

ABSTRACT

This study is carried out to determine the possibility of using the Iraqi Bentonite raw material for bleaching the cottonseed oil and to study the effect of treatment with acid and caustic on the process of bleaching as well as the effect of the particle size, the degree of temperature and the time required for the process.

The Iraqi local material was examined by X-ray diffraction (XRD) and infrared spectroscopy (IR) techniques, also chemical and mineral analysis were used to determine the clay characteristic.

Two methods of adsorption were used the physical and chemical adsorption. For the physical adsorption method, two groups of Bentonite samples were prepared (A&B). For group A, the Bentonite with percentage (70%, 75%, 80%, 85%, and 90%) mixed with sulfuric acid (H_2SO_4) using different percentage (30%, 25%, 20%, 15%, and 10%) with concentration 4N for 6 hours. While sample of group B different concentration of H_2SO_4 with normality 4N and 8N were mixed with a specific amount of Bentonite for a time 3.5 hours and 6 hours. In the second group (C), the Bentonite treated with (Na_2CO_3) to get the following values of pH (8.5, 9.5, 10.5, and 12.5) for a time 3.5 hours and of pH (10.5, 12.5, and 14.5) for a time 6 hours. The process of bleaching of cottonseed oil then performed by using all the groups A,B, and C using concentration 0.3% and 0.7% for time periods 3.5 hours and 6 hours.

The red color degree for the cottonseed oil was measured using Lovibond color glasses before and after bleaching. Also the free fatty acid (F.F.A), the pH of the treated Bentonite, and the pH, density of bleached oil. The value of the physical and chemical adsorption were calculate using two equations, Frenlich and Langmuir, and the constant of the equations were determined, the result of the study reveals that the best color was

obtained by using the chemical adsorption method (group C). As the color degree of cottonseed oil changed from (16-red) before bleaching to (7-red) after bleaching with the sample (C_7) of the pH value 7.6. In the case of using the physical adsorption method. The best value of color (9.01-red) was produce using sample A_1 with concentration 0.7% and pH value 1.45 for a time 3.5 hours. While in group B, the best value produce by using sample B_4 , where the degree of color was (9.2-red) using concentration 0.7% with pH value 1.5 and time 3.5 hours.

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List of symbols

Symbols	Identity
A _o	The Adsorption of Unbleaching Oil
A _t	The Absorbance of Bleaching Oil at Time t
a, b	The Langmuir Isotherms Constants
C	The Amount of Residual Substance
c	The Velocity of The Light
d	The Interplanner Distance
e	Electron Charge
Eq.wt	The Equivalent Weight of Solution
F.F.A	The Amount of Free Fatty Acid
FTIR	For Transition Infrared Diffraction
h	Plank's Constant
K	The Frenlich Constant
Ni	The Percentage of Solution Before Dilution
Nj	The Percentage of Solution After Dilution
m	The Amount of Adsorbent
N	The Percentage of Solution
n	The Frenlich Constant
P	The Equilibrium Pressure for A Given Amount of Substance Adsorbed
Sp.Gr	The Specific Gravity of Solution
W	The Weight of Solution
V	The Volume of Solution
Vi	The Volume of Solution Before Dilution
Vj	The Volume of Solution After Dilution
X	The Relative Amount of Substance Adsorbed
Xe	The Residual Relative Amount at Equilibrium
XRD	X-ray Diffraction

The Greek Symbols

Symbols	Identity
λ	The X-Ray Wavelength
λ_0	The Minimum X-Ray Wavelength
Θ	The Angles by Bragg's Law
α, β	Alpha Carotene of Pigments of Oil
ν	The Frequency of the Continuous Spectrum
ν_0	The Maximum Frequency of the Continuous Spectrum
V	The Voltage of the Kinetic Energy

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قسم الفيزياء

دراسة استعمال المواد المحليه في تقصير الزيوت النباتيه

رسالة

مقدمة إلى كلية العلوم - جامعة النهرين

وهي جزء من متطلبات نيل درجة الماجستير في الفيزياء

من قبل

رشا شكيب مكيه

بكالوريوس ٢٠٠٣ (جامعة النهرين)

بإشراف

د. أزهار جواد داوود

١٤٢٧ هـ

٢٠٠٦ م

ربيع الأول

نيسان

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ وَأَقِيمُوا الصَّلَاةَ وَآتُوا الزَّكَاةَ وَمَا تُقَدِّمُوا لِأَنْفُسِكُمْ مِنْ

خَيْرٍ تَجِدُوهُ عِنْدَ اللَّهِ إِنَّ اللَّهَ بِمَا تَعْمَلُونَ بَصِيرٌ ﴿ صدق

اللَّهُ الْعَظِيمُ

﴿ البقرة: ١١٠﴾

الخلاصه

يهدف البحث الى دراسه امكانيه تحسين قابليه استخدام ماده البنتونايت المحليه العراقيه لقصر الزيت النباتي لبذره القطن و دراسه تاثير المعامله بالحامض والقاعده عن اداء البنتونايت وكذلك تاثير الحجم الحيبي للمسحوق المستخدم ودرجه الحراره والزمن لحدوث عمليه القصر. تم تشخيص ماده البنتونايت الاوليّه باستخدام تقنيه حيود الاشعه السينيه XRD وتقنيه تحليل مطياف الاشعه تحت الحمراء IR، كما اجريت تحاليل كيميائيه ومعدينيه للماده لتحديد نمط الاطوار الفعاله في البنتونايت الاولي.

قسمت الدراسه الى مجموعتين مجموعته التقصير الفيزياوي والكيمياوي . المجموعه الاولي التي استخدمت فيها التقصير الفيزياوي تمت معامله البنتونايت بالحامض (H_2SO_4) ، حيث تحتوي هذه المجموعه على مجموعتين (A&B) طبقا لنسب المضافه من البنتونايت ومحلول حامض الكبريتيك (H_2SO_4). حيث تمثلت المجموعه (A) باضافه البنتونايت بنسب مئويه (70% , 75%) (10% , 15% , 20%) (H_2SO_4) مع كميات من حامض الكبريتيك (80% , 85% , 90 %) (25% , 30%) بتركيز 4N لمدة ٦ ساعات . وفي مجموعته (B) تمت المعامله باضافه البنتونايت مع تراكيز مختلفه من حامض الكبريتيك (H_2SO_4) 4N,8N بازمان مختلفه ٣,٥ و ٦ ساعات. اما المجموعه الثانيه التي استخدمت فيها التقصير الكيمياوي (C) حيث عوملت اطيان البنتونايت

مع كاربونات الصوديوم اللامائية (Na_2CO_3) بالاعتماد على حصول الاس الهيدروجيني على القيم

(8.5,9.5,10.5) بزمن قدره ٣,٥ ساعات و(10.5, 12.5 , 14.5) بزمن قدره ٦ ساعات

اجريت عمليه قصر زيت بذره القطن باستخدام البنتونايت المعامل للمجاميع (A, B, C) باستخدام

نسب (0.3 % , 0.7 %) لفته زمينه ٣,٥ و ٦ ساعات.

تم قياس درجه اللون للزيت بجهاز لوفيبوند لقياس اللون الاحمر لزيت بذره القطن قبل وبعد عمليه

القصر وقياس كميته الحموضه الدهنيه الحره ،الكثافه للطين المعالج والكثافه للزيت المقصور. واجريت حسابات

الامتزاز بالطرق الفيزياويه والكيميائيه باستعمال معادلتى فرنديش و لانكماير للامتزاز ودراسه ثوابت

المعادلات لتوضيح عمليه القصر للزيت.

بعد اجراء البحث تم التوصل الى ان افضل النتائج كانت باستخدام البنتونايت المعالج بالتقصير

الكيمياويه (GroupC) في النموذج C7, تم الحصول على تغير اللون الزيت من (16-red) للون

الزيت قبل القصر الى (٧-red) بالنسبه للون الاحمر للزيت بعد القصر في الجزء القاعدي بقيمه

pH=7.6. اما عند استخدام الطريقه الفيزياويه (Group A&B) اظهرت احسن النتائج للزيت

المقصور بالحامض كانت في المجموعه A حيث ان درجه اللون للنموذج A١ تساوي (9.01-red)

باستعمال اعلى تركيز % ٠,٧ بقيمه pH=1.45 بفته زمينه 3.5 ساعات. اما في المجموعه B

ظهرت احسن النتائج في النموذج B٤ بدرجه حامضيه ٩,٢ حيث ان درجه اللون الاحمر يساوي

(9.2-red) عند اعلى تركيز للبنتونايت المعامل بالحامض % 0.7 بقيمه الاس الهيدروجيني ١,٥ وزمن

خلط قدره ٣,٥ ساعات.

CHAPTER THREE

EXPERIMENTAL WORK

3.1 RAW MATERIAL

The Raw Materials used for this study are: Bentonite, Sodium Carbonate, and Cottonseed oil.

3.1.1 BENTONITE CLAY

AL-Sofra Iraqi Bentonite clay supplied by "The Company of Geology survey in Iraq". The mineral and chemical analysis of this crude clay was carried by company of geology survey in Iraq are listed in the Tables 3.1, 3.2 respectively. The phase structure for these minerals are measured by XRD Tech. by using (SIEMENS X-RAY DIFFRACTION, UNIT MODEL D-500, KV=40, CU $K\alpha$ = line, $\lambda=1.542^{\circ}\text{A}$). This test made in University of Baghdad, the College of Science, the Geology Department. The result is shown in Figure 3.1 for this material.

