Activation of Iraqi Bentonite Powder with H_2SO_4 and its Application in Oils Bleaching

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Abstract
In this work an Iraqi bentonite powder; obtained from Al-Anbar/Akashat region; was activated using H_2SO_4 solution. The mass percentage of H_2SO_4 used in the activation process was varied between (0 - 70%).The activation process was carried out by heating the bentointe powder in H_2SO_4 solution for 1 hour at 90^oC. The result revealed that optimum acid activation occurred when (10%) acid was used in clay mixture.

Bleaching efficiency was calculated from measurement of absorbance of UV light by crude colored oil before and after treatment with activated clay. This results obtained exhibited the values of surface area and pore volume were (59.9) m^2/g and (0.1309) m^3/g respectively for the crude bentonite, after the activation with (10%) acid these values changed to (200) m^2/g and (0.5056) m^3/g respectively. On the other hand maximum surface area (350) m^2/g was obtained by using (70%) acid activation. Other properties such as density, acidity, pH and oil retention were determined and found close to that of commercial type.

Keywords: *Bentonite, acid activation, bleaching efficiency, Clay, XRD.*

1- Introduction
Bleaching is an important step in the refining of fats and vegetable – animal oils for industrial applications. In edible oil processing bleaching is responsible for clarified oil that is more stable and also more attractive to the consumer. Clarification is usually performed in an adsorption process which preferentially uses acid – treated clays to remove undesirable oil components. Bleaching primarily removes coloring pigments such as chlorophylls and carotenes but peroxides and other impurities (e.g. soap, trace prooxidant metals and

phosphatides) are also important targets of the bleaching process. Such light – colored oil influences consumers preferences but are also beneficial for quality and stability (1).

Natural or acid activated clay is composed mainly of smectite, an aluminosilicate mineral. It is well known that bentonites in their natural state have limited sorbing capacity. This ability is greatly enhanced by treatment with strong acids.

When bentonites are acid activated as a result of treatment with hot mineral solutions, hydrogen ions attack the aluminosilicat layers via the interlayer regions (2). This attack alters the structure, chemical composition and physical properties of the clay while increasing the adsorption capacity. Betonites are used as industrial raw materials in more than 25 application areas (3, 4), including the production of selective adsorbents (5, 6) bleaching earth (7, 8), catalyst beds (9), carbonless copy paper (10) and medication (11). They are also used as binders in foundries and in ceramic production since they produce muds of high plasticity with water (12, 13). The physico- chemical properties of bentonites play a major role in all these applications. Bentonites may be subjected to high temperature when used in these applications and their physicochemical properties may change as a result of thermal treatment (14).

On the other hand, acid activation of clays has attracted considerable attention in recent years. Acid activated smectites are used as catalysts, catalyst beds, adsorbents and bleaching earth in industry (14). One reason for this interest is that acid – activated clays exhibit significantly different physicochemical characteristics compared to their non – activated counterparts. One of these physicochemical properties is surface area. The surface area and the porous structure of bentonites can be changed to the desired extent by acid activation (15, 17). During acid activation, the structure of the raw clay is opened and becomes porous. At the same time H^+ ion 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 (18). The main aim of this work was to enhance the bleaching activity of Iraqi bentonite after activation by sulfuric acid. The study is also aims to discuss the variation of some of physicochemical properties of Iraqi bentonite after acid treatment.

2- Experimental

2-1 Materials

Bentonite (CaB) was obtained from the bed in the Al-anbar region in Iraq. Its basic clay mineral is calcium montmorillonite (CaM). Bentonite was supplied by Iraqi National Company for Geological Survey and Mining. Analytically pure H_2SO_4 (98%) was supplied by Biosolve Company. Vegetable oil (Supplied by State Company of vegetable oils /Baghdad – Iraq) and mineral transformer spent oil (supplied by ministry of Electricity/Middle Region of Electricity Distribution State Company).n-Hexane supplied by GCC Company (UK).

