁻⁴	6.38	0.0528	
X2-oxalic acid concentration	1.445*10 ⁻⁴	1	1.445*10 ⁻⁴	2.44	0.1791	
X3-time	2.101*10 ⁻⁴	1	2.101*10 ⁻⁴	3.55	0.1184	
X1X2	1.225*10 ⁻⁵	1	1.225*10 ⁻⁵	0.21	0.6684	
X1X3	9.000*10 ⁻⁶	1	9.000*10 ⁻⁶	0.15	0.7128	
X2X3	2.250*10 ⁻⁶	1	2.250*10 ⁻⁶	0.038	0.8532	
X12	2.895*10 ⁻³	1	2.895*10 ⁻³	48.86	0.0009	
X22	4.459*10 ⁻³	1	4.459*10 ⁻³	75.25	0.0003	
X32	2.039*10 ⁻³	1	2.039*10 ⁻³	34.41	0.0020	
Residual	2.962*10 ⁻⁴	5	5.925*10 ⁻⁵			
Lack of Fit	9.625*10 ⁻⁵	3	3.208*10 ⁻⁵	0.32	0.8148	not significant
Pure Error	2.000*10 ⁻⁴	2	1.000*10 ⁻⁴			
Cor Total	9.244*10 ⁻³	14				

$R^2 = 0.9680$, Adj. $R^2 = 0.9103$, Adequate Precision = 12.033, CV = 3.29%, Standard Deviation = $7.697*10^{-3}$.

A model *F*-value of 16.78 with (Prob > F) equal 0.0032 for response Y_1 (Fe_2O_3 %) verified the sufficiency of the model as shown from Table (7). From the ANOVA table, the model terms X_1, X_{12}, X_{22} and X_{32} were observed to be statistically significant. However, the model terms $X_2, X_3, X_1X_2, X1X3$ and $X2X3$ were statistically insignificant. The main factor sulfuric acid concentration had a significant effect on the Fe_2O_3 %. The coefficient of determination (R^2) of the model for response Y_1 was noted as 0.9680 which suggested that the fitted polynomial equations had a good degree of fitness of the model and only about 0.032 of the total variation cannot be explained by the fitted model. The “pred R -squared” of 0.7847 was in reasonable agreement with the “adj R -squared” of 0.9103 because the difference between these values is within 0.2 which confirmed good predictability of the model. Moreover. For response Y_1 the standard deviation of the model was $7.697*10^{-3}$. This confirm the goodness of the model since the smaller the value of standard deviation the better is the model because the predicted value obtained will be found closer to the actual value. “Adequate precision” is a measure of the signal to noise ratio and a value greater than or equal to 4 is always desirable. In the present analysis, a value of 12.033 indicated sufficient model discrimination. On the other hand, a

relatively lower value of the coefficient of variation (CV = 3.29 %) indicated good precision and reliability of the model.

Results of ANOVA (response of Y2: (TiO₂ %)) is shown in Table (8). It indicates that the model was highly significant as the Fisher F-test (F model, S_{2reg}/S_{2err} = 13.73) with a very low probability value [(P > F) = 0.005]. The main effect X₁, X₃; the two-level interactions of sulfuric acid concentration and oxalic acid concentration (X₁X₂); the second-order effect of leaching time(X₃₂) were the significant model terms. Other model terms were statistically insignificant. It was found that the coefficient of determination (R²) was 0.9611, which was very high and indicates a good correlation. As well, the adjusted R² value (0.8911) was also high to advocate the significance of the model, which ensured a satisfactory adjustment of the experimental data to the polynomial model. The difference between adj R-squared and pre R-squared value was more than 0.2 which indicates a blocking effect for which model reduction was necessary. “Adequate precision” is a measure of the signal to noise ratio and a value greater than or equal to 4 is always desirable. The ratio of 13.8333 for response Y2 indicates an adequate signal and so the model could be used to navigate the design space. Simultaneously, a low value of the coefficient of variation (CV = 7.66 %) denoted good accuracy and reliability of the model [24, 25].

Table (8): ANOVA for response surface quadratic model of Y2 (TiO₂ %).

