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Study on the Activation of Saudi Natural Bentonite, Part II: Characterization of the Produced Active Clay and Its Test as an Adsorbing Agent

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Abstract. The active clay (Saudi-bentonite) produced by the acid activation of Saudi natural clay was characterized with respect to chemical composition and physical properties. The obtained results were compared with commercial active clay being used in bleaching edible oils. Also, the adsorptive ability of clay to remove some coloring matter was investigated.The chemical composition of the produced active clay was found to be close to that of the commercial clay with slightly higher iron and silicon oxides percentages and a lower percentage of aluminum oxide. The activated clay has an average surface area of 267.5 m^2/g and a bulk density of 720 kg/m^3. These results are very close to those of the commercial active clay. The adsorption of the coloring matter present in edible oil and a basic dye (methyl violet) on activated Saudi-bentonite was found to follow the Freundlich equation. The values of the constants were found to be dependent on the matter being adsorbed. However, the clay failed to remove acidic dyes from aqueous solutions because of the acidic nature of the clay.

Notation

C_o	initial dye concentration (mg/L)
C_e	residual (equilibrium) concentration (mg/L)
N	normality of sodium hydroxide
OR	oil retention
V	volume of sodium hydroxide used in titration (mL)
W	weight of clay (S-B) (g)
W_C	weight of cake (g)
x/m	mass fraction of dye on solid (mg/g)

1. Introduction

In part I of this work [l], the results of the activation of Saudi natural bentonite mineral with sulfuric acid were presented as well as the result of the apparent kinetics of the activation reaction. The produced Saudi-bentonite was tested against an active commercial clay for bleaching corn oil. The results showed a highly active clay which will be referred to as Saudi- bentonite.

Bentonite clays are used in preparation of drilling mud [2] and in making models for molten metals casting such as cast iron [3]. But one of the most important uses of bentonite clay is in the bleaching of edible and mineral oils. The active bentonite has the ability to adsorb coloring organic matter on its surface. As an adsorbent, the clay must possess high surface area per unit mass and must have an active surface. During acid activation, the structure of the raw clay is opened and becomes porous. At the same time H^+ replaces other metallic ions in the structure such as Fe^{+3}, Al^{+3}, Ca^{+2},........etc. giving the resulting clay a highly active structure which is acidic in nature [41].

In this paper, characterization of Saudi-bentonite clay is undertaken. Chemical analysis, specific surface area, bulk density, pH....etc. are all determined experimentally for Saudi bentonite as well as the active clay (clay B) being used by a local edible oil refinery. All results will be presented in comparative form so as to give credibility to the obtained data and discussion. Finally, the adsorptive capability of Saudi-bentonite was studied not only with regard to oils but also to organic dye. This is done to check the possible use of the activated Saudi-bentonite in the treatment of dye house effluents.

2. Experimental

2.1 Specific surface area

Specific surface area was measured using Quantasorb JR instruments supplied by quantum Corp., U.S.A. according to the B.E.T. method [5].

2.2 Apparent bulk density

The method adopted by Al-Zahrani et al. [6] was used.

2.3 Oil retention [7]

100 g of oil and 10 g of clay were mixed together and heated up to 120 °C in 5 minutes then kept at this temperature for 5 minutes. The mixture was filtered using a vacuum system for 30 minutes. The filtered cake is then weighed.

$$\%OR = W_C\,(100 - \%H_2O \text{ in cake}) - 10\,(100 - \%.H_2.O \text{ in clay}) / 10 \qquad (1)$$

where OR represents oil retention, W_C is the weight of cake (g). The percent H_2O in cake and in clay was determined by drying in an oven at 110 °C until the change in weight is negligible.

2.4 pH

10 g of clay were added to 100 mL of distilled water. The mixture was stirred vigorously. The pH of the clay suspension was then measured via a 891-pH meter.

2.5 Acidity

In the acidity test [7], 10 g of clay were boiled for 3 minutes with 100 mL distilled water then filtered and washed with another 100 mL of distilled water. The combined filtrate and wash liquid is then titrated with 0.1N NaOH solution to phenolphthalein end point. The acidity is then calculated as percent weight NaOH per gram of clay:

$$\text{Acidity} = [(V \times N \times 40) / W_c] \times 100 \quad (2)$$

where V is the volume of sodium hydroxide used in titration (mL), N is normality of sodium hydroxide and W is weight of clay (g)

2.6 Adsorption experiments

2.6.1 Adsorption of coloring substances from edible oil

To study the adsorption of coloring matter by the activated Saudi-bentonite clay, five adsorption experiments were conducted using a dosage of clay from 0.25 to 2 g.