2-2 Characterization

2-2-1 X-ray diffractometry (XRD)

Standard Phllips type PW1877 Automated powder diffractometer was used with Cu-Kα radiation and a pure Silicon powder as a standard for studying the composition and diffraction pattern of clay.

2-2-2 Preparation of activated clay

Local bentonite clay was first ground and then dried at 105 ˚C for 4 hours. Eight Samples, each having a mass of (20) gm, were taken from the dried CaB. The first sample was mixed with (400) ml distilled water and a suspension was prepared. Other samples were mixed with (400) ml of H2SO4 solutions which had different concentrations, such that the mass percentage of the H2SO4 in the bentonite – acid mixture would be (5, 10, 20, 30, 40, 50, 60, and 70 %). The acid activation was performed by heating a total of 8 suspensions in a shaking water bath at 97 ˚C. The activated samples were filtered under vacuum and the precipitate was washed with distilled water until it was free of SO4-2 ions. The samples which were then dried for (24) hours at 105 ˚C were labeled and stored in polyethylene bags to be used later in the bleaching experiments. The bleaching experiments were carried out using the above prepared samples with unbleached vegetable oil (Supplied by State Company of Vegetable oils /Baghdad – Iraq) for the first set of experiments, and with unbleached mineral transformer spent or used oil (supplied by Ministry of Electricity/Middle Region of Electricity Distribution State Company) for second set of experiments, Then bleaching efficiency was determined using the following expression:

$$BE(\%) = \frac{A_{unbleached} - A_{bleached}}{A_{unbleached}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where Aunbleached and Ableached are the absorbencies of unbleached and bleached oil respectively, UV spectrophotometer model (180) Shemadzue was used for determining the absorbencies. The spectral rang used in this experiment was (200-800) nm and wavelength used (490) nm was determined from Figure (1).Figure (1) shows the absorbance as function of wave length.

2-2-3 Preparation of bleached oil

(100) g of refined unbleached oil was placed in (250) ml flask, and 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, during stirring, until its temperature reached 70 ˚C. A known weight of the activated Iraqi bentonite was added. The flask was heated until its temperature reached 90 ˚C and was maintained at this temperature for (30) minutes. The oil was immediately filtered under gravity using Whatman filter paper no. 42 (15 cm diameter) diluted with n-hexane then absorbance of color was measured using a UV- spectrometer.

2-2-4 Specific surface area

Specific surface area was measured using instrument model Q-surf (9600) according to the B.E.T. methods.

2-2-5 Apparent bulk density

This measurement was carried out according to ASTM method D2854- 83.

2-2-6 Oil retention

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

$$\% OR = W_c\ (100 - \%\ H_2O \text{ in Cake}) - 10\ (100 - \%\ H_2O \text{ in Clay}) / 10 \qquad (2)$$

Where OR represents oil retention, Wc is the weight of cake (g). The percent of H2O in cake and in clay was determined by drying them in an oven at 110 ˚C until the change in weight was negligible.

2-2-7 pH and Acidity measurement

10 g of clay was added to 100 ml of distilled water. The mixture was stirred vigorously. The pH of the clay suspension was then measured via pH meter.

In the acidity test (19), (10) g of clay was boiled for 3 minutes with (10) ml distilled water then filtered and washed with another (100) mL of distilled water. The combined filtrate and wash liquid were then titrated with (0.1) N NaOH solution to phenolphthalein end point. The acidity is then calculated as precent weight of NaOH per gram of clay

Acidity= $[(V \times N \times 40) / W_c] \times 100$…………………………………………………….. (3)

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).

2-2-8 Adsorption of coloring substances from oil

To study the adsorption of coloring matter by the activated Iraqi – bentonite clay, five adsorption experiments were conducted using a dosage of clay from 0.5 to 10 g .In each case similar procedure of preparation bleached oil is used.