The bands and structure of the crude Bentonite has been made by using (SHIMADZU FOURIER TRANSULATION INFRARED MODEL FTIR 8300 (Kyoto, Japan)). The IR spectrum for Bentonite raw material is shown in Figure 3.2.

Table 3.1 The Mineralogy of the Iraqi Bentonite (AL-SOFRA group).

Minerals	Percentage
Montmorillonite	79%
Attapulgate	7%
Calcite	5%
Apatite	5%
Gypsum	2%
Halite	1%
Quartz	1%

Table 3.2 Chemical Composition of Iraqi Bentonite (AL-SOFRA group)

Material	Bentonite Raw Material (wt %)	Food Grade (wt%) ^[69]
SiO ₂	56.77	61.08
Al ₂ O ₃	15.67	21-22
Fe ₂ O ₃	5.12	-----
CaO	4.48	2.0-2.5
MgO	3.42	3-4
Na ₂ O	1.11	3.7-4.2
K ₂ O	0.60	-----
L.O.I	1	-----

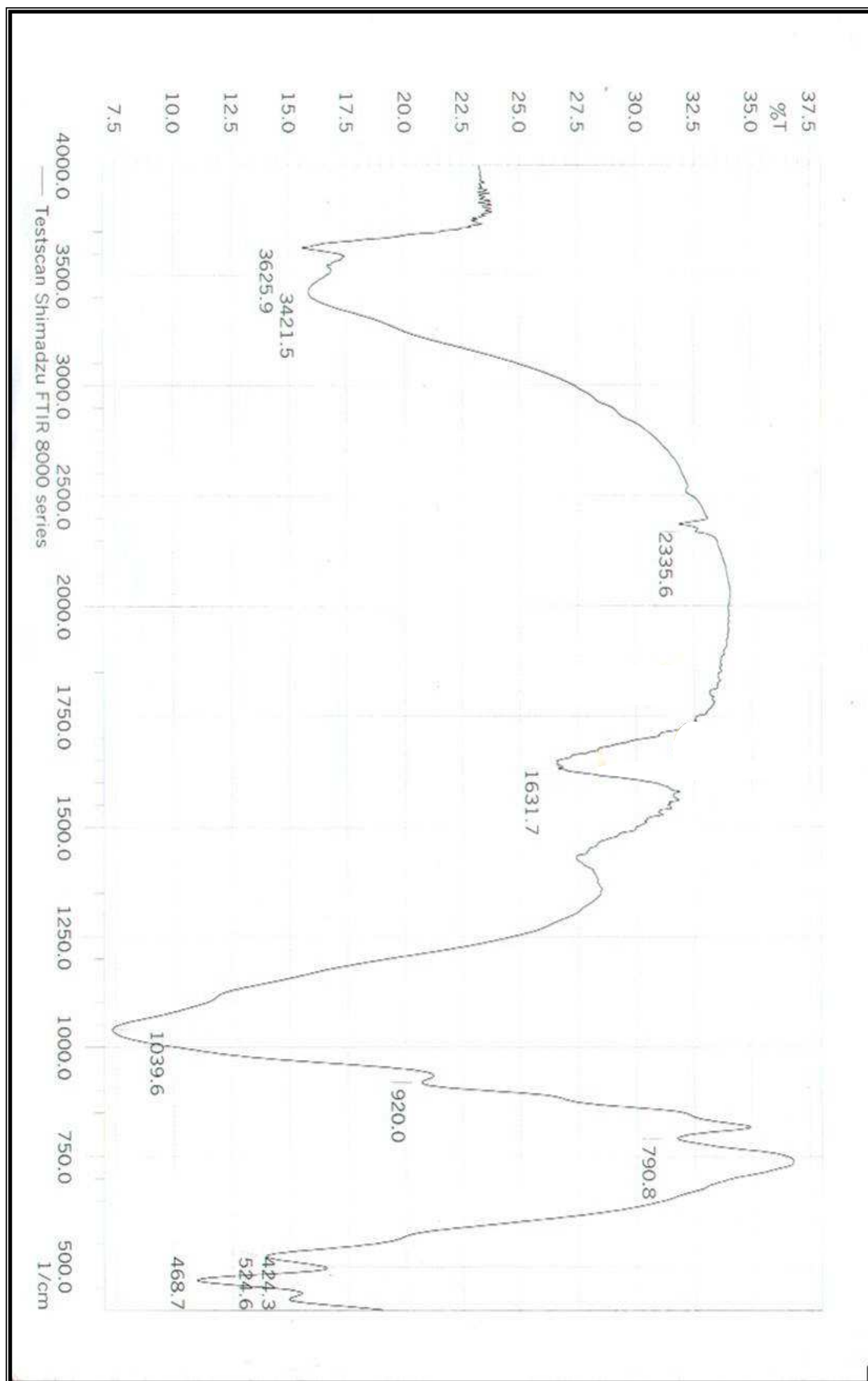


Figure 3.2 IR analyses for Bentonite raw material

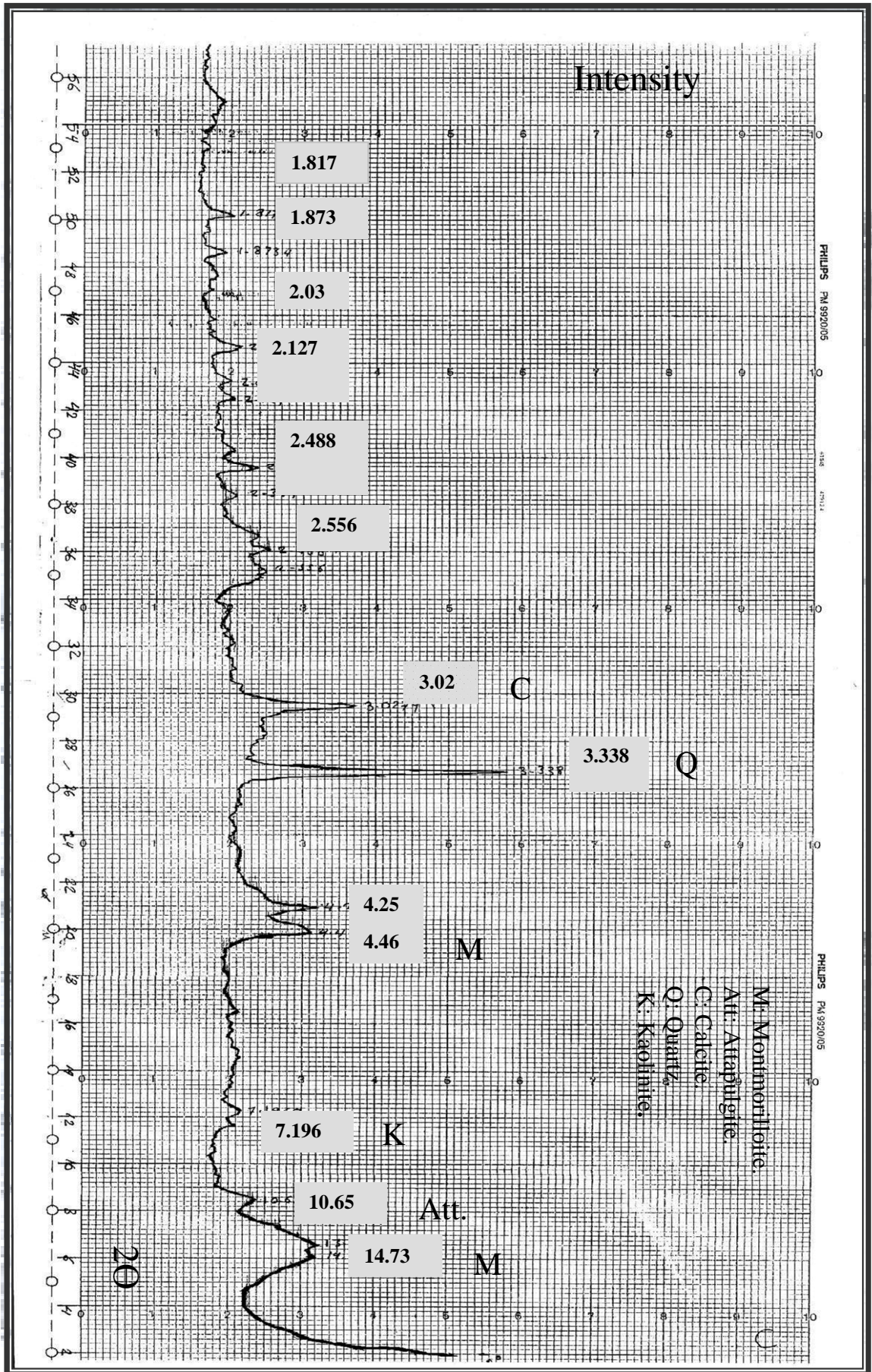


Figure 3.1 XRD pattern for Bentonite raw material

3.1.2 SODIUM CARBONATE " Na_2CO_3 "

Sodium carbonate used type (Riedel-deHaën, 5092A). Sodium Carbonate is a white, crystalline and hygroscopic powder with a purity of > 98%. Sodium Carbonate has melting point of 851 °C, it decomposes when heated at temperature greater than 400 °C, and sodium carbonate is a strong alkaline compound with pH of 11.6 for 0.1 M aqueous solution ^[68, 69].