100 g of refined unbleached corn oil were placed in 250-mL flask, then a magnetic stirring bar was carefully inserted into the flask which was placed on a magnetically-stirred hot plate. A thermometer was inserted in the flask to monitor the temperature. The flask was heated, while stirring, until its temperature reached 70 °C. The known weight of the activated Saudi bentonite was added. The flask was heated until its temperature reached 90 °C and maintained at 90 ± 2 °C for 30 minutes. The oil was immediately filtered under gravity using Whatman filter paper no. 42 (15-cm diameter) then its color was measured using a PFX990 Lovibond Tintometer.

2.6.2 Adsorption of organic dyes

The adsorption of two types of dyes (acidic and basic), which are used in industry, on the activated Saudi-bentonite was investigated. The adsorption experiments were carried out at room temperature (22 ± 1°C). At first, the required equilibrium (contact) time was determined by following the residual dye concentration in solution with time. It was found that equilibrium was attained very quickly and 15 minutes were enough to establish the state of equilibrium. To determine the adsorption isotherm experimentally the following procedures were followed:

Five conical flasks each containing 100 mL of aqueous dye solution of known concentration and different weights of clay (0.25 - 2 g) were placed in a thermostated shaker for 15 minutes. The conical flasks were removed from the shaker then filtered. The first portion of filtrate was discarded and the dye concentration was measured spectrophotometrically. The equilibrium concentration of the dye adsorbed on the clay was calculated by material balance as follows:

$$x / m = (C_o - C_e) \qquad (3)$$

where (x/m) is the mass fraction of dye on solid (mg/g), C_o is initial dye concentration (mg/l) and C_e is residual (equilibrium) concentration (mg/1).

3. Results and Discussion

3.1 Chemical composition

The chemical analysis of the raw clay, activated clay and imported clay were determined experimentally in the labs of Ministry of Petroleum & Minerals at Jeddah. The results of the analysis are given in Table 1. For comparison purposes, the analyses shown in Table 1 are adjusted by the exclusion of volatile matter represented by loss on ignition from the data. The results are given in Table 2. Columns 1 and 2 in Tables 1 and 2 show the result of the activation process. Sulfuric acid reacts with the different cations forming sulfate, which reduces the percentage of such oxide in the activated clay. The removal of such cations was responsible for producing the active structure of clay as was explained earlier[1]. Comparison between the chemical composition of Saudi-bentonite and clay B (the commercial clay) shows that the differences in composition are small and they are due to the difference in the origin of each clay.

Table 1. Chemical analysis of raw, activated and commercial clays as done by Ministry of Petroleum and Mineral Resources Laboratory

Compound	Raw local clay %	Activated local clay (Saudi-bentonite) %	Commercial active clay (clay B) %
SiO_2	52.88	66.2	57.33
Al_2O_3	17.59	11.71	13.04
Fe_2O_3	10.15	3.0	1.43
TiO_2	1.1	1.5	0.25
CaO	1.26	<0.05	2.03
MgO	2.3	0.73	1.7
Na_2O	1.26	0.12	<0.05
K_2O	0.64	0.48	0.64
MnO	0.15	0.05	<0.05
SO_3	<0.05	<0.05	1.73
P_2O_3	0.27	<0.05	<0.05
L.O.I.	11.4	15.3	22.28

Table 2. Chemical analysis of raw, activated and commercial clays after exclusion of all volatile matter (L.O.I)

Compound	Raw local clay %	Activated local clay (Saudi-bentonite) %	Commercialactive clay (clay B) %
SiO_2	59.74	78.16	73.76
Al_2O_3	18.73	13.83	16.78
Fe_2O_3	11.47	3.54	1.84
TiO_2	1.24	1.77	0.32
CaO	1.42	<0.06	2.61
MgO	2.60	0.86	2.18
Na_2O	1.42	0.14	<0.06
K_2O	0.72	0.57	0.82
MnO	0.17	0.06	<0.06
SO_3	<0.06	<0.06	2.22
P_2O_3	0.31	<0.06	<0.06

3.2 Physical characterization

Table 3 summarizes the results obtained for different characteristics of Saudi bentonite clay. The results are shown along with those of clay B for comparison. It is clear from the data reported in Table 3 that the activated Saudi bentonite has similar properties as those of the commercial clay (clay B) being used in the bleaching of edible oils.