3- Result and discussion

3-1 XRD results

The chemical analysis of Iraqi bentonite clay and XRD of both raw and activated clay were determined in the labs of Ministry of industry (State Company of Surveying and Mining). The composition of Iraqi raw clay is given in Table 1. As shown in Table 1,the bentonite is mainly composed of (SiO2, Al2O3, Fe2O3, CaO, MgO, Na2O3, K2O, P2O, SO2, Cl, LiO3, Na2O and CaO) which reflects the contents of cationic interlayer in monomorillonite as well as the different contents of CaO and Na2O can classify a bentonite as either Ca-bentonite or sodium bentonite [24].

Iraqi bentonite shows high content of CaO (4.48) and Na2O/CaO ratio is less than 1, which indicates the presence of Ca-bentonite. The diffractogram of raw sample indicated that the sample consisted of predominantly, substantial amount of quartz, feldspar, calcite, and Dolomite. The XRD pattern of raw clay and activated clay is shows in Figure (2). This result shows a structural change caused by high percentage of (70% acid activation). The intensity of line 2theta = (8.5˚) corresponde to the basing (001) shows a little decrease in intensity while M is diminished. On the other hand, a peak at 2theta of (27˚) is strengthed from activated sample due to amorphous silica.

3-2 Clay Bleaching performance

Analysis of Visible spectra of neutralized (unbleached oil) and oil sample treated with different acid mass percent of activated bentonite (10%-70%) were recorded in the wavelength region between (320) nm and (800) nm as shown in Figure (3).

Absorbance and bleaching efficiency curves of transformer used oil are reported in Figure (3 &4), (similar behavior was obtained with edible oil) the weakest bleaching value are given by the crude clays, on the other hand, the clays activated with different percent of acid present satisfactory values which exceed (75%).

This curve makes it possible to determine a clarification optimum activation with (10%) acid, which shows the highest value. The reduction in efficiency at activation over (50%) acid is mainly due to the intense destruction of the layer and interlayer space of activated clay this may give the interpretation of the descending in efficiency curve above (50%) acid. Moreover the other important factor in removal color and other impurities from oil is clay to oil ratio, in this case the removal of color from the oil increases until a maximum value is reached, and such result is shown in Figure (5). The residual filtrated cake from bleaching transformer using oil gave a black color which indicates the high efficiency of activated clay in removal a wide range of impurities in spent oil.

3-3 Density

The results of density measurement of activated clay are shown in Figure (6). The exhibited results show a steep decrease in density as acid % in bentonite acid mixture increased. According to this trend, clay mineral property is changed as the acid activation progresses.

The results obtained for different characterizations of Iraqi bentonite clay together with commercial active clay for comparison are summarized in table (2). The activated Iraqi bentonite properties agree well with those of the commercial clay.

4_ Conclusion

Bentonite from Al-Anbar governorate, west of Iraq, shows a predominated of calcium which allowed to characterize the sample mainly as calcium bentonite. Acid activated bentonite has a potential of decolorizing both edible and mineral used transformer oil. The most efficient bleaching capability of bentonite was obtained by activating with (10-40%) sulfuric acid at which the bleaching efficiencies fall within the range of (75-80%) expected of acid activated imported clay. Local clay can be activated using different acid (H_2SO_4) to clay ratio, to obtain bleaching clay of very good quality.

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Table (1) Chemical composition of Iraqi Bentonite.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O	SO_2	CL	LiO_3
56.77	15.67	5.12	4.48	3.42	1.11	0.6	0.65	0.59	0.57	9.49

Table (2) Physical Properties of raw, activated and commercial clays.

