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Study on the Activation of Saudi Natural Bentonite, Part I: Investigation of the Conditions that Give Best Results and Kinetics of the Sulfuric Acid Activation Process

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Abstract. The Kingdom of Saudi Arabia has many natural clay deposits of the montmorillonite type which are susceptible to activation. The activation of the Saudi natural bentonite with sulfuric acid was studied experimentally and the activity of the produced clay for bleaching of corn oil was tested and compared with that of commercial active clay. The conditions that give best results for the sulfuric acid activation were found to be: 45% by wt acid concentration, liquid to solid ratio of 5:1 (mL/g), clay particle size of -325 mesh (95% passing), at the acid boiling point for 15 minutes and mixing rate of 200 rpm. It was found that using a lower acid concentration requires more time to reach the same degree of activation as that when a higher acid concentration was used. The produced active clay (Saudi-bentonite) has a comparable bleaching power to that used commercially. The oil bleached with Saudi-bentonite clay is of qualities similar to that bleached by commercial clays. The apparent kinetics of the heterogeneous reaction were also studied. It was found that the reaction between sulfuric acid and clay is a zero order reaction with an apparent activation energy of 430 cal/mol.

Notation

A	Arhenius constant
C_A	concentration of sulfuric acid (mol/L)
E	activation energy (cal/mol)
PB	percent bleaching
R	gas constant = 1.987 (cal/mol K)
r_A	rate of reaction (mol/L min)
r_{A0}	initial rate of reaction (mol/L min)
R_i	color of the oil after bleaching with the imported clay in red units
R_l	color of the oil after bleaching with the local activated clay in red units
R_v	color of the refined corn oil (unbleached) in red units
T	reaction temperature (K)

Introduction

Naturally occurring clays are aluminosilicate minerals containing sodium, potassium and calcium, in which magnesium and iron may be substituted for aluminum. Few of these clays possess decolorizing properties and are used for bleaching purposes. The majority do not possess such decolorizing power. But some clays (montmorillonite) may be activated by some form of treatment and their bleaching power can be improved. Activation of clays can essentially be accomplished by calcination, reaction with mineral acids or a combination of both techniques[1, 2].

During the calcination process, the water in the clay mineral is driven out as the temperature is increased leaving in its place a porous structure with increased internal surface area. As the temperature rises up to 500-700°C, the structure is modified and the OH-O bonds are destroyed with the resultant structure having higher adsorptive properties and becoming an active one. However, higher temperatures may alter or destroy the structure[3]. Bakr, *et al.* [4], studied the suitability of some Egyptian clay for bleaching cottonseed oil. One of the methods investigated was by calcination. They found that the most suitable temperature for activation was 700°C and the calcination time to be 2 to 4 hours. Al-Zahrani [3] studied the thermal activation of natural local clay, which was carried out at different temperatures ranging from 500 to 800°C and for different periods of time ranging from 0 to 8 hours. It was found that the percentage of bleaching increased with time until it reached a maximum value of 17.5% when the temperature is 600°C and the time of calcination is 8 hours.

Acid treatment of clays changes the clay structure by creating new pores resulting in an increase of surface acidity through the replacement of cations like A^{3+}, Fe^{3+} and Ca^{2+} from the structure with H^+ [5]. During clay activation with mineral acids two basic reactions occur [6]:

1. The acid first dissolves part of Al_2O_3 as well as of CaO, MgO,... etc., from the lattice. This causes an opening of the crystal lattice and an increase in internal surface area.
2. The second reaction is the gradual exchange of the Ca and Mg ions, located at the surface of the crystal against hydrogen ions from the mineral acid.

For the above reasons, acid-activated clay is almost saturated with H^+ and exhibits strong acidic character. Activation of clay can be done using any mineral acid, but activation with hydrochloric and sulfuric acids is the most common procedure. Al-Zahrani [3] reported that clays activated with sulfuric acid exhibit better bleaching properties than those activated with hydrochloric acid. Anthony, *et al.* [7], determined the conditions that give best results for acid activation of some selected Nigerian clays. They found that the bleaching activity was highest when one part of the clay was mixed with three parts of 1.4 - 2.7 M HCl or 0.5 - 1.0 M H_2SO_4, refluxed for 2 - 6 hours then dried to 5 - 15% moisture content.

Murad, *et al.* [8], studied the potential of Qena clay as a bleaching agent for cotton oil. Clay samples were subjected to HCl treatment at different temperatures and clay to acid ratios. They reported that the treatment with an acid of normality 1 - 2 N combined with low temperature (30-70°C) resulted in low bleaching efficiency of clay whereas at a higher temperature (90°C) the efficiency increases .

The present work deals with the activation of local Saudi clay by leaching with sulfuric acid. Saudi Arabia is rich with clay minerals. The sodium bentonite mineral "montmorillonite" can be found at different locations throughout the Kingdom. This clay has a mineralogical structure that is suitable for activation. The variables affecting the activation process are investigated in order to reach the conditions which give best results for the reaction. Also, the kinetics of the reaction were studied.

Experimental

The activation experiments were carried out in a laboratory-size stirred batch reactor (ID = 11 cm) shown in Fig. 1. The reactor is a 700-mL round-bottom Pyrex flask with a special Pyrex lid that fits tightly on the flask top. The lid is clamped to the flask with a clip. The lid that covers the flask has four necks. The function of each one of the necks is as follows:

i) A glass condenser is connected through a ground joint to the first neck. The water vapor and acid fumes are condensed then returned to the reaction vessel as the reaction is carried out at the boiling point of the acid.
ii) A two-plaids glass stirrer (impeller diameter = 5 cm) extends into the reactor through the central opening. The stirrer is driven by a variable speed motor.
iii) The third neck is used for introducing the clay to the acid when the temperature reaches the boiling point. It is also used to withdraw samples to monitor the reaction progress with time.
iv) The last opening in the lid is used for inserting temperature-sensing element. A mercury glass thermometer is used for temperature measurement with an accuracy of ±1°C. This is used to monitor reaction temperature.