Table 3. Physical properties of raw, activated and commercial clays

Clay type	Surface area (m^2/g)	Bulk density (kg/m^3)	%Oil retention	pH	Acidity
Raw local clay	64.7	1111.1	21	8.1	0.0
Activated local clay (Saudi-bentonite)	267.5	720	57.2	3.2	0.12
Commercial active clay (clay B)	226	740	35	3.1	0.36

In order for the activated Saudi-bentonite to be considered as a bleaching clay for edible oil, the bleached oil must be of similar qualities as those bleached with commercial clays. Several tests were conducted by a local edible oil refinery for characterization of the oil bleached with the activated Saudi bentonite and the commercial clay. The results are shown in Table 4. It shows that oil bleached with activated Saudi bentonite is of similar qualities to those of oil bleached with commercial clays.

Table 4. Comparison of characteristics of unbleached oil and that oil bleached with activated local clay and imported active clays.

Bleaching clay type	Free fatty acid	Peroxide value	Gas chromatography				
			C:16	C:18.0	C:18.1	C:18.2	C:18.3
Activated local clay (Saudi-bentonite)	0.061	1.1	12.77	1.12	27.22	53.42	0.039
Commercial active clay	0.066	1.1	13.16	1.23	27.26	56.67	0.37
Unbleached oil	0.056	2.0	12.9	1.13	27.36	57.98	0.4

3.3 Adsorptive properties

The bleaching of oil by the action of clay is actually an adsorption, on the surface of the clay, of the organic coloring matter [9]. The clay used in these experiments was prepared under the pre-determined optimum conditions [1]. Figure 1 shows the bleaching curve of the clay. As the ratio of the clay to oil increases, the removal of color from the oil increases until a maximum value is reached.

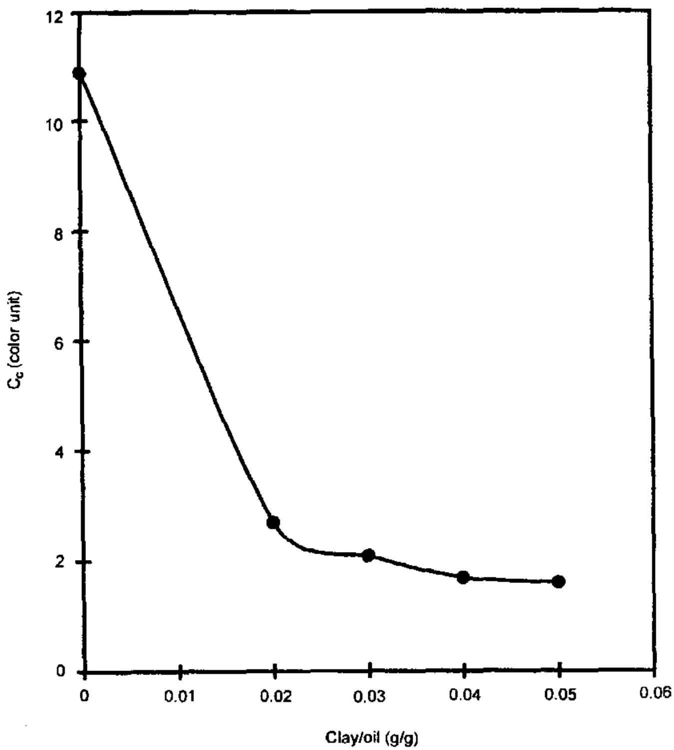

Fig. 1. Bleaching curve of oil bleached with the activated Saudi-bentonite clay.