Clay Type	Surface area (m^2/g)	Density (Kg/m^3)	Oil Retention (%)	pH	Acidity
Raw clay	59.9	1105	21	8.1	0
Activated clay	240.03	740	49.7	3	0.16
Commercial clay	220	750	35	3.1	0.36

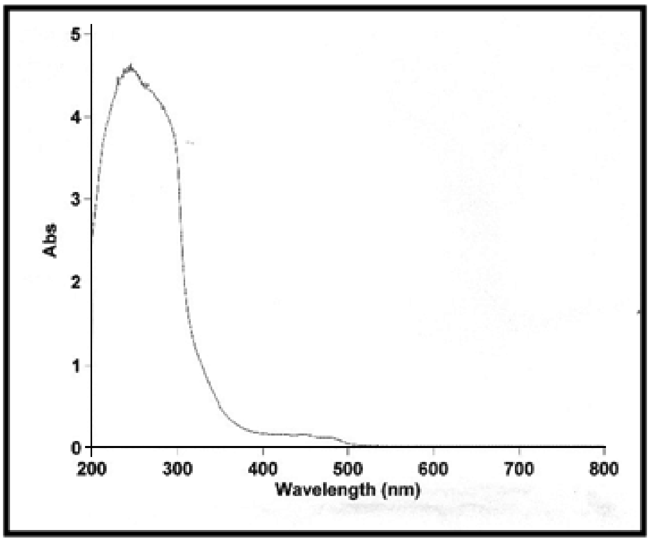

Fig (1) Visible spectra of unbleached edible oil

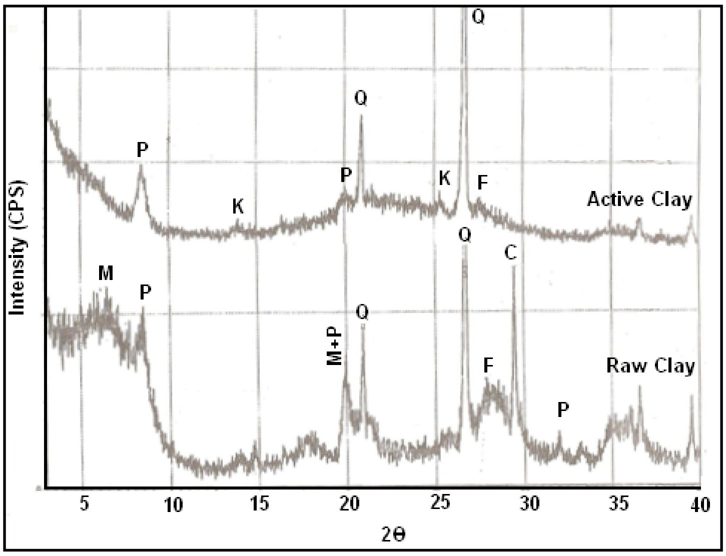

Fig (2) XRD of raw and activated clay (M: Montmorillonite, Q: quartz, F: feldspar, K: kaolinite, P: Polygorskite)