2.1 Procedures

2.1.1. Activation experiments

The raw clay was dried and ground to the required size (-325 mesh with 95% passing). The required amount of acid was placed in the reactor vessel shown in Fig. 1. The volume of the reactants should be neither more than two thirds nor less than one third of the volume of the vessel. The contents of the reactant were then heated via a heating mantel until it began to boil then 40 g of the grounded clay (-325 mesh with 95% passing) were added to it. The stirrer was started and adjusted at the required speed and the mixture was heated under total reflux for the required time. Samples of 50 mL each were taken after 15, 30, 45, 60, 120 minutes, filtered then washed with hot distilled water till free from acid then dried at 105 °C for one hour. The activation experiments were carried out at three different temperatures. These were: room temperature (22 ± 1°C), acid boiling point (dependent on acid concentration), and at the mid point which is the arithmetic average between room temperature and the acid boiling point. The experiments were conducted using sulfuric acid concentrations of 25%, 35%, 45% and 55% by weight. The bleaching power of the activated clay was then measured by conducting a bleaching test on corn oil.

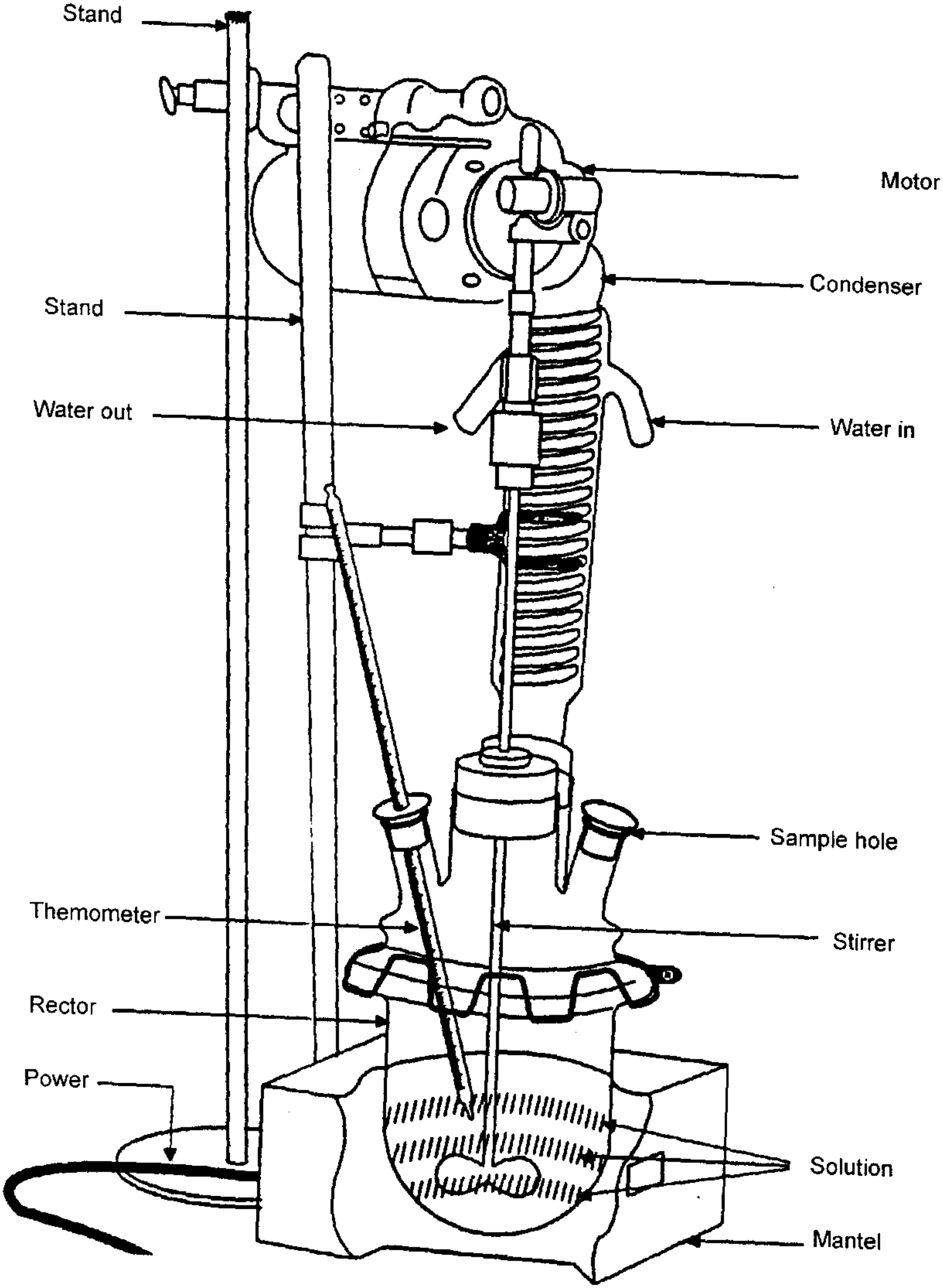

Fig. 1. Batch reactor assembly.