3.1.3 COTTONSEED OIL

The cottonseed oil was supplied by "The general company for vegetable oils industry of Iraq". The characteristic of the used Cottonseed oil is shown in table 3.3.

Table 3.3 The Specification of the used Cottonseed oil (Food Grade)

Analytic	Weight percent
F.F.A	1% Max
Moisture contents	12% Max
Oil content	19% Max
Impurities	2% Max
PH	5-7 Max

3.2 TREATMENT OF BENTONITE

Two methods of bleaching were used, the first is physical adsorption method and the second is the chemical adsorption method.

3.2.1 THE PHYSICAL BLEACHING METHOD

The samples prepared using this method is divided in two groups, A and B.

Group A

This group of the Bentonite is mixed with acid as the following:

1. Taking about 200gm of crude Bentonite material using [STAUTION, 462AL] and grinding them using Porcelain ball mill. Powders of granular sizes in the range (38-75 μ m) by using different sizes are prepared .The percentages of powders used are 25% of granular size 38 μ m, 75% of granular size 63 μ m and 25% of granular size 75 μ m. These powders then mixed with 1000ml of distilled water for 30 minutes at 90 $^{\circ}$ C using [STURT SCIENTIFIC MAGNETIC STIRRER HOTBLATB, made in GREAT BRITAIN] using magnetic stirrer [model (GREAT BRITAIN, SERIAL 11750)] with 500rpm.
2. Sulfuric acid [KODAK, REAGENTACS, UN1830, MW98.08, and MADE IN U.S.A.] was taken with 4N, and then distilled with 100ml of water.

The following relation is used to calculate the proper normality [⁵⁴]:

$$N = \frac{W * SP .Gr .}{Eq .Wt} \times \frac{1000}{Vml} \dots\dots\dots (3 - 1)$$

Where N: is the percentage of solution before dilution.

Sp.Gr: is the specific gravity of acids.

W: is the weight of solution.

Eq.wt: is the equivalent weight.

Vml: is the volume in milliliter.

By using dilution equation given by:

$$N_i V_i = N_j V_j \quad \dots\dots\dots (3 - 2)$$

Where V_i : is the volume of solution before dilution.

N_j : is the percentage of solution after dilution.

V_j : is the volume of solution after dilution.

3. Variety of amounts of Bentonite solution and dilution H_2SO_4 were mixed to get five groups A_1 to A_5 as shown in Table 3.4.

4. The reaction for each group was carried out for 6 hours at a temperature between (80-90°C).

Table 3.4 Preparation of samples A_1 to A_5

Group A	Sulfuric Acid Dilution %	Bentonite Solution / %
A_1	30	70
A_2	25	75
A_3	20	80
A_4	15	85
A_5	10	90

5. The color samples of the five samples (A_1 to A_5) were changed from yellow to grey. Then the PH of each group was measured as show in Table 3.5.

6. The solid material was separated by using filter paper. Dried using Furnace [GCA/PRECTSIONSCIENTIFC, MODEL 16] at (70°C) for 12 hours. The dried powder was milled using ball mill of porcelain body with different size of sphere, following by using the powder for particle size less than 75 μ m.

Table 3.5 PH of samples

Samples	PH
A ₁	1.08
A ₂	1.36
A ₃	1.63
A ₄	2.05
A ₅	2.32

Group B

An amount of Crude Bentonite (400gm) was calcined at 400°C using furnace [GALLEN VAUK TYPE, FR610] for 3 hours. The calcined powder then sieved to get grains size less than 74 μ m. Four groups of samples (B₁ to B₄) were prepared using 100gm of the sieved powder with sulfuric acid of (4N and 8N) for two different time intervals 2 hours and 3.5 hours as shown in table 3.6.

Table 3.6 Preparation of samples (B₁ to B₄).

Group B	Bentonite Powder /g	Sulfuric Acid Dilution	Mixing Time /hr
B₁	100	4N	2
B₂	100	4N	3.5
B₃	100	8N	2
B₄	100	8N	3.5

The mixing process was performed by using magnetic stirrer of 500rpm and heating at 90^oC. Then, the same steps 4, 5, 6 in group A were repeated for the groups (B₁ to B₄). The measurement pH for the groups (B₁ to B₄) are given in table 3.7.

Table 3.7 The PH of samples

Samples	PH
B ₁	3
B ₂	2.9
B ₃	1.9
B ₄	1.8

3.2.2 THE CHEMICAL ADSORPTION METHOD

Seven samples were prepared (group C) to be used for applying the chemical adsorption methods. In this group Bentonite mixed with sodium carbonate. The step of the process were taking an amount of Bentonite equal to 150gm and mixed with distilled water to get slurry. Then Na₂CO₃

dissolved in distilled water and added to the mixture until the pH of the mixture reached 8.5 with continue of mix and heating up to 90°C by using magnetic stirrer 500rpm for a period of 3.5 hours. Then by using the same method for another three samples with pH 9.5, 10.5, 12.5 were prepared (C₁ to C₄). Then another set of samples were prepared with pH 10.5, 12.5, and 14.5 (group C₅ to C₇) using steps 1, and 2 as shown but for 6 hours as defined in table 3.8. All the seven samples (C₁ to C₇) then dried in furnace at 70 °C for 6 hours. Each of final material of the 7 groups then grinded using ball mill for four hours, then sieved to get grains size of 63µm.

Table 3.8 The preparation condition of samples C₁ to C₇.

Group C	PH of sodium Carbonate	Mixing Time /hr
C ₁	8.5	3.5
C ₂	9.5	3.5
C ₃	10.5	3.5
C ₄	12.5	3.5
C ₅	10.5	6
C ₆	12.5	6
C ₇	14.5	6

3.3 THE ADDITION OF OIL

In this part an amount of cottonseed oil equal to 200gm were heated to be in the temperature range (70-90°C), which is lower than the boiling degree of the oil. Two values of concentrations 0.3% and 0.7% of the previously prepared samples of groups (A) and groups (B) were used.

Each Bentonite group defined concentration was mixed with 200gm of cottonseed oil by a three-neck glass flask [200ml, type WITEG GERMANY]. The mixture then heated in heating Mantle [ACHTUNG, TYPE WM/MRZ/2], the process carried out with using Mechanical Mixer [KARL_KOIB, IRA-WERK, TYPE D-6072], for a time of 3.5 hours. Each final sample gets a different color. 100 gm of each sample of groups (C₁ to C₄) was mixed with 200gm of cottonseed oil using the same aperture used in step one for a time 3.5 hours. 100gm of each sample of groups (C₅ to C₇) was mixed with 200gm of cottonseed oil as in step two but for a time of mixing about 6 hours. The oil of all the samples mentioned above separated from the Bentonite using vacuum method (ELNOR, type B.2990 WESPELAAR-Belgium, made in Belgium), the degree of color of the oil samples of the original and modified were conducted by (THE GENERAL VEGETABLE OIL INDUSTRY OF IRAQ) .

3.4 OPERATION PROCEDURE

A certain amount of the treated Bentonite samples mixed with an amount of cottonseed oil in three neck glass, for a certain time with average temperature (70^oC), this procedure repeated for each group of samples. The degree of color then measured for all the samples to determine the effect both the temperature and time of heating on the bleaching process. The schematic diagram of bleaching apparatus is shown in Figure 3.3.

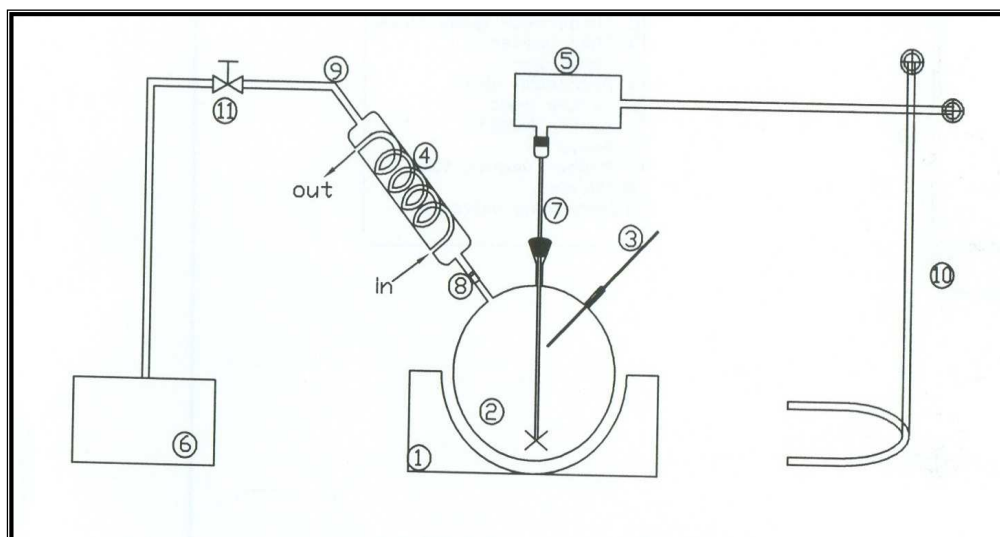


Figure 3.3 Schematic diagram of bleaching apparatus

- | | |
|----------------------------|--|
| 1. Heating mantle | 2. Three-neck glass flask |
| 3. Thermometer | 4. Condenser |
| 5. Mechanical mixer | 6. Vacuum pump, 7. Sealing rubber |
| 8. Adaptor | 9. Rubber vacuum tube |
| 10. Stands | 11. Controlling valve. |

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 THE RESULTS OF MEASUREMENTS

Bentonite local materials are treated using two methods, the first is divided into two groups (Group A and B) and the second is sodium activation process (Group C). According to the concentration of acid and clay concentration, nine samples were prepared for group A and B, and seven samples were prepared for group C, According to pH value.