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.076	9	8.435*10 ⁻³	13.73	0.0050	significant
X ₁ -sulfuric acid concentration	0.016	1	0.016	26.66	0.0036	
X ₂ -oxalic acid concentration	7.605*10 ⁻⁴	1	7.605*10 ⁻⁴	1.24	0.3166	
X ₃ -time	6.612*10 ⁻³	1	6.612*10 ⁻³	10.76	0.0219	
X ₁ X ₂	0.024	1	0.024	39.35	0.0015	
X ₁ X ₃	3.063*10 ⁻³	1	3.063*10 ⁻⁴	0.50	0.5118	
X ₂ X ₃	2.256*10 ⁻³	1	2.256*10 ⁻³	3.67	0.1135	
X ₁ ²	1.753*10 ⁻³	1	1.753*10 ⁻³	2.85	0.1520	
X ₂ ²	3.801*10 ⁻⁵	1	3.801*10 ⁻⁵	0.062	0.8135	
X ₃ ²	0.024	1	0.024	39.22	0.0015	
Residual	3.073*10 ⁻³	5	6.145*10 ⁻⁴			
Lack of Fit	2.806*10 ⁻³	3	9.353*10 ⁻⁴	7.02	0.1273	not significant
Pure Error	2.667*10 ⁻⁴	2	1.333*10 ⁻⁴			
Cor Total	0.079	14				

R² = 0.9611, Adj.R² = 0.8911, Adequate Precision = 12.833, CV = 7.66%, Standard Deviation = 0.025

3.2.3 Model accuracy check

A normal plot of residuals between the normal probability (%) and the internally studentized residuals is presented obtained. In this way, the residuals can be checked to determine how well the model satisfies the assumptions of ANOVA. The studentized residuals can be used to measure the standard deviations separating the experimental and predicted values. Figures (6) and (7) show the relationship between the normal probability (%) and the internally studentized residuals. The straight line means that no response transformation is required and that there was no apparent problem with normality [26].

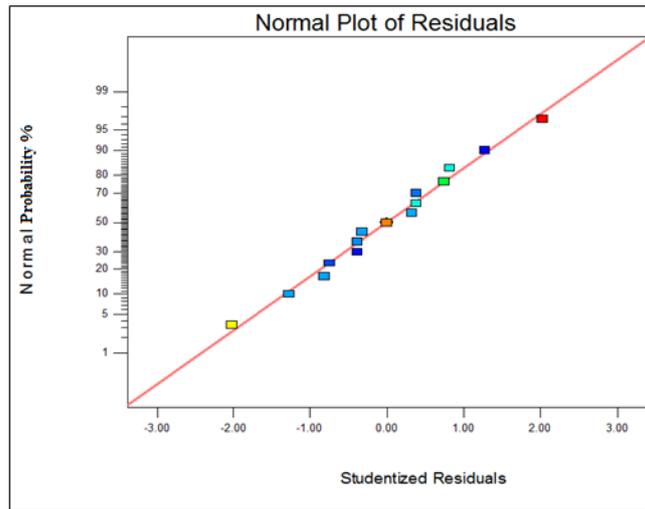


Figure 6. Normal plot of studentized residuals for Fe_2O_3 (%).

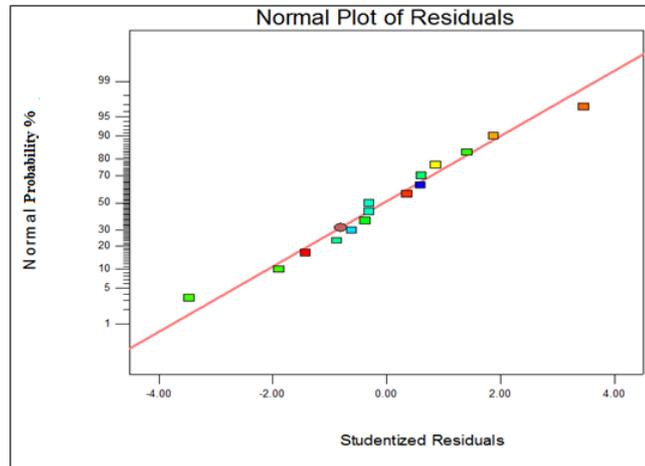


Figure 7. Normal plot of studentized residuals for TiO_2 (%).