2.1.2. Bleaching test [9]

100 g of refined unbleached corn oil were placed in 250-mL flask, then a magnetic stirring bar was carefully inserted into the flask. The flask was placed on a magnetically-stirred hot plate. A thermometer was inserted in the flask. The hot plate was turned on and the stirring was adjusted until agitation was moderate. The flask was heated until the temperature reached 70°C, then 2 grams of the activated clay were added and heating was continued to 90°C. The flask was maintained at 90 ± 2°C for 30 minutes. The oil was immediately filtered under gravity using Whatman filter paper No. 42 (15 cm diameter). The filtered oil was placed in a cell to measure the color using PFX990 Levibond Tintometere. The percent bleaching power (BP) of the produced clay was compared to a reference active clay supplied by a local oil refinery as follows:

$$\% \text{ Bleaching power (PB)} = (R_v - R_l) / (R_v - R_i) \times 100 \qquad (1)$$

where R_v is the color of the refined corn oil (unbleached) in red units, R_l is the color of the oil after bleaching with the local activated clay in red units and R_i is the color of the oil after bleaching with a commercial clay used in a local edible oil refinery.

2.1.3. Reaction kinetics

The change of acid concentration with time during the activation process was done to study the kinetics of the reaction. The activation experiment was carried out at a known temperature. Samples were withdrawn at different time intervals. The concentration of the free acid was determined by titration with 1.0 N NaOH solution. The rate of reaction was taken as the slope of the tangent of the time-concentration curve at any time "t".

Results and Discussion

3.1 Activation process

The effects of temperature, concentration of sulfuric acid, time of reaction, particle size, liquid to solid ratio and degree of mixing on the activation of clay were studied. Replicates of many of the experiments showed an experimental error in bleaching power of less than 2%. The bleaching power is taken as an indication of the activity of produced active clay.

The effect of temperature is presented in Fig.2 for experiments conducted with 45% by wt. acid. It is obvious from this figure that the activation reaction does not proceed to any appreciable degree at low temperatures. At the boiling point of H_2SO_4 acid, a truly active clay is produced. The percent bleaching of the produced clay increases with reaction time until it reaches a maximum (101% at 15 minutes), then it starts to decrease with increasing reaction time.

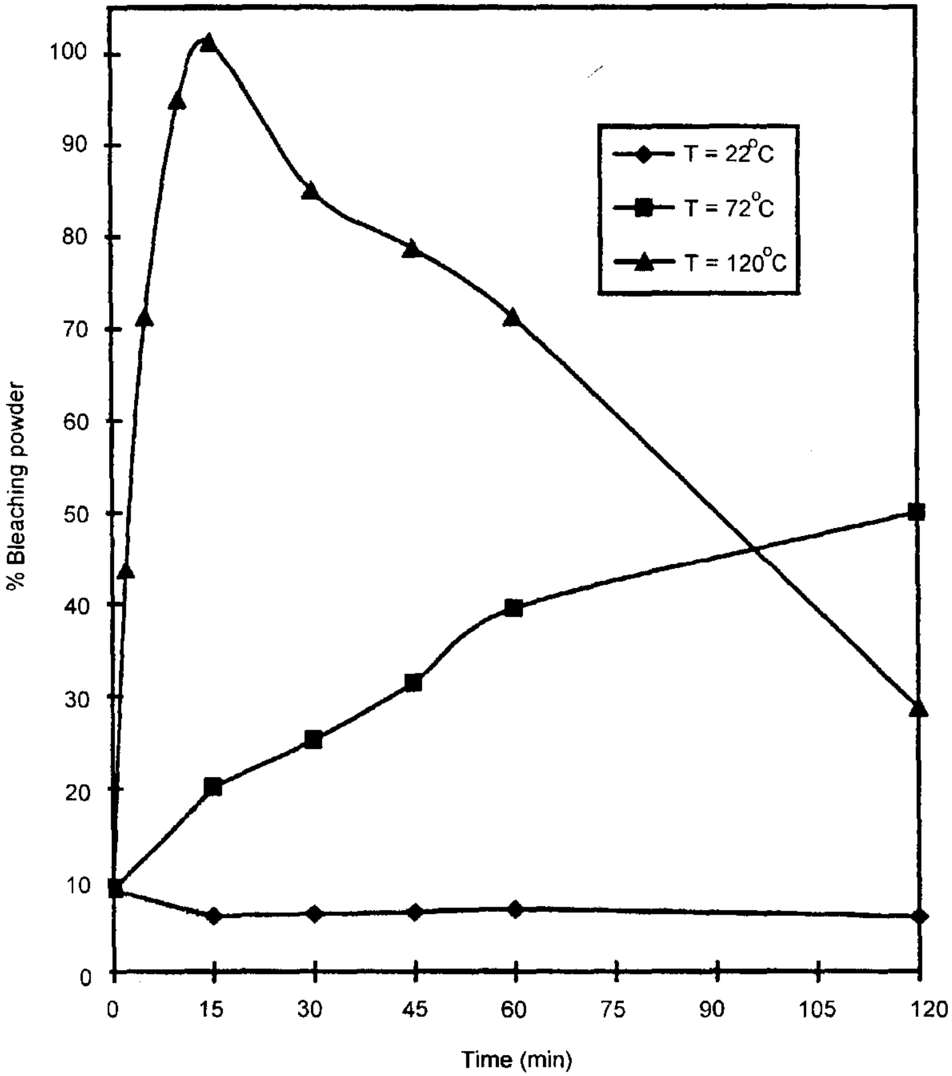

Fig. 2. Percent bleaching v.s. reaction time at different temperatures. H_2SO_4 conc. = 45% by wt., mixing = 200 r.p.m., liquid to soild ratio = 5:1 (mL/g) and grain size = -325 mesh (95% passing).