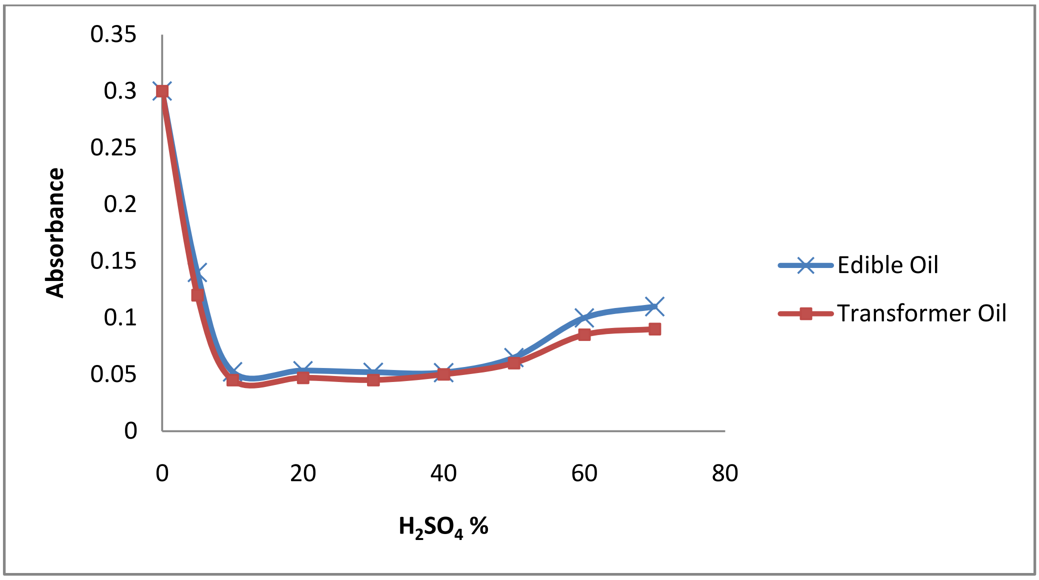

Fig (3) Absorbance of oil color by the mass percent of acid in the bentonite

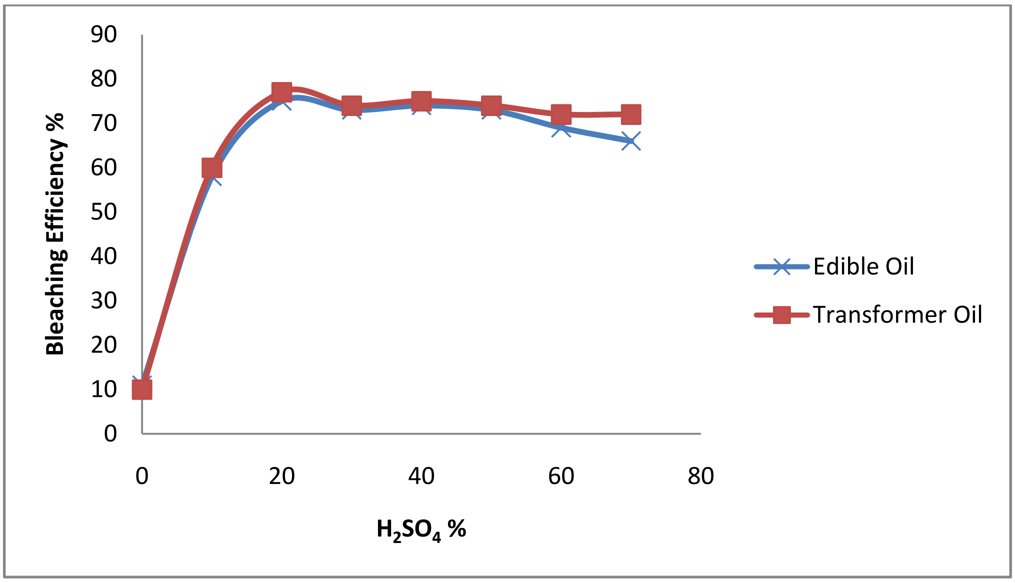

Fig (4) Bleaching efficiency curve of bentonite at different percent of acid

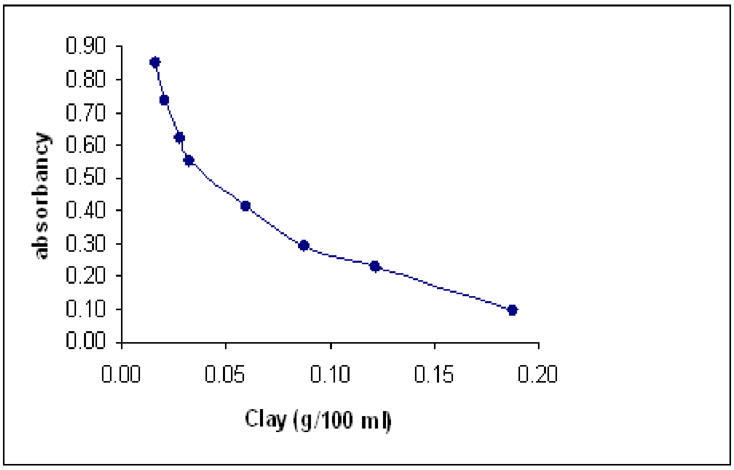

Fig (5) Variation of absorbance of oil color as a function of mass increase of activated bentonite (10% activated clay is used)