To obtain an adequate model, an accuracy check is necessary. The model accuracy was checked by comparing the predicted and actual experimental values. The predicted versus actual plots for responses Y1 and Y2 are shown in Figures (8) and (9). The experimentally obtained data for each run is the actual value whereas the predicted value is evaluated from the model using the proposed prediction equation. From both plots, it was observed that the most of the data points are well distributed near to the straight line, which suggested an excellent relationship between the experimental and predicted values of the responses.

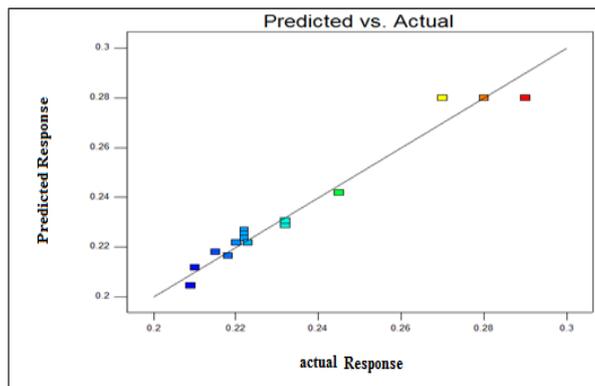


Figure 8. Plot of actual response versus predicted response for Fe_2O_3 (%).

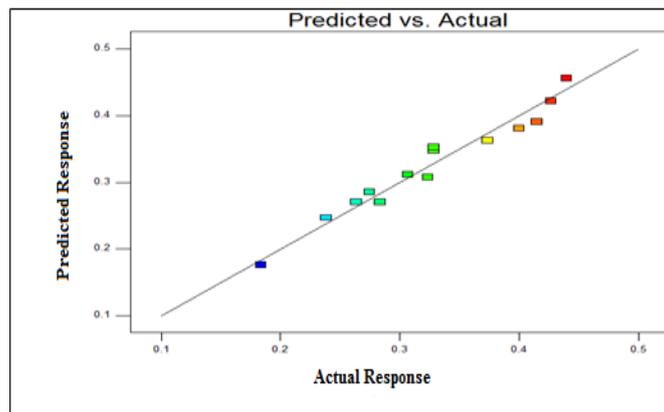


Figure 9. Plot of actual response versus predicted response for TiO₂ (%).

3.2.4 Interaction effect of process variables on responses

The 3-D response graphs for the Fe₂O₃ are depicted in some figures to indicate relation between parameters. The 3-D plots were generated using Design-Expert® Software, Version 9.0 (Stat-Ease, Minneapolis, USA) by varying two parameters within the range and keeping the other variable at constant level. Figure (10) demonstrates the no significant mutual interaction between sulfuric acid concentration (X₁) and oxalic acid concentration (X₂) for Fe₂O₃ % response at constant time (3hours). It was noted that as the sulfuric acid concentration increases from 1–5 molar and oxalic acid concentration decreases to 10g/l, the Fe₂O₃ loss was high i.e. 0.623–0.177%. Results from 3-D surface plot when keeping the sulfuric acid concentration and oxalic concentration in the mentioned range at constant time indicates that the best results are obtained at 5 molar sulfuric acid concentrations, 10 g/l oxalic acid concentration and at a time 3 hour. These results indicated that the sample is easily amenable to sulfuric acid leaching and the design shows significant sulfuric acid concentration and in significant interaction between variables. This may be attributed to the consumption of a great part of sulfuric acid in side reactions.