Similar plots to that shown in Fig. 2 were obtained which show the effects of acid concentration and time of reaction on the bleaching power of the active clay. Increasing acid concentration or time of reaction beyond a certain point results in decreasing the activity of the produced clay. Table 1 contains values of maximum bleaching power and the corresponding acid concentrations and reaction times. It shows that the best conditions correspond to an acid concentration of 45% and a time of reaction of 15 minutes. The maximum bleaching power at other concentrations (25% and 35%) are identical to that at 45%. However, the reaction times in both cases are longer which make these conditions at 25% and 35% undesirable.

Table 1. The optimum time of activation for different acid concentrations

Sulfuric acid Concentration (%)	Time of activation	Percent bleaching power (%)
25	60	100
35	35	100
45	15	101
55	10	91

During the acid activation reaction, sulfuric acid reacts with the Al^{+3}, Fe^{+3} and Ca^{+3} removing them from the lattice and produces a porous structure. Also, H^+ replaces the ions in the structure and increases the cation exchange capacity of the clay [5]. However, on prolonged heating with high concentration of sulfuric acid as is the case when the acid concentration is 55% wt., the attack on the internal structure by the acid begins and the activity of the clay starts to decline. Reaction times longer than those listed in Table 1 lead to similar results.

The effect of particle size on the activation process was also investigated. Clays of sizes -100 mesh and -325 mesh (95% passing) were tested at different acid concentrations. A sample of these results is given in Fig. 3. When the grain size of the clay is reduced, the total area exposed to reaction with the acid increases which increases reaction rate. Therefore, more pores will be created which results in increasing the bleaching power of the clay.

Liquid to solid ratio (mL/g) effect on the bleaching power of the clay was studied using an acid concentration of 45%. Grain size, agitation and time and temperature of reaction were kept constant at: -325 mesh (95% passing), 200 rpm., 15 minutes and 120°C (boiling point), respectively. The results of varying liquid to solid ratio in the range of 3:1 to 7:1 are shown in Fig. 4. Three replicates of each data point were made and the error in bleaching power was less than 2%. As the liquid to solid ratio increases to 5:1, the bleaching power of activated clay increases, while further increase to 7:1 results in a decrease in the bleaching power, therefore the liquid to solid ratio that gave the best result is 5:1. At low liquid to solid ratio, the contact between the acid and the clay is less than when the ratio is more and the rate of reaction is slow. Increasing the liquid to solid ratio above 5:1 increases the amount of sulfuric acid, which causes the destruction of the skeleton of the clay. However, liquid to solid ratio has a small effect on bleaching power compared to the effect of temperature, time and acid concentration.

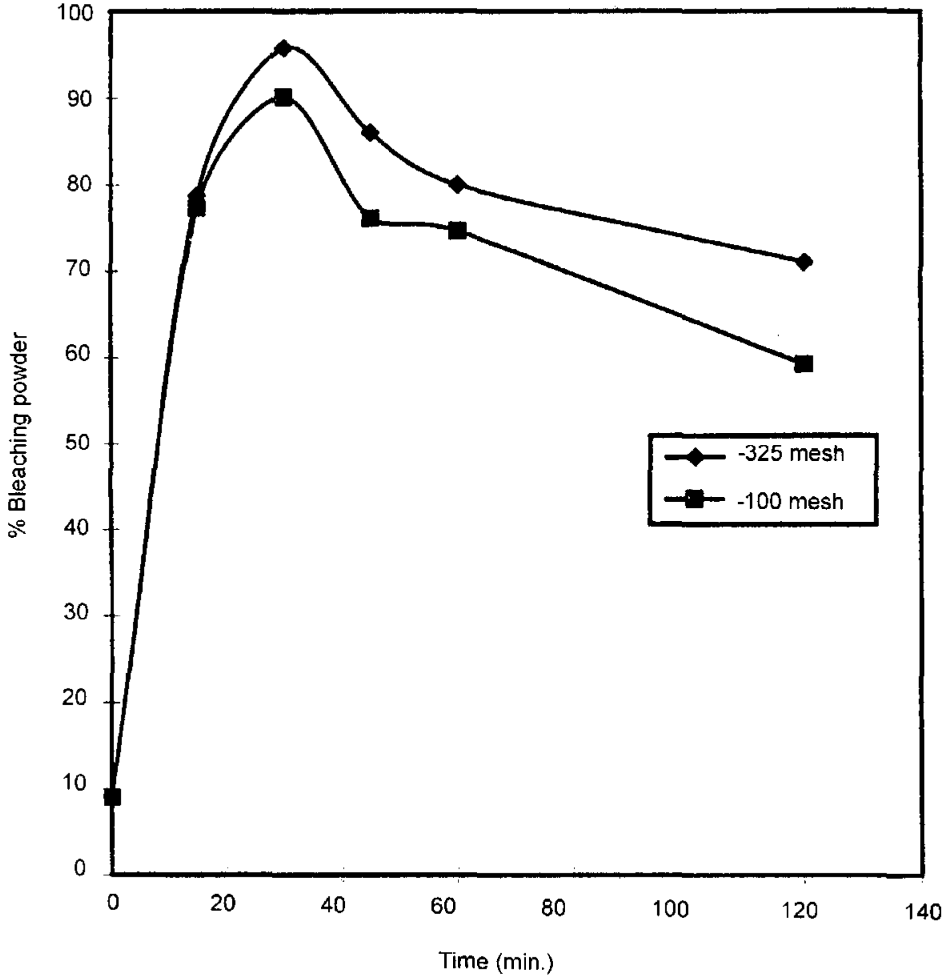

Fig. 3. Percent bleaching v.s. reaction time for grain size -100 and -325 mesh (95%) passing). H_2SO_4 conc. = 35% by wt., temperature = boiling, mixing = 200 r.p.m. and liquid to solid ratio = 5:1 (mL/g).