4.1.1 MEASUREMENT OF GROUP A

1. The pH, F.F.A, the bleaching color and the density for group A were measured and the results of these measurements are shown in table 4.1. The values of bleaching color vs. pH of the Cottonseed oil were plotted as shown in Figure 4.1. Figure 4.2 is a plot of the values of free fatty acid (F.F.A) vs. pH of the Cottonseed oil, and Figure 4.3 is the values of treated oil density vs. pH of the cottonseed oil.

2. The calculated values of the amount of substance adsorbed (X), residual relative amount at equilibrium X_e , the amount of adsorbent per mass percent X/m , $X/(X/m)$, $\text{Log } X_e$, and $\text{Log } (X/m)$ are given in table 4.2. The values (n , a , b , and k) which are Langmuir constants and Freundlich constants were calculated from two figures, the first is between the values of X_e against $X_e/(X/m)$, Figure 4.4 and the second is between $\text{log } (X/m)$ against $\text{log } X_e$, Figure 4.5. Langmuir constants a and b were calculated from Figure 4.4 where the slope gives $1/a$ and the intercept is

equal to b/a . The Freundlich constants were calculated from Figure 4.5, where the slope is equal to n and the intercept is equal to $(\log k)$. Where K is a general measure of the active decolorization power of the adsorbent, and n is an indication of its characteristic manner of adsorption. The whole values are given in table 4.3.

Table 4.1 Values of pH_{oil} , F.F.A, and Density of the bleaching color of Cottonseed Oil with concentration 0.3%, 0.7% of Bentonite at temperature $70^{\circ}C$ (group A).

Sample	0.3%					0.7%				
	A ₁	A ₂	A ₃	A ₄	A ₅	A ₁	A ₂	A ₃	A ₄	A ₅
PH_{oil}	1.51	1.93	2.32	3.12	3.51	1.45	1.75	1.99	2.5	2.21
F.F.A	6.51	5.21	4.75	3.12	2.21	6.22	5.01	4.63	2.99	2.11
Density (gm/cm³)	0.77	0.79	0.82	0.87	0.89	0.71	0.73	0.75	0.82	0.88
Bleaching color	9.2	9.8	10	11.5	12.5	9.01	9.2	9.82	10.1	11.5

Table 4.2 The values of the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) for the bleaching of Cottonseed Oil with concentrations 0.3%, 0.7% of Bentonite at temperature $70^{\circ}C$ (group A).

values	0.3%					0.7%				
	A ₅	A ₄	A ₃	A ₂	A ₁	A ₅	A ₄	A ₃	A ₂	A ₁
X	0.37	0.42	0.47	0.51	0.54	0.43	0.43	0.47	0.53	0.54
X_e	0.62	0.57	0.52	0.49	0.46	0.56	0.56	0.52	0.47	0.45
X/m	1.25	1.41	1.58	1.7	1.8	0.62	0.63	0.68	0.76	0.78
X_e/(X/m)	0.5	0.4	0.33	0.29	0.25	0.91	0.9	0.76	0.61	0.58
Log X_e	-0.2	-0.24	-0.27	-0.3	-0.3	-0.25	-0.25	-0.28	-0.33	-0.34
Log X/m	0.09	0.15	0.199	0.23	0.25	-0.20	-0.20	-0.16	-0.11	-0.10

Table 4.3 Langmuir isotherm constants (*a* and *b*) and Freundlich isotherm constants (*n* and *K*) for the bleaching of Cotton-Seed Oil with concentration 0.3, 0.7% of Bentonite at temperature 70°C (group A).

Langmuir constants				Freundlich constants			
A		b		n		k	
0.3%	0.7%	0.3%	0.7%	0.3%	0.7%	0.3%	0.7%
-2.34	-1.29	-3.42	-3.8	-1.18	-1.04	0.73	0.34

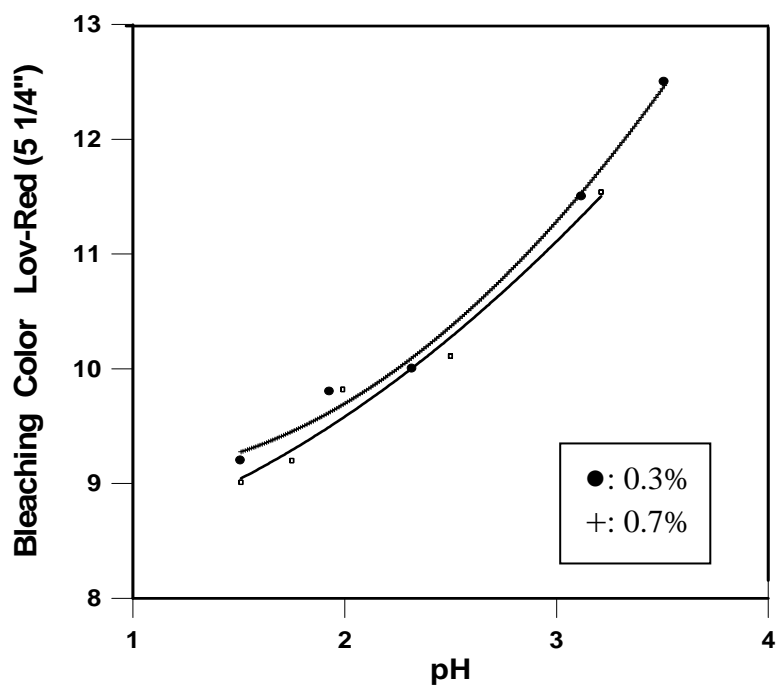


Figure 4.1 The bleaching color of cottonseed oil dependence on Bentonite solution pH in group A.

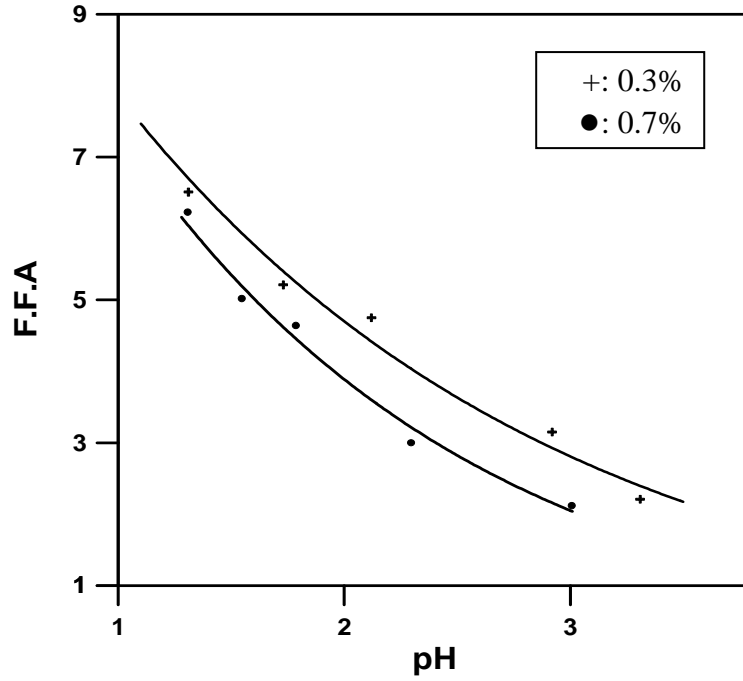


Figure 4.2 The variation of the Free Fatty Acid of Cotton-Seed Oil with the pH-Bentonite Solution of group A.

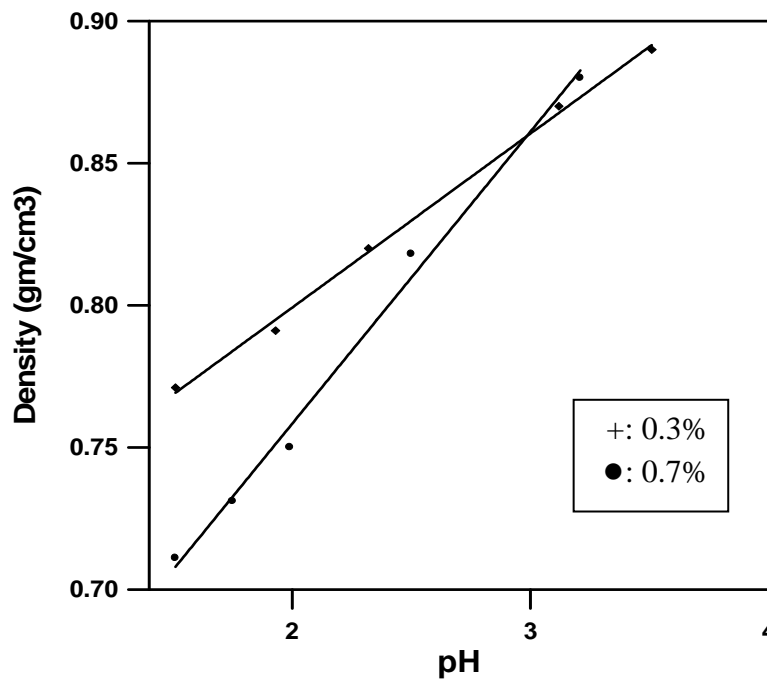


Figure 4.3 The variation of Density of Cotton-seed Oil with the pH-Bentonite Solutions of group A.