3.3.1 Adsorption of coloring substances in edible oil

The adsorption of a solute from a dilute liquid solution by solid adsorbent is often described by Freundlich isotherm. Earlier work [9, 10] had shown that the adsorption of color impurity in oil on clay is described by the equation:

$$x/m = K\,C_e^{\,n} \tag{4}$$

where x is the mass of substance adsorbed at equilibrium, m is the mass of adsorbent, C_e is equilibrium concentration and k and n are constants. Plotting the values of ln(x/m) against C_e in accordance with the logarithmic form of the Freundlich isotherm:

$$\ln(x/m) = \ln K + n \ln C_e \tag{5}$$

will yield a straight line if the adsorption process follows the Freundlich equation. The results of adsorption of unbleached oil on the produced clay are shown in Figure 2. The reading of the color by the PFX990 Lovibond Tintometer is taken to represent the concentration of color in oil (C_e) [10]. The Figure shows that the data follows the Freundlich isotherm since a straight line was obtained. The value of n is equal to 1.35 whereas the value of K is calculated to be 105.5. The high value of K indicates that activity or decolorizing properties of the active clay are high. This value is close to the value 108.89 reported by Paradas *et al.* [11] for the adsorption of chlorophyll-a from acetone solution on bentonite clay activated with sulfuric acid. The value of n is in agreement with the values reported in the literature [10, 11] for active clay suitable for bleaching oils.

According to the above discussion and comparison with published literature, it is possible to conclude that the Saudi-bentonite has excellent bleaching properties that compare closely to those of the best active clays reported in the literature.

3.3.2 Adsorption of dyes on activated clay

One of the recent trends in the treatment of effluents containing coloring organic matter is to use an active clay instead of active carbon. The low cost of active clay as compared to activated carbon has made this alternative worth investigating.

Acid dye (acid bordeaux B)

The adsorption of acid dye on activated clay gave poor results. No noticeable removal of color was observed. This may be attributed to the acidic nature of the clay.

Basic dye (methyl violet)

The adsorption of methyl violet from dilute aqueous solution was investigated. and the results are shown in Figure 3 as a plot between equilibrium residual concentration in solution versus the dosage of active clay. It shows that the clay will be relatively effective in removing first portions of color from solution.

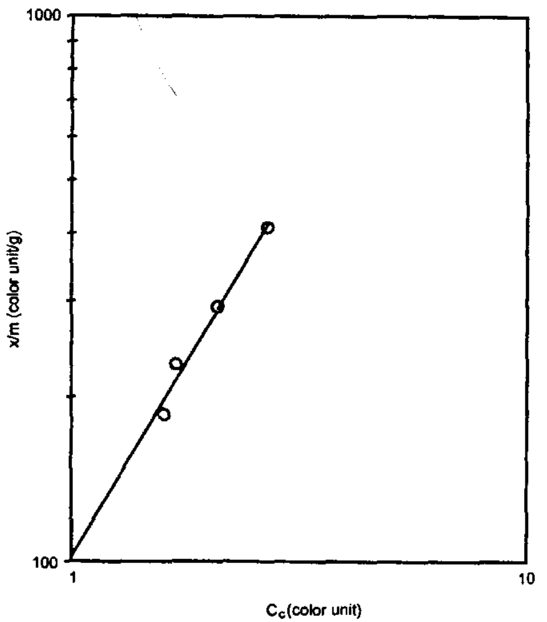

Fig. 2. Adsorption of oil color on the activated clay samples.

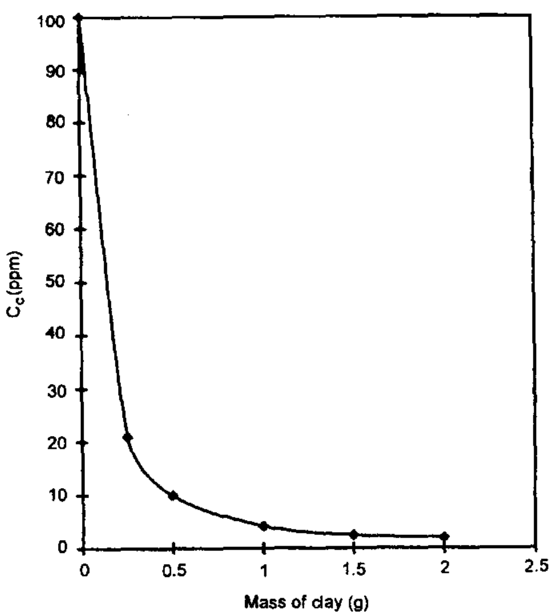

Fig. 3. Residual concentration of methyl violet as a function of clay dosage used in adsorpition experiments.

Figure 4 represents the plot of log x/m versus log Ce. The resulting straight line indicates that the adsorption process follows the Freundlich isotherm. The values of the constants n and K are 1.356 and 4.6, respectively. The high value of n explains the fast initial removal of color by activated Saudi-bentonite clay [11].