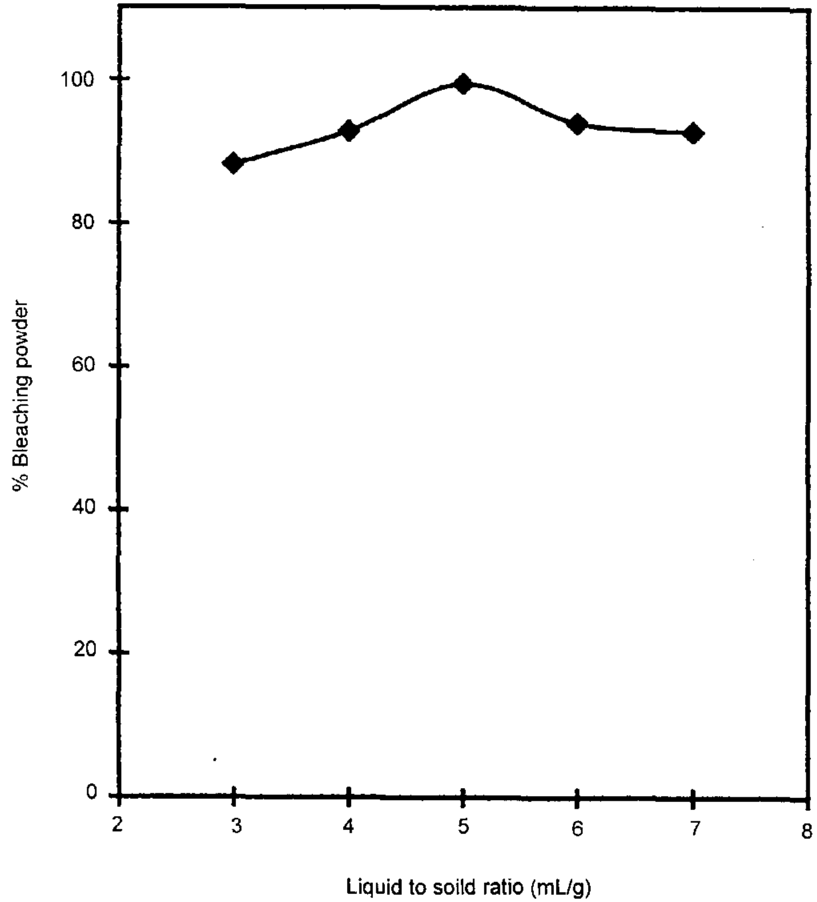

Fig. 4. Percent bleaching v.s. liquid to solid ratio (mL/g). H_2SO_4 conc. = 45% by wt., temperature = boiling, mixing = 200 r.p.m., reaction time = 15 minutes and grain size= -325 mesh (95% passing).

The results of clay activation at different degrees of mixing are shown in Fig. 5. Grain size, acid concentration, liquid to solid ratio and time and temperature of reaction were kept constant at: -325 mesh, 45% by wt., 5:1., 15 minutes and 120°C, respectively. Replicates indicated that the error in bleaching power was less than 2%. As agitation increases to 200 revolution per minute (rpm.) the bleaching power of the activated clay increases. A further increase in agitation to 300 rpm caused the bleaching power of the clay to decrease. As degree of agitation increases the contact between the acid and the clay increases and external mass transfer resistance decreases, hence reaction rate increases. This leads to an increase of surface area of produced active clay, which results in increasing the bleaching power. However, increasing the degree of mixing more than 200 r.p.m. causes less contact between the sulfuric acid and the clay due to high speed and vortex formation around the agitator.