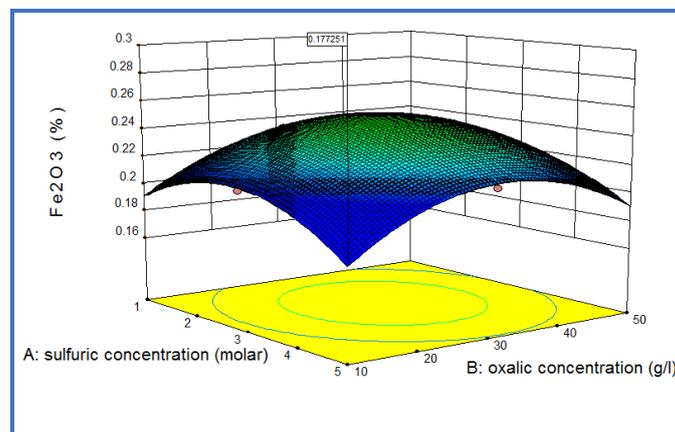


Figure10. The combined effect of interaction between sulfuric acid concentration (X₁) and oxalic acid concentration (X₂) for Fe₂O₃ content (%) at constant time (3) hrs.

Figure (11) demonstrates the significant mutual interaction between sulfuric acid concentration (X₁) and oxalic acid concentration (X₂) for TiO₂ % response at constant time (2hours). It is noted that as the sulfuric acid concentration increases from 1–5 molar and oxalic acid concentration decreases to 10 g/l, the Fe₂O₃ loss was high i.e. 1.669 – 0.178%. These results indicated that the sample is easily amenable to sulfuric acid leaching and the design shows significant sulfuric acid concentration, time and in significant oxalic acid concentration. The design indicates significant interaction between sulfuric acid and oxalic acid, sulfuric acid and time and no significant relationship between oxalic acid and time. This may be attributed to the consumption of a great part of sulfuric acid in side reactions with increase time and the stability of oxalic acid at a constant value.

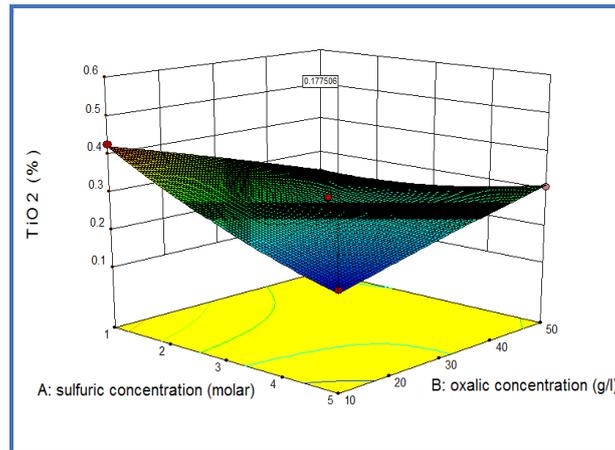


Figure (11): The combined effect of interaction between sulfuric acid concentration (X1) and oxalic acid concentration (X2) for TiO₂ content (%) at constant time (2) hrs.

3.2.5 Process optimization

In processing of (-25 μm) kaolin by leaching with sulfuric acid and oxalic acid, relatively low Fe₂O₃ content (%) and TiO₂ content (%) value is desired since the low iron oxide and titanium oxide contents improve the competitiveness of kaolin fraction in the commercial market. However, it was difficult to optimize the two responses under the same conditions because the interest regions of them were different. So, the best possible goal for each response was determined by Numerical optimization of the overall desirability function using mentioned Design-Expert1 Software. To achieve the maximum desirability, parameters were set as minimize without a target. The obtained predicted optimal values for the independent variables were as follows: X₁: Sulfuric acid concentration = 4.99252 molar, X₂: Oxalic acid concentration = 10.0083 g/l and X₃: time = 2.28294 hrs. to achieve minimum iron oxide content of 0.201492 % and titanium oxide content of 0.183944 % as shown in Figure (12) with overall desirability of 1.00.

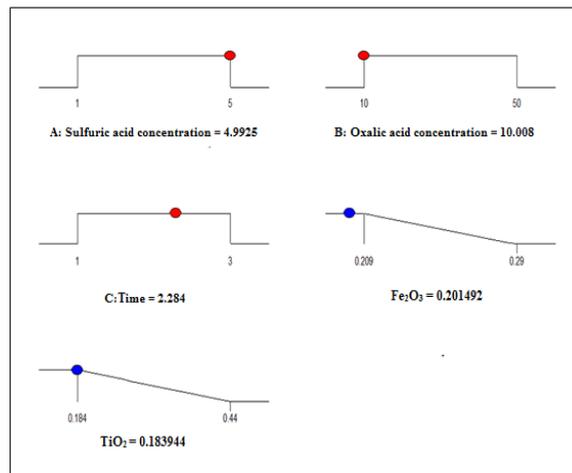


Figure (12): Optimized process condition.