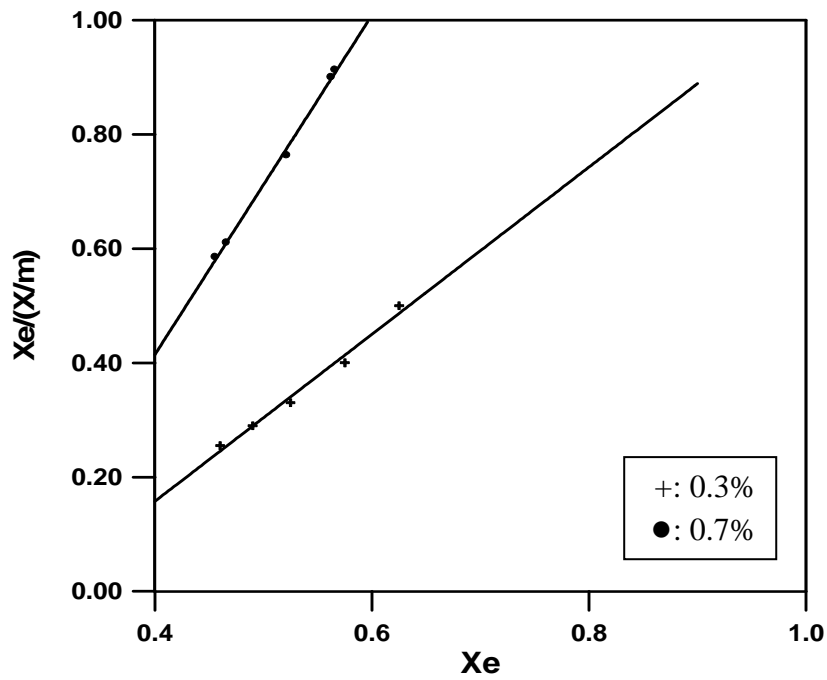


Figure 4.4 Langmuir Isotherms For the Bleaching of Cottonseed Oil With Bentonite at temperature 70°C of group A..

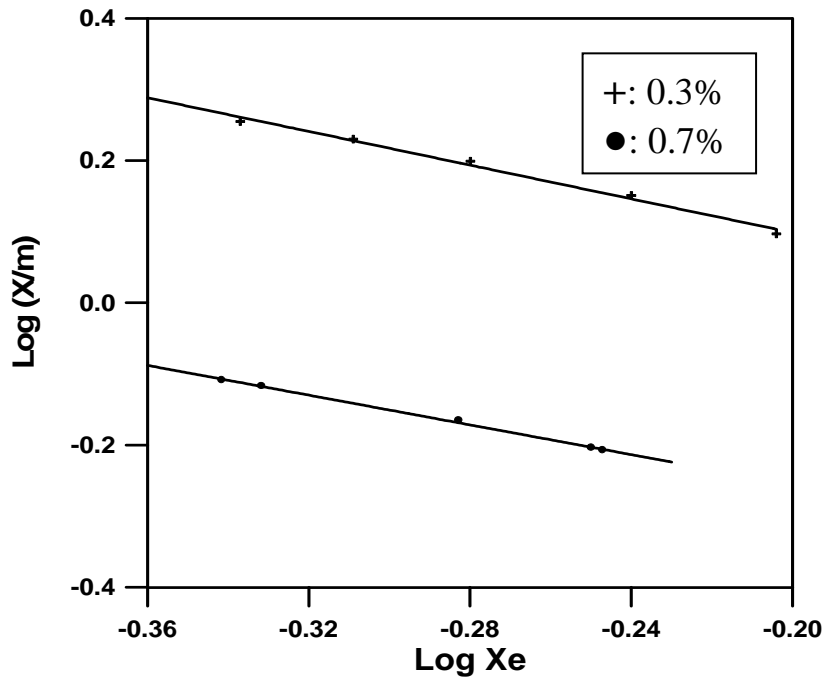


Figure 4.5 Freundlich Isotherms For the Bleaching of Cottonseed Oil With Bentonite at temperature 70°C of group A.

4.1.2 MEASUREMENT OF GROUP B

1. The measurements carried out in group A (pH of cottonseed oil, the F.F.F, Density, and bleaching color) are repeated for group B. The results are listed in table 4.4, and the values of bleaching color, the values of F.F.A, and the values of Density were plotted vs. pH of cottonseed treated are show in Figures 4.6, 4.7 and 4.8.

Table 4.4 The values of pH_{oil}, F.F.A, and Density of the bleaching color of Cotton-Seed Oil with concentration 0.3%, 0.7% of Bentonite at temperature 70°C (group B).

Sample	0.3%				0.7%			
	B ₁	B ₂	B ₃	B ₄	B ₁	B ₂	B ₃	B ₄
PH _{oil}	3.61	3.51	2.53	2	2.9	2.52	1.59	1.5
F.F.A	2.25	2.24	3.22	3.5	3.43	4.01	4.2	4.31
Density (gm/cm ³)	0.89	0.87	0.85	0.79	0.84	0.82	0.79	0.75
Bleaching color	13	12.2	11.2	12.2	11.5	10.1	9.8	9.2

2. The calculated values of X, X_e, X/m, X_e/(X/m), Log X_e, and Log X/m are given in table 4.5. Two figures were plotted to calculate the Langmir constant and Frenlich constants. Two figures are plotted of the value of X_e against the values of X/m. The first for samples B1 and B2, and the second for B3 and B4 .From the slop of these figures we get 1/a and the intercept gives b/a. On the other hand the Frenlich constants were calculated from the graphs between log X_e vs. Log X/m .The slope of these figures are equal to n and the intercepts are equal to (log k).See table 4.6.

Table 4.5 The values of the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) for the bleaching of Cottonseed Oil with concentrations 0.3%, 0.7% of Bentonite at temperature 70°C (group B).

values	0.3%				0.7%			
	B ₁	B ₂	B ₃	B ₄	B ₁	B ₂	B ₃	B ₄
X	0.35	0.39	0.44	0.39	0.42	0.49	0.51	0.54
X_e	0.65	0.61	0.56	0.61	0.57	0.5	0.49	0.46
X/m	0.35	0.39	0.44	0.39	0.42	0.59	0.51	0.54
X_e/(X/m)	1.85	1.56	1.27	1.56	1.32	0.84	0.96	0.85
Log X_e	-0.18	-0.21	-0.25	-0.21	-0.24	-0.29	-0.3	-0.33
Log X/m	-0.45	-0.4	-0.35	-0.4	-0.37	-0.22	-0.29	-0.26

Table 4.6 Langmuir isotherm constant (a and b) and Frenlich isotherm constants (n and K) for the bleaching of Cottonseed Oil with concentration 0.3, 0.7% of Bentonite at temperature 70°C (group B).

Samples	Langmuir constants		Frenlich constants	
	a	b	n	k
B1	-0.367	-2.589	-1.59	-0.176
B2	-0.389	-2.637	2.2	0.135
B3	-0.819	-3.64	-1.1	0.231
B4	-0.75	-3.56	-1.158	0.22

4.1.3 Measurement for group C:

1. The measurement for groups A and B were also carried out for group C, and the results are given in table 4.7 and Figures 4.13, 4.14 and 4.15.
2. The values of Langmuir and Frenclish constants were calculated from table 4.8 and the Figures 4.16, 4.17 and 4.18. The values of a, b, n, and K are given in table 4.9.

Table 4.7 the values of pH_{oil} , F.F.A, and Density for the bleaching color of Cotton-Seed Oil at a temperature $70^{\circ}C$ (group C).

Samples	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
pH_{oil}	5.21	6	6.4	7	6.5	7.21	7.6
F.F.A	2.31	2.23	2.12	1.92	2.11	1.83	1.77
Density (gm/cm ³)	0.62	0.57	0.54	0.5	0.62	0.58	0.56
Bleaching color	7.5	7.3	7.21	7.11	7.11	7.02	7

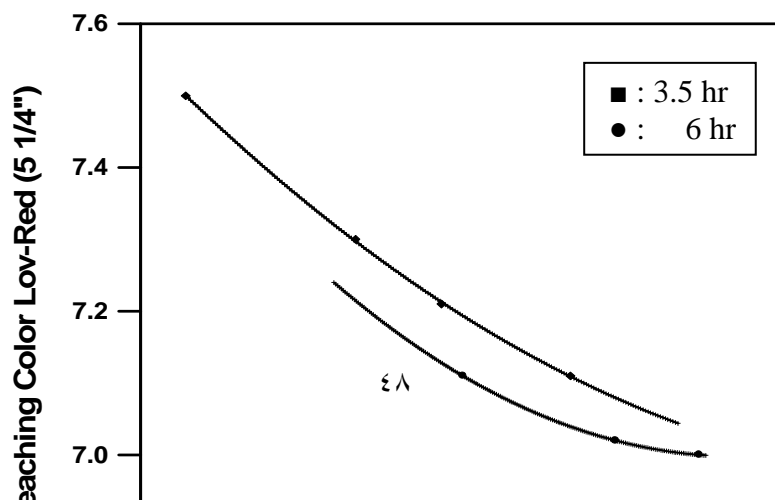
Values	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
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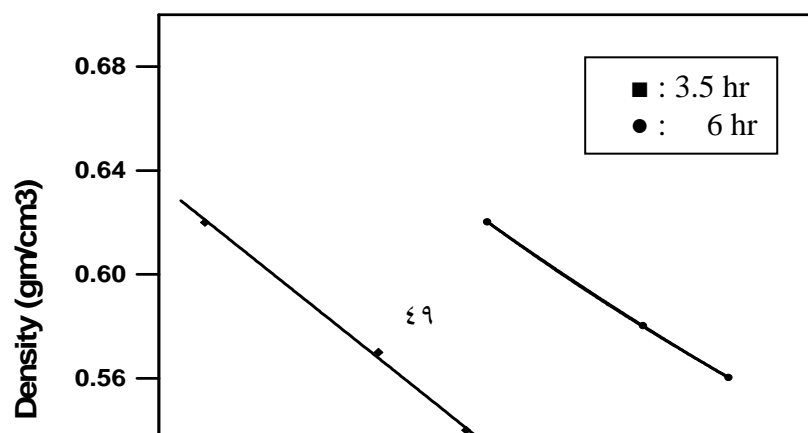
Table 4.8 The values of the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) for the bleaching of Cotton-Seed Oil at a temperature 70oC (group C).