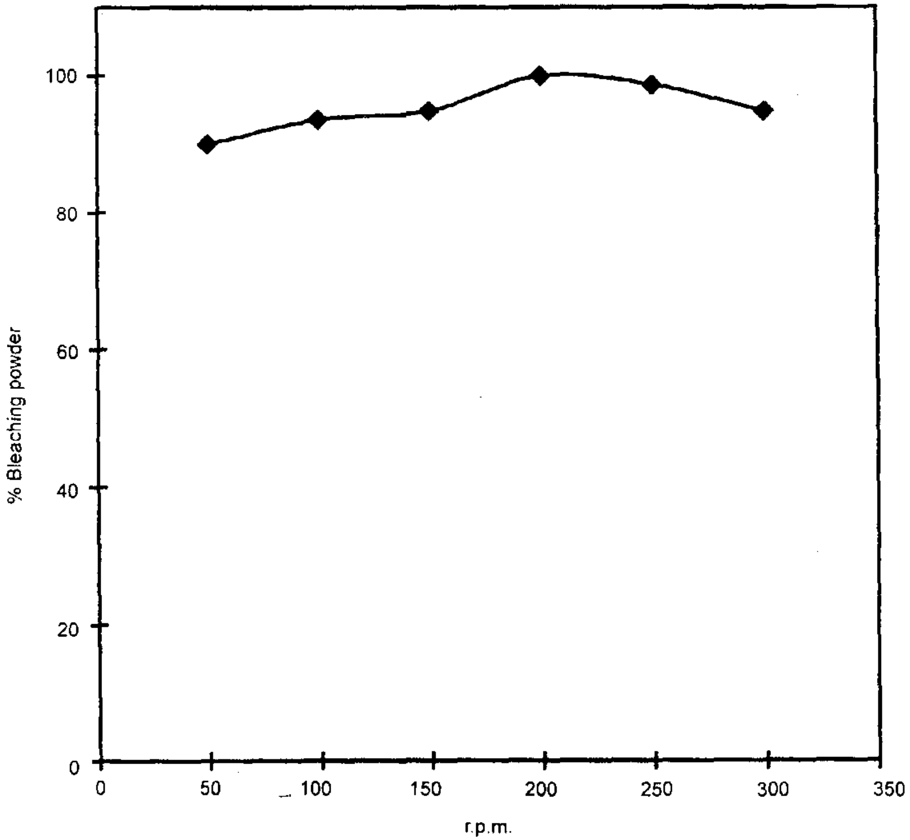

Fig. 5. Percent bleaching v.s. degree of agitation. H_2SO_4 conc. = 45% by wt., temp. = boiling, liquid to soild ratio = 5:1 (mL/g), reaction time = 15 minutes, and grain size = -325 mesh (95% passing).

3.2 Apparent kinetics of the activation reaction

Reaction between clay and sulfuric acid is a heterogeneous one in which a liquid (sulfuric acid) contacts a solid (clay particles), reacts with it, and transforms it into liquid and solid products. Because of the small size of the clay particles, solid particles are assumed unchanged in size during reaction which therefore can be considered as unreacted core solid-liquid reaction. Reaction between sulfuric acid and clay particles according to this model, which was developed by Yagi and Kuni, occurs in five steps as follows [10]:

1. Diffusion of sulfuric acid through the liquid film surrounding the clay particle to the surface of solid.
2. Penetration and diffusion of sulfuric acid through the blanket of ash to the surface of unreacted core.
3. Reaction of sulfuric acid with solid at this reaction surface.

4. Diffusion of liquid products through the ash back to the exterior surface of the solid.
5. Diffusion of liquid products through the liquid film into the main body of fluid.

In order to determine the apparent kinetics of the heterogeneous reaction, it is treated as a homogeneous one. The experiments were done under conditions that eliminate the mass transfer resistance. This is accomplished by good mixing of the fine grained solid with the liquid. The reaction rate is calculated from the concentration-time curve as that shown in Fig. 6. The data obtained were then analyzed by the initial rates method and differential method of analysis of reaction rate [10, 11].

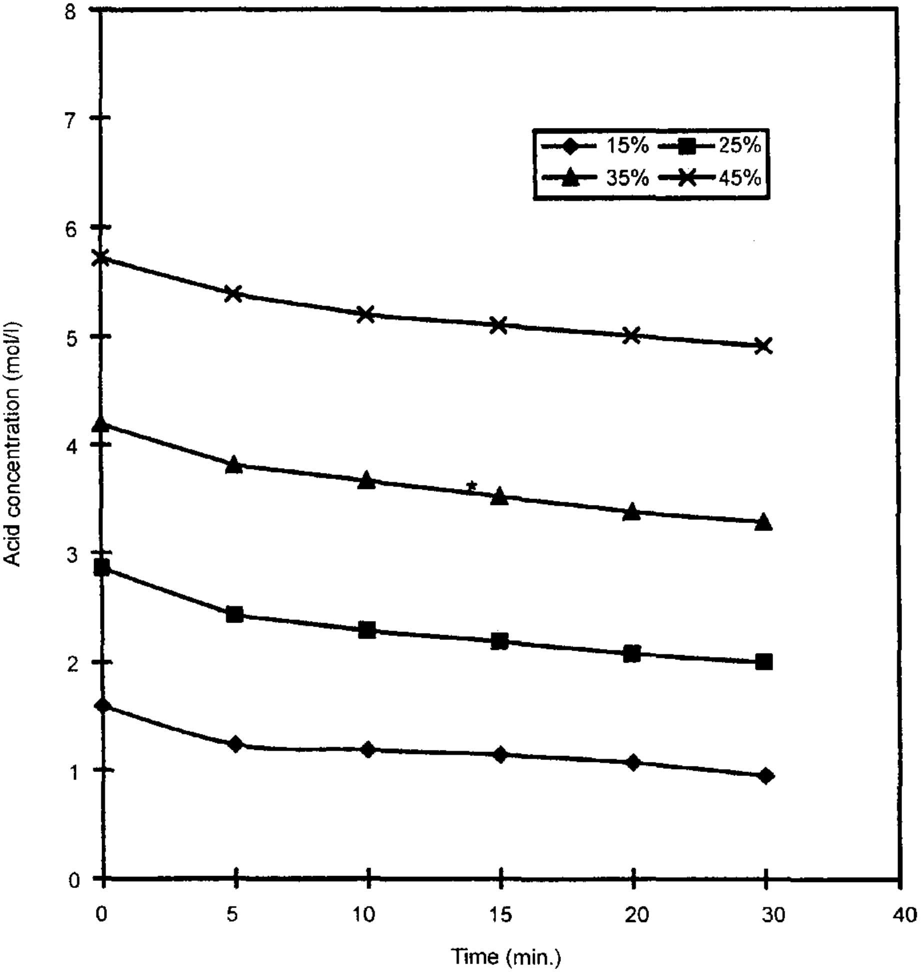

Fig. 6. Change of sulfuric acid concentration with time at different initial concentrations. Mixing = 200 r.p.m., liquid to solid ratio = 5 : 1 (mL/g) and grain size = -325 mesh (95% passing).