The validity of this prediction was examined by performing an experiment using the predicted optimal values. The iron and titanium contents obtained in this experiment were 0.209 and 0.184 % as shown in Table (9). Overall, the experimental values were in close agreement with the obtained calculated values from the models. As a result, RSM proved to be an effective method to optimize the experimental conditions under consideration.

Table (9): Model Validation.

Sulfuric concentration (molar)	Oxalic concentration (g/l)	Time (hr)	Fe ₂ O ₃ %		TiO ₂ %	
			Predicted	Experimental	Predicted	Experimental
4.99252	10.0083	2.28294	0.201492	0.209	0.183944	0.184

Table (10) shows ten experiments of the predicted optimal values for the independent variables taken by mentioned Design-Expert1 Software to achieve low iron and alumina contents.

Table (10) shows experiments of the predicted optimal values for the independent variables

NO	Sulfuric acid concentration (g/l)	Oxalic acid concentration (g/l)	Time (hr)	Fe ₂ O ₃ %	TiO ₂ %
1	4.99375	10.4999	2.17292	0.206884	0.18336
2	4.99502	10.8905	1.80831	0.207798	0.181953
3	4.99252	10.0083	2.28294	0.201492	0.183944
4	4.96387	10.6353	1.84284	0.208003	0.181307
5	4.99274	10.1879	1.86469	0.205447	0.177991
6	4.91382	10.3471	2.02661	0.208272	0.180831
7	5	10	2	0.204375	0.176
8	4.96081	10.4757	1.77051	0.207175	0.18286
9	4.98599	10.0215	2.20465	0.203026	0.18077
10	4.95219	10.9319	2.07905	0.208252	0.181982

4. CONCLUSIONS

The aim of this study was the removal of impurities from -25 μm kaolin obtained from the attrition of wadi-Qena Kaolinitic white sand ore by dispersion and leaching. In this regard, two group of experiments were made. The first group includes selective dispersion and flocculation experiments. The results showed that a kaolin product containing 0.542 % Fe₂O₃ and 0.924 TiO₂ were obtained and physical properties improved such as brightness increased from 76.45 to 81.32, Iso-brightness increased from 84.15 to 86.85, whiteness increased from 91.73 to 93.18, redness decreased from 0.22 to 0.17 and yellowness decreased from 5.84 to 3.96. Secondly in an attempt to decrease the Fe₂O₃ % and TiO₂ % contents in -25 kaolin product leaching processes was carried out. Also Process optimization of the experimental conditions (sulfuric acid concentration, oxalic acid concentration and time) was carried out by means of Box-Behnken design (BBD) of Response surface methodology (RSM). Two responses (iron oxide and titanium oxide content) were chosen to be the responses. Quadratic model which expressed the functional relationship between the two responses and the three independent variables were obtained by ANOVA. The correlation coefficients (R²) of 0.9680 and 0.9611 for iron oxide % and titanium oxide % showed the good fit of the experimental data to the model. It was found that iron oxide response was in significantly influenced by interaction between variables and titanium oxide response was significantly influenced by interaction between sulfuric acid and oxalic acid, sulfuric acid and time and insignificantly affected by interaction between oxalic acid and time. Simultaneous optimization was performed on the basis of the desirability function to determine the optimal conditions of variables for desired iron oxide and titanium oxide contents. The best minimum iron oxide % (0.201492) and minimum titanium oxide content % (0.183944) were found at optimum process conditions. These conditions are, sulfuric acid concentration (4.99252 molar), oxalic acid concentration (10.0083 g/l) and time (2.28294 hr). These optimum values of

Fe₂O₃ % and TiO₂ % were further validated by actually performing an experiment at the optimized values of parameters and were found in good agreement with the values predicted by models.

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