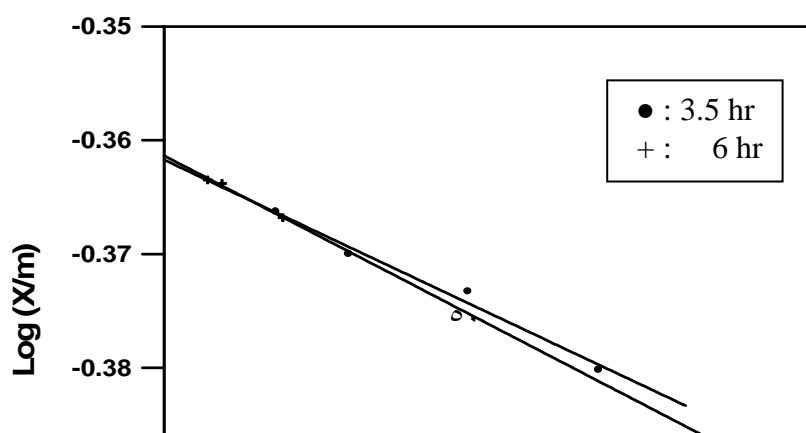
$X_e/(X/m)$	0.888	0.86	0.84	0.82	0.827	0.81	0.8
Log X_e	-0.42	-0.43	-0.44	-0.449	-0.44	-0.45	-0.456
Log X/m	-0.38	-0.37	-0.37	-0.36	-0.36	-0.36	-0.363

Table 4.9 Langmir isotherm constant (a and b) and Frenlich isotherm constants (n and K) for the bleaching of Cotton-Seed Oil at temperature 70°C (group C).

Langmuir constants				Frenlich constants			
a		b		n		k	
3.5hr	6hr	3.5hr	6hr	3.5hr	6hr	3.5hr	6hr
-1.795	-3.626	-7	-11.27	-0.44	-0.495	0.269	0.257







4.2 DISCUSSION OF RESULTS

The results of our work proved that the Iraqi Bentonite clay can be used in the process of bleaching the cottonseed oil after treatment by several processes which had be done in this study.

The results of measurements of samples A are given in Table 4.10, Figure 4.1 shows that the best degree of red color of bleaching oil is achieved at low pH (i.e. by increasing oil acidity). Where the degree of color was reduced from (12.5-red) to (9.2-red) as the pH decreased from 3.51 to 1.51 for samples with concentration 0.3%. On the other hand the free fatty acid (F.F.A) was increased from 2.21 to 6.51 as shown in Figure 4.2. The density of the oil decreased from 0.89 gm/cm^3 to 0.77 gm/cm^3 as the value of pH decreases see Figure 4.3. The degree of red

Table 4.10 The result of the measurement of group A

P h	Sample	0.3%	0.7%
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		A ₁	A ₂	A ₃	A ₄	A ₅	A ₁	A ₂	A ₃	A ₄	A ₅
	PH _{oil}	1.51	1.93	2.32	3.12	3.51	1.45	1.75	1.99	2.5	2.21
	F.F.A	6.51	5.21	4.75	3.12	2.21	6.22	5.01	4.63	2.99	2.11
	Density gm/cm ³	0.77	0.79	0.82	0.87	0.89	0.71	0.73	0.75	0.82	0.88
	Bleaching red color	9.2	9.8	10	11.5	12.5	9.01	9.2	9.82	10.1	11.5
Adsorption Parameter	X	0.54	0.51	0.47	0.42	0.37	0.54	0.53	0.47	0.43	0.43
	X _e	0.46	0.49	0.52	0.57	0.62	0.45	0.47	0.52	0.56	0.56
	a	-2.34					-1.29				
	b	-3.42					-3.8				
	n	-1.18					-1.04				
	k	0.73					0.34				

color of the bleached oil was improved slightly for samples of group (A) by using higher concentration (0.7%). For a range of pH from 2.21 to 1.45, the degree of color decreased from (11.5-red) to (9.01-red) where the F.F.A increased from 2.11 to 6.22 and the density of oil is decreased from 0.88 to 0.71 gm/cm³.

The results of measurement of samples of group B are listed in Table 4.11. The plot of the values of red color degree of bleaching oil with the pH values, Figure 4.6 shows the same results obtained for samples of group A, the degree of color improved with using low pH (i.e. increasing the acidity). Also these values of red color degree improved with the increase in concentration and normality for samples B₃ and B₄ (which have higher concentration 0.7% and higher normality 8N). The degrees of

Physi cal Para	Sample	0.3%				0.7%			
		B ₁	B ₂	B ₃	B ₄	B ₁	B ₂	B ₃	B ₄

		F.F.A	2.25	2.24	3.22	3.5	3.43	4.01	4.2	4.31
Adsorption Parameter s	Density gm/cm³	0.89	0.87	0.85	0.79	0.84	0.82	0.79	0.75	
	Bleaching red color	13	12.2	11.2	12.2	11.5	10.1	9.8	9.2	
	X	0.35	0.39	0.44	0.39	0.42	0.49	0.51	0.54	
	X_e	0.65	0.61	0.56	0.61	0.57	0.5	0.49	0.46	
	Sample	B1		B2		B3		B4		
	a	-0.36		-0.389		-0.819		-0.75		
	b	-2.589		-2.637		-3.64		-3.56		
	n	-1.59		-2.2		-1.1		-1.158		
	k	-0.176		0.135		0.231		0.22		

color are better than those of samples B1 and B2 (which have concentration 0.3% and normality 4N). The value of F.F.A in Figure 4.7 shows an inverse relation between F.F.A and pH values. Which is the same result obtained for samples of group A. The relation of density with pH values are shown in Figure 4.8, where the density is decreasing with increasing the pH values. So using low pH will improve the color and density of bleached oil.

The results of the Bentonite clay treated with sodium carbonate (Na_2CO_3) of group C are given in Table 4.12. The results show an improvement in the red color degree, the F.F.A, and the density of the bleached oil for samples C₁ to C₄, it can be noticed that the degree of red color improved from (7.5-red) to (7.11-red) as the pH changed from 5.21 to 7 (i.e. increasing of causticity) as shown in Figure 4.14. Also the

Table 4.12 The result of the measurement of group C

Physical Parameters	Samples	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
	PH _{oil}		5.21	6	6.4	7	6.5	7.21
F.F.A		2.31	2.23	2.12	1.92	2.11	1.83	1.77
Density gm/cm ³		0.62	0.57	0.54	0.5	0.62	0.58	0.56
Bleaching red color		7.5	7.3	7.21	7.11	7.11	7.02	7
Adsorption Parameters	X	0.62	0.63	0.64	0.64	0.64	0.64	0.65
	X _e	0.37	0.36	0.36	0.35	0.35	0.35	0.35
	a	-1.79			-3.626			
	b	-7			-11.27			
	n	-0.44			-0.495			
	k	0.269			0.257			

values of density of bleached oil decreased from 0.62 gm/cm³ to 0.5 gm/cm³, see Figure 4.15. For samples C₅ to C₇, the values of the red color and F.F.A and density are better than those of samples C₁ to C₄ (i.e. by increasing the time of mixing, and increasing the causticity). The best values obtained of red color degree (7-red), with F.F.A 1.77, are that of sample C₇. In the preparation of this sample, the time of mixing was 6 hours, and the caustic concentration was 7.6. A value of color equal to 7 and F.F.A equal to 1.77 can be consider a very good results compared with values used for the Iraqi oil production slandered, where the degree of red color oil is (7-red), and F.F.A is 1% max..

For groups A&B, the activation of Bentonite with hot mineral acid (H₂SO₄) strongly increases the adsorption, bleaching, and catalytic power also increase the specific surface area. This treatment of Bentonite has replaces exchangeable cation (K⁺, Na⁺, and Ca⁺) by (H⁺) in the interlamellar space and also leaches out part of Al⁺³, Fe⁺³, and Mg⁺² ions from the octahedral sheet of the lattice structure, which renders the clay

physically more porous and electrochemically more active. This results leads to the increasing in the surface area and consequently increase in the ability of Bentonite to adsorb the color components from oil ^[70, 71]. The results produce for group A which have grains of different sizes (38 μm , 63 μm , and 75 μm) are better than those produced by samples of group B, which have granular size of 75 μm only, This improvement in the results is due to the increases in the adsorption ability of the clay because of the increase in the surface area of the clay granules. The increase in amount of adsorbent concentration leads to the improvement of the color of cottonseed oil which is due to the increasing of speed of adsorbent ^[72].