3.2.1 Reaction order

The method of initial rates could be used to determine the reaction order and specific rate constant. Figure 6 shows the time-concentration-curves at different initial concentrations. The corresponding initial rates of the reaction are calculated and plotted as a function of acid concentration as shown in Fig. 7. The slope of the resulting straight line is almost zero which represents the apparent order of the chemical reaction.

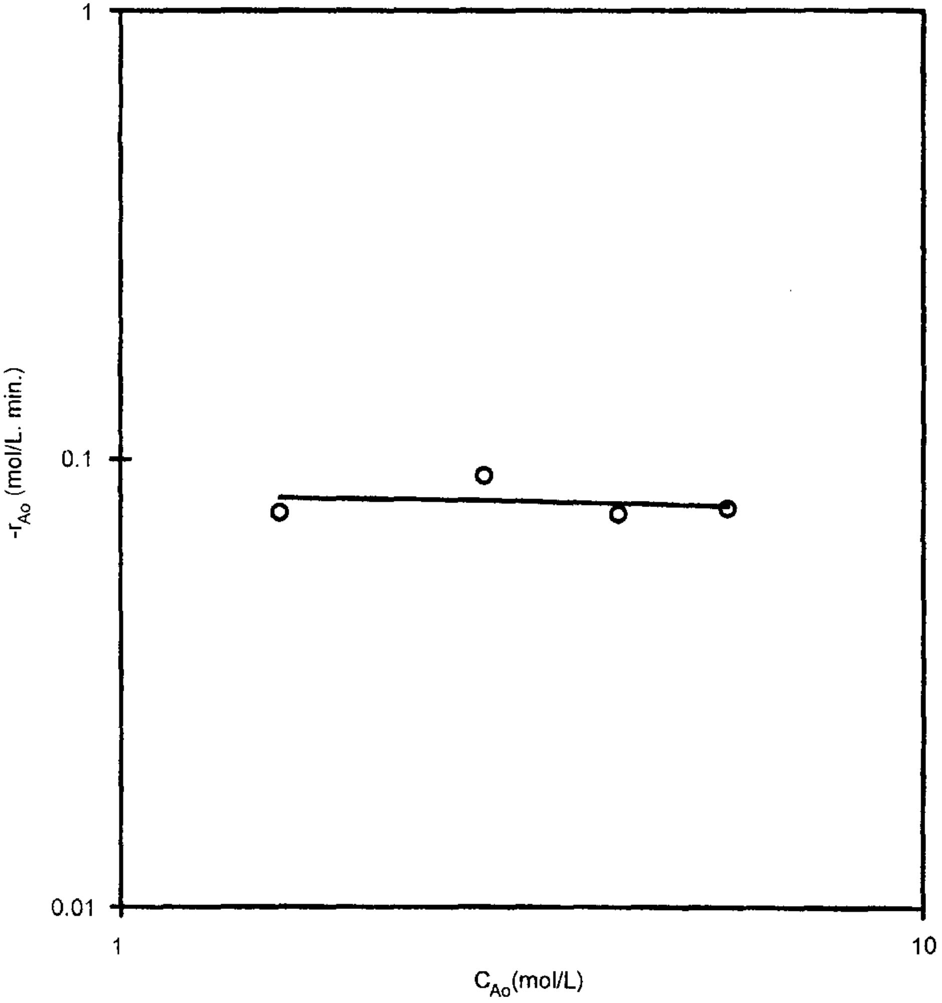

Fig. 7. Initial reaction rate v.s. initial acid concentration.

The differential method of analysis is also applied for the determination of the reaction order. Table 2 shows the experimental data obtained for the rate of reactions at 80, 100 and 120°C. The results are plotted according to logarithmic form of the general rate equation:

$$\ln(-r_A) = \ln k + n' \ln C_A \tag{2}$$

where r_A is reaction rate (mol/L min.), n' is the apparent reaction order, k is reaction rate constant and C_A is the concentration of sulfuric acid (mol/L). The values of n' and k at different temperatures are listed in Table 3.

Table 2. The change of sulfuric acid concentration with time at different temperatures. C_{A0} = 5.83 mol/L, mixing = 200 r.p.m., liquid to solid ratio = 5 : 1 (mL/g) and grain size = -325 mesh (95% passing)

Reaction Temperature (°C)	Time (minute)	C_A (mol/L)	$-r_A$ (mol/L min)
80	0	5.83	0.029
	15	5.52	0.014
	30	5.39	0.0045
100	0	5.83	0.0385
	15	5.40	0.019
	30	5.21	0.0007
120	0	5.83	0.057
	15	5.2	0.027
	30	4.97	0.0072

Table 3. Calculated values of n' and k for the reaction of raw clay with H_2SO_4

Temperature (K)	n'	K
353	0.047	0.0289
373	0.055	0.0385
393	0.064	0.0573

The average apparent order of the reaction can be calculated as 0.055, which is in agreement with the value obtained by initial rates method. In other words, the reaction can be considered zero order with respect to sulfuric acid concentration. The apparent reaction rate is therefore independent of the acid concentration. This is due to the excess acid used in the activation process. Therefore, the diffusion step rather than the chemical reaction step determines the overall rate of reaction.