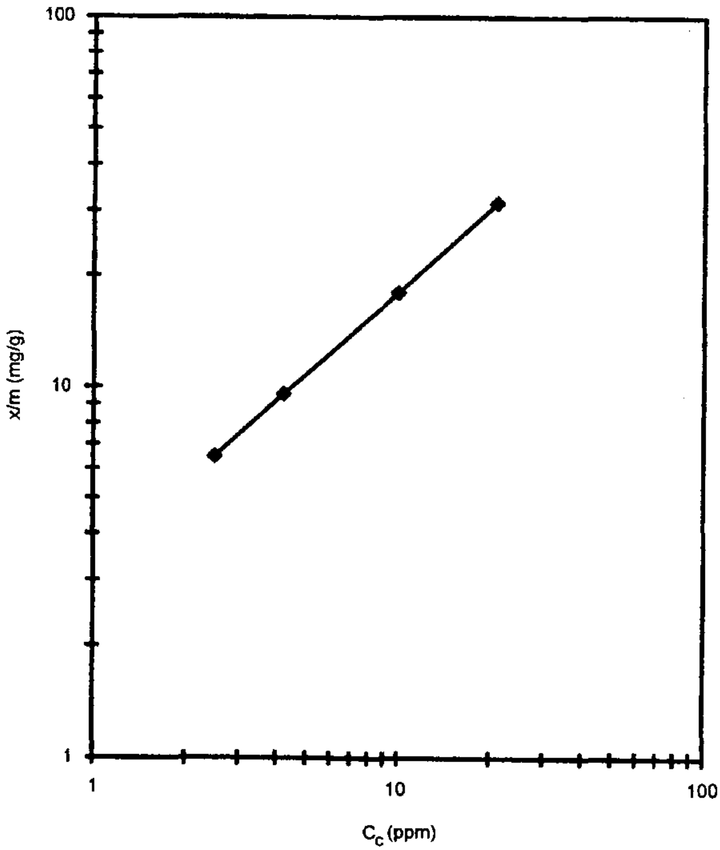

Fig. 4. Adsorption of methyl violet color on activated clay samples.

Conclusion

Saudi-bentonite prepared from Saudi-local raw clay by acid leaching is an active clay. It can be used for bleaching edible oil. The bleached oil has qualities similar to those bleached by commercial clays. The properties of Saudi-bentonite are compared with commercial active clay (clay B) and found to have similar properties but it possesses larger specific surface area. The produced Saudi-bentonite can be used for the removal of basic dyes from aqueous solution. The adsorption of the color from edible oil and the basic dye from an aqueous solution is found to follow the Freundlich isotherm. The adsorption of an acidic dye on the activated Saudi-bentonite clay gave poor results.

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دراسة حول تنشيط خام البنتونيت السعودي
٢- خواص البنتونيت المنشط واختباراته كعامل ممتز

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جدة ٢١٤١٣ ، المملكة العربية السعودية

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

ملخص البحث. تمت دراسة خواص البنتونيت السعودي المنشط وتعيين تحليله الكيميائي وخواصه الطبيعية ؛ كما تم عمل دراسة مقارنة بين استخدام كلا من البنتونيت السعودي المنشط وطفلة تجارية نشطة في عمليات تبييض زيوت الطعام ٠

وبينت نتائج الدراسة أن التحليل الكيميائي للبنتونيت المنشط مقارب للطفلة التجارية مع ارتفاع طفيف في نسبة أكاسيد الحديد والسليكون ، وانخفاض في نسبة أكسيد الألمنيوم ، وكانت المساحة السطحية المتوسطة للبنتونيت السعودي المنشط ٢٦٧,٥ م٢/جم٠ وهذه الأرقام مقاربة جدا لأنواع الطفلة التجارية النشطة .

كما تمت دراسة لاستخدام البنتونيت السعودي المنشط في امتزاز كلا من المواد الملونة الموجودة بالزيوت الغذائية وصبغة قاعدية (الميثيل البنفسجي) وكانت النتائج تتبع معادلة فروندليش ، و وجد أن قيمة ثوابت المعادلة تعتمد على نوعية المواد الممتزه ، كما بينت الدراسة أن البنتونيت السعودي المنشط لا يصلح لامتزاز الصبغات الحامضية من المحاليل المائية نتيجة طبيعة طفل البنتونيت الحامضية.