In the case of using chemical bleaching method (group C), it was found that the value of bleaching red color of cottonseed oil is better than that of groups A & B. Where Na_2CO_3 treatment of Bentonite depends essentially on an ion exchange reaction; ions in the Bentonite are replaced by alkali ions. Na_2CO_3 treatment created an active Bentonite with a higher swelling capacity and increased plasticity ^[13].

The reason of the variation of free fatty acids with pH of Bentonite is due to an inverse relation between clay pH and free fatty acid increase in the oil during bleaching. The hydrogen ion causes some hydrolysis of the oil glycosides to free fatty acid and glycerin. For this reason an optimum balance must be observed by the clay manufacture between a low pH for maximum adsorptive capacity on the chlorophyll type oils, and a high pH for minimum hydrolytic effect on any fat and oil ^[18]. Also, the increase in the time of mixing has responsible effect on decreasing the value of free fatty acid ^[70]. The reduction in the bleaching oil density is due to the removal of color pigments which have a considerable weight in the oil ^[27].

The Langmuir constants for the samples of all groups (A, B, and C) are given in Tables 4.1, 4.2, and 4.3. It can be noticed that all the values of a and b are negative which indicate that there is no chemical

adsorption, according to reference ^[11]. In other words there are no bonds produced between molecules or atom, as the bonding requires high activation energy about 300-500 kJ/mol.

The value of Freundlich constants for all samples of all group (A, B, and C) are given in Tables 4.1, 4.2, 4.3, (the values of K indicate activity of decolorization power of the adsorbent. The highest value of K is 0.73 for group A with concentration 0.3% and the highest value of K for group B is equal to 0.231 for sample B₃. For samples of group C is the highest value of K is equal to 0.269. The value of K for all samples is positive which indicates that a process of physical adsorption taken place and there is an attraction between the adsorptive surface and the adsorbed molecules or atom. The energy required for physical adsorption is less than 20kJ/mol and there is no need for high activation energy ^[11]. This study shows the Freundlich adsorption equation to be applicable in the bleaching of cottonseed oil. The aim of this study was concentrated about the efficiency of bleaching the oil. But there are many parameters dealing with this process so that this research will be away to extend in future work.

4.3 CONCLUSION

1. The quantity of adsorption on the Bentonite clay surface increased with the decrease of the grain size of the adsorbent.
2. The chemical adsorption method can be used only for bleaching the oil used in making the soap. Because the sodium carbonate material working on oxidizing all the color pigments in the oil and change it to colorless materials which can not be removed easily from the oil.
3. The physical adsorption method is much easier and doesn't need a long time filtration. Also all the dissolved or colloidal pigments can be removed easily.
4. In the case of using chemical adsorption for oil bleaching (group C), the best result obtained is a color degree equal to (7-red) at pH 7.6 and F.F.A is 1.77 where the oil density is equal to 0.56.
5. In the case of using physical adsorption, the best result obtained was in group A. the value of the color is (9.01-red), at pH 1.45, the value of F.F.A is 6.22 and the density of oil is 0.71. Which in group B, the best value of color is (9.7-red) with the highest value of F.F.A equal to 4.31 at pH value 1.5 and the density of oil is 0.75.
6. The high value of F.F.A in the oil can be treated by using Alkaline. It is foam preferred to use NaOH instead of Na_2CO_3 , because the produced during treatment is lower and can be settled easily leaving the oil with high efficiency.

4.4 FUTURE WORKS

1. Use another treatment method and other additive to study the effect on improving the color of bleaching oil.
2. Study the effect of particle size by using surface area techniques on the adsorption efficiency.
3. Study the effect of using higher values of temperature during the mixing process on the efficiency of the oil bleaching.

CHAPTER ONE

INTRODUCTION

1.1 BENTONITE CLAY

The term Bentonite was first applied by Knight 1898 to particularly highly colloidal plastic clay found near Benton in the cretaceous beds of Wyoming in U.S.A ^[1].

Bentonite is a rock composed essentially of clay minerals of the Smectite (montmorillonite group). Other smectite group minerals include hectorite, saponite, beidellite, and nontronite. They consist of individual crystallites, the majority of which are <2 μ m in largest dimension ^[2].

Depending on the nature of their genesis, bentonites contain a variety of accessory minerals in addition to montmorillonite. These minerals may include quartz, feldspar, calcite and gypsum. The presence of these minerals can impact the industrial value of a deposit, reducing or increasing its value depending on the application ^[3].

Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water, creating a gelatinous and viscous fluid. Its color ranges from white to light olive, green, cream, yellow, earthy red, brown and sometime sky blue when fresh but yellowing rapidly with exposure to air when, wet it is highly plastic and slippery ^[4].

The special properties of bentonite (hydration, ion exchange, swelling, water absorption, plasticity, and thixotropy) make it a valuable material for a wide range of uses and applications ^[2].

1.2 STRUCTURE OF BENTONITE

Bentonite is Hydrated Alumino Silicates, which is the main mineral smectite (montmorillonite group). A simple formula for montmorillonite is $[(\text{OH})_2 \text{Al}_2 \text{Si}_4\text{O}_{10}]$ or $[\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}]$. Smectite are clay minerals, they consist of individual crystallites the majority of which are three layers clay mineral. They consist of two tetrahedral layers and one octahedral layer (2:1) ^[4].

The principle building element of montmorillonite are two dimension arrays of silicon-oxygen tetrahedral and two dimension arrays of aluminum or magnesium oxygen-hydroxy octahedral. In the silicon oxygen sheets, the silicon atoms are coordinated with four oxygen atoms. The oxygen atoms are located on the four corner of a regular tetrahedral with the silicon atom in the center. The silicon-oxygen sheet is called the tetrahedral sheet or the silicon sheet. In Al - Mg - O or OH sheets, the Al or Mg atoms are coordinated with six oxygen atoms or OH groups which are located around the Al or Mg atoms with their center on six corners of a regular octahedral. This sheet is called octahedral sheet or the alumina or magnesium octahedral sheet ^[5]. A schematic representation of the atom arrangement is "unit cell" is shown in Figure 1.1 for (2:1) layer clay of Bentonite, the structure is usually referred as the Hofmann structure. In the tetrahedral sheet tetravalent Si is some times partly replaced by trivalent Al ^[6].

In the octahedral sheet, there may be replacement of trivalent Al by divalent Mg without complete filling of the third vacant octahedral position. Al atoms may also be replaced by Fe, Cr, Zn, Li and other atoms. Such substitution of electropositive elements by those of lower valence result in an excess of negative charge of the layers. The net negative charge is compensated by the adsorption of cations on the layer surfaces, both on

the interior and the exterior surface of the stock [7].

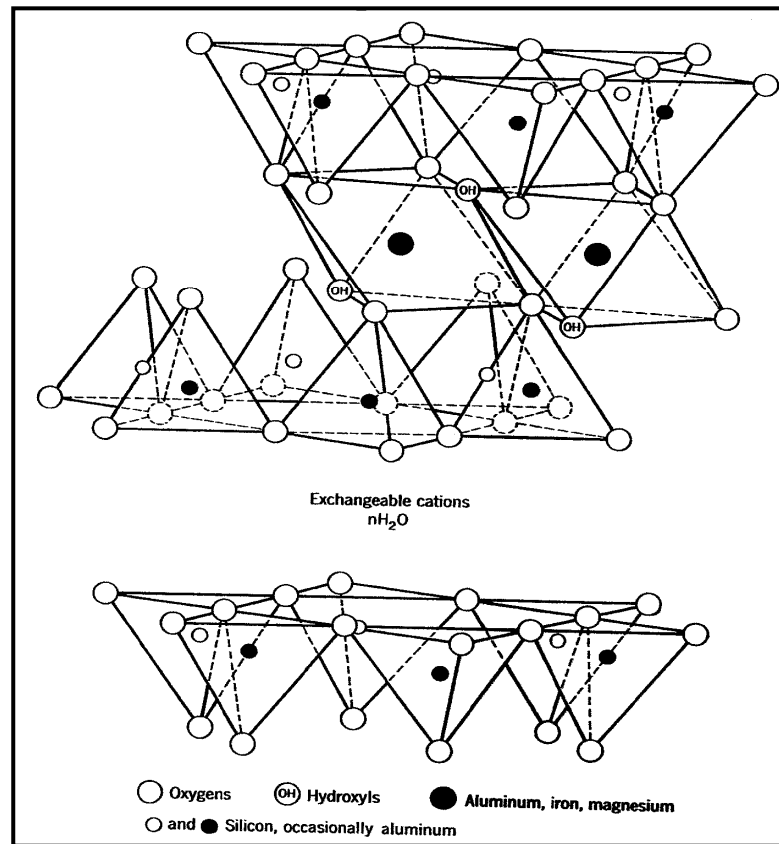


Figure 1.1 Diagrammatic Sketch of the Structure of Montmorillonite [6].