3.2.2. Activation energy

The apparent activation energy of the sulfuric acid reaction with clay is determined from experimental data using Arhenius equation.

$$k = k_o\, e^{-E/RT} \tag{3}$$

and

$$\ln k = \ln k_o - E/RT \tag{4}$$

where k_o is Arhenius constant, E is the activation energy in cal/mol, R is gas constant (= 1.987 cal/mol K) and T is the reaction temperature in K.

Figure 8 shows the plot of lnk versus 1/T. The slope of the straight line obtained is -93.57 K. Therefore, the value of the apparent activation energy was found to be 430 cal/mol. This low value substantiates the claim that the reaction is limited by diffusion.

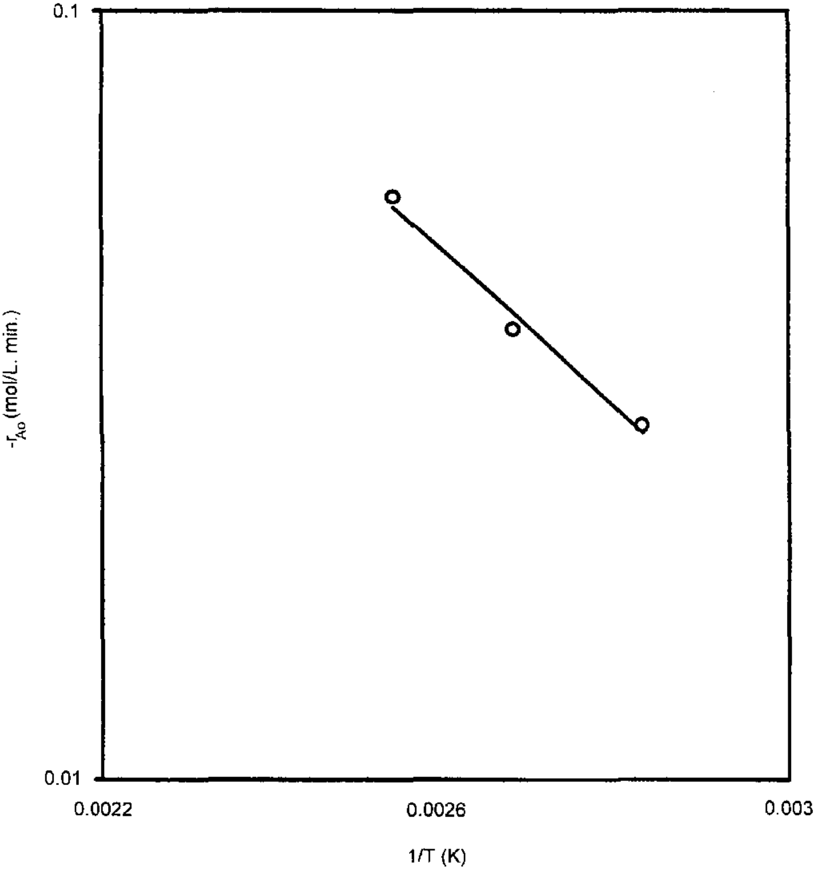

Fig. 8. Reaction rate constant versus 1/T.

Conclusion

Local Saudi sodium bentonite can be treated with sulfuric acid to give an active clay that can be used for bleaching of refined edible oils. The conditions that give best results for activation are:

acid concentration = 45% H_2SO_4 by wt., temperature of reaction = 120 °C (boiling point of the acid), time of reaction = 15 minutes , liquid to solid ratio = 5:1, Grain size = -325 mesh (95% passing) and mixing rate = 200 rpm.

The produced active clay under such conditions has a bleaching power comparable to commercial active clays. The apparent order of the heterogeneous reaction between sulfuric acid and clay is zero and the activation energy is 430 cal/mol.

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دراسة حول تنشيط خام البنتونيت السعودي

١– دارسة أفضل الظروف وحركية التنشيط باستخدام حامض الكبريتيك

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قسم الهندسة الكيميائية ، جامعة الملك عبد العزيز ، ص.ب ٩٠٢٧ .
جدة ٢١٤١٣ ، المملكة العربية السعودية

(قدم للنشر في ٠٣/١١/١٩٩٩م ، وقبل للنشر في ٠٨/٠٤/٢٠٠٠م)

ملخص البحث. تتواجد في المملكة العربية السعودية الكثير من خامات الطفلة من نوع مونتمورلونيت القابل للتنشيط . تم إجراء دراسة معملية حول تنشيط خام البنتونيت السعودي باستخدام حامض الكبريتيك ، و تمت مقارنة نشاطية الناتج مع نشاطية الطفلة التجارية في تبييض زيت الذرة ، ووجد أن أفضل ظروف التنشيط باستخدام حامض الكبريتيك كالآتي : (تركيز الحامض ٤٥٪ بالوزن ، نسبة السائل إلى الصلب ٥ : ١ (ملل / جم)، حجم الحبيبات ٩٥٪ تمر من منخل −٣٢٥ فتحة عند درجة حرارة الغليان لزمن ١٥ دقيقة وسرعة التقليب ٢٠٠ لفه في الدقيقة . وقد وجد أن استخدام تركيزات أقل من الحامض تتطلب زمن أطول للوصول لنفس درجة تنشيط الخام بالمقارنة باستخدام تركيزات أعلى من الحامض .

كما وجد أن البنتونيت السعودي المنشط مكافئ في خواصه للطفلة التجارية سواء في النوعية أو في قوة التبييض . وقد بينت دراسة حركة التفاعل غير المتجانس بين البنتونيت السعودي وحامض الكبريتيك أنه من النوعية ذات درجة تفاعل صفر وأن طاقة التنشيط الظاهريه تساوى ٤٣٠ سعر لكل جزئ.