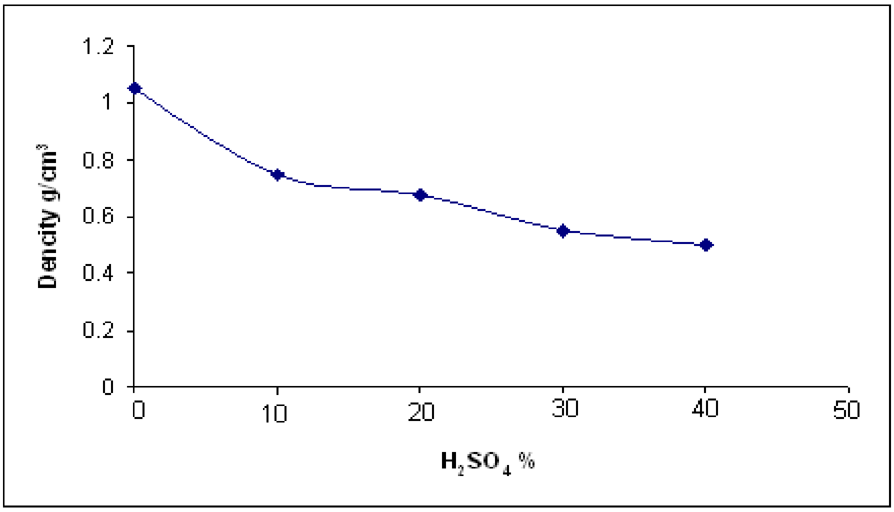

Fig (6) Variation of density of bentonite as a function of mass percent of acid in bentonite

تنشيط اطيان البنتونايت العراقية بواسطة حامض الكبريتيك وتطبيقاته في قصر الزيوت

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الخلاصة

في هذا البحث تم تنشيط مسحوق البنتونايت العراقي (الذي تم الحصول عليه من محافظة الانبار- منطقة عكاشات) باستخدام محلول حامض الكبريتك وكانت النسبة المئوية للحامض المستخدم تتراوح بين (0- 70%) وقد تمت عملية التنشيط لمسحوق البنتونايت وذلك بتسخينه في محلول الحامض لمدة ساعة وبدرجة حرارة90م. تبين من النتائج التي تم الحصول عليها ان احسن نتيجة كانت عند استخدام حامض بنسبة وزنية هي(10 %) كذلك تم التعرف على كفاءة عملية القصر التي تم حسابها من قياس امتصاصه محلول الزيت الخام للاشعة فوق البنفسجية قبل وبعد اجراء عملية التنشيط بالاطيان المنشطة.

اظهرت النتائج ايضاً ان قيم المساحة السطحية والحجم المسامي كانت (59,9) م^2/غم و (0,1309)م^3/غم على التوالي بالنسبة للبنتونايت الخام غير المعالج اما تلك القيم التالية (200) م^2/غم و (0,5056)م^3/غم بالتتابع بعد عملية التنشيط بالحامض وبنسبة وزنية (10%).

واظهرت النتائج ايضاً ان اكثر مساحة سطحية (350م^2/غم) تم الحصول عليها عندما جرى التنشيط باستخدام نسبة وزنية للحامض قدرها (70%). تم في هذا البحث ايضاً قياس بعض الخواص الاخرى مثل الكثافة، الحامضية وكمية الزيت المتبقي ووجد ان نتائجها مقاربة لتلك المعروف بالنسبة للنوع التجاري.