1.3 TYPES OF BENTONITE

There are three types of Bentonite, natural calcium Bentonite or calcium montmorillonite, natural sodium Bentonite or sodium montmorillonite, sodium activated Bentonite or sodium activated montmorillonite [8].

In natural calcium Bentonite, the vast majorities of the montmorillonite according in abundance world wide, are of the calcium type and referred to as calcium Bentonite. Calcium Bentonite contains calcium in its structure, has a far lower capacity to swell when wet and usually exhibits great

adsorptive characteristics. Calcium Bentonite is often characterized by much lower swelling and liquid limit values compared to natural sodium Bentonite ^[1].

Natural sodium Bentonite as the name suggests occurs with sodium as the predominant exchange cation. Sodium Bentonite contains sodium in its structure, has strong swelling properties (ability to swell to many times its dry volume when wet) and possesses a high dry-bonding strength. Sodium Bentonite is characterized by high swelling, high liquid limit and high thermal durability.

Sodium activated Bentonite is produced by the substitution of calcium ions by sodium ions. This transformation can be achieved by the addition of a soluble sodium salt to calcium Bentonite ^[1, 9].

1.4 APPLICATIONS OF BENTONITE

The applications of Bentonite includes ^[2, 4]:

- Preparation of the drilling mud.
- Purification and color reduction of fat, oils and waxes.
- Plasticizer in ceramic clay bodies.
- Binder of foundry sand.
- Agent in water and effluent purification.
- Bleaching agent industrial, bleaching agent in lubricant oil recycling.
- Bleaching earth or fuller's earth, bleaching clay, soap clay.
- Dependence on their chemistry and molecular structure can be altered by acid leaching to lender them useful as catalysts for petroleum cracking or for bleaching animal little such as cat litter.
- Small amount of Bentonite are used in the absorption of oil and greases, in paint, and paper industry.

1.5 LITRUTURE SURVEY

Bentonite is widely used in a variety industrial applications. They are components in many commercial products. Also, the presence of Bentonite components in clay and soils may significantly affect the properties of such material ^[10] .

HüSEYİN TOPLLAR (1996) ^[11] studied the adsorption isotherms of the bleaching of sunflower-seed oil. Since the heat evolved during adsorption ($0.33-1.07 \text{ kJ mol}^{-1}$) was less than 20 kJ mol^{-1} , the forces between the adsorbent and adsorb ate appear to be Van Der Waals forces, and this type of adsorption is physical or Van Der Waals adsorption. He showed that the forces between adsorbent and adsorbate appear to be Van der Waals forces, and showed that Frenclish equation is more applicable than the Langmuir equation to the experimental adsorption isotherms for the bleaching of sunflower-seed oil with Bentonite.

HAMİD JAZAYERİ and MEHRAN REZAEİ (2001) ^[12] studied the acid activation of Bentonite clays. The purpose of the study was to execute investigation for Bentonite samples from Iran, to determine the benefic ability as well as the possibility of its activation by sulfuric acid, in order to produce industrial samples of bleaching earth for bleaching test with vegetable and mineral oil.

N.YILDIZ, A. CALIMLI (2001) ^[13] studied the alteration of three Turkish Bentonite by treatment with Na_2CO_3 and H_2SO_4 . The resulting materials were analyzed by X-ray diffraction (XRD) and infrared (IR) spectroscopy. The analyses of treated samples with Na_2CO_3 and H_2SO_4 showed that the structure of Bentonite completely changed following treatment. These changes showed differences depending on exchangeable cations, clay type, and the ratio of additives.

EDWARD SOBSAZK and IRENA SLEDZ (2002) ^[14] has studied the yield of fatty impurities separation from bleaching earth by extraction method, in which they used ethanol, isopropanol in alkali medium at NaOH or KOH. The method of vegetable oil bleaching by adsorption of impurities using activated Bentonite involves the necessity of its regeneration. Studied on the yield of fatty impurities extraction by ethanol, isopropanol at the temperature 35; 50; 65°C in alkaline medium at NaOH or KOH concentration range from 0.015 to 0.415 mole/dm³ of alcohol have been carried out. They found that ethanol solution with 0.323 mol/dm³ of alcohol NaOH concentration is excellent extraction solvent

TüLAY ALEMDAROĞLU, YÜKSEL SARIKAYA, et al (2003) ^[15] investigate the surface acidity of a Bentonite modified by acid activation thermal treatment. The experimental data were evaluated by Langmuir adsorption equation and the total number of surface acid centers ($n_m/\text{mol g}^{-1}$) was determined. The variation in n_m values as a function of the mass percent of H₂SO₄ used in activation (10% - 70%) and its correlation with variation in surface area (A) and pore volume (V) as a function of the mass percent of H₂SO₄ were investigated for acid – activation KB samples . The variation in n_m values as a function of thermal treatment temperature (200°C-1300°C) and its correlation with variation in A and V as a function of thermal treatment temperature were investigation for thermally treated KB samples. They found that the variation of specific surface area and surface acidity as a function of the mass percent of the acid used in activation were more or less, parallel to each other for the case of acid-activation Bentonite samples.

E.L.FOLETTO, et al (2003) ^[16] studied the performance of an Argentinean acid-activation Bentonite in the bleaching of soybean oil. They found that the Bentonite clay can be activated with H₂SO₄ (4N, 8N) at 90°C

for 2 and 3.5 hours. They found that time and acid concentration increases the degree of destruction of the Bentonite structure. Activated samples were tested in order to verify their capacity to bleach soybean oil and were compared to standard commercial bleaching clay. Tasted samples are more efficient in bleaching than the standard.

ÖHMI (2005) ^[17] studied countercurrent bleaching of rap seed oil. He found that this process is suitable for any oil and the process can be integrated easily to existing plant and can be used without any restriction for the alkaline and physical refining.

1.6 AIM OF THE STUDY

1. Study the ability of Bentonite local material to be used as bleaching of agent vegetable oil.
2. Study the effective parameter in the process of manipulation of Bentonite material (i.e. acidity and caustic for clay, bleaching red color, free fatty acid of oil, density of oil, particle size of clay, temperature, and time).
3. Study the process parameter for bleaching with respect of this parameter.
4. The calculation of Freundlich and Langmuir constants which are a , b , n and K , where:

a is a measured for maximum adsorption corresponding to complete monolayer converge and b is Langmuir constants related to bonding energy of adsorption and represents the quantity of adsorption to adsorbents for a unit equilibrium concentration.

K : is a general measure of the active decolorization power of the adsorbent, and n is an indication of its characteristic manner of adsorption.

CHAPTER TWO

THEORETICAL PART

2.1 BLEACHING PROCESS

The bleaching process is an important step in refining vegetable oils. This step means the removal of undesired components from the oil by adsorption. This enables the produce of light colored and stable oil, acceptable to consumers.

The term refining refers to any purifying treatment designed to remove free fatty acids, phosphatides, or mucilaginous material, or other gross impurities in the oil, it excludes bleaching and deodorization. The term bleaching is reserved for treatment designed solely to reduce the color of the oil, very little material is removed from the oil by bleaching. A bleaching treatment is commonly applied to oils after purification has been largely accomplished by refining. Deodorization is the term used for treatment intended primarily for the removal of traces of constituents that give rise to flavors and odors.

Due to its sorption and catalytic properties; Bentonite is widely used in a variety of industry. The clay utilized as adsorbent, catalyst and catalyst support and decolorizing agent in oil refining, and in the pharmaceutical industries. It is well know that Bentonite in their natural state have limited sorping capacity. This ability is greatly enhanced by treatment with a strong acid ^[18].

Clay minerals are used extensively as bleaching agent for mineral and vegetable oils adsorbent. The decolorization is made by two types of clay minerals: fuller's earth and acid activated Smectite clays or acid activation Bentonite.

Activation with hot mineral acids strongly increases the adsorptive, bleaching and catalytic power and increase specific surface area^[19]. The acid treatment (activation) of Bentonite replaces the exchangeable cations (K^+ , Na^+ , and Ca^{2+}) by H^+ in the interlamellar space and also leaches out apart of Al^{3+} , Fe^{3+} , and Mg^{2+} ions from the octahedral sheet to the lattice structure (i.e. hydrogen ion attack the aluminosilicate layers via the interlayer rejoin). This process alters the structure, chemical composition and physical properties of the clay while increasing its adsorption capacity, the surface area and consequently the ability of Bentonite to adsorb the coloring component from the oil^[20, 21].

The clay bleaching earth work based on its character of adsorption and ion exchange. The adsorb influenced by some factors as follows: particle size, adsorbent polarity, surface area, pore volume, and pore size. The increase in specific surface area and pore volume improves the adsorption capacity of metal impurities, phosphatides and color bodies^[22].

The most important and generally practical method of refining is treatment of the oil with an alkali. Alkali refining effects an almost complete removal of free fatty acids, which are converted in to oil insoluble soaps. Other acids substances likewise combine with the alkali, and there is some removal of impurities from the oil by adsorption. Other acids substances is same removal of impurities from the oil by adsorption on the soap formed in the operation. Moreover, all substances that become insoluble on hydration are removed^[23, 24]. To develop the surface of Bentonite, they are treated with an inorganic chemical. There is Na_2CO_3 . Bentonite contain inorganic exchange cation such as Na^+ , Mg^{+2} , and Ca^{+2} that are strongly hydrated in the present of water. Na_2CO_3 treated of Bentonite depends on essentially on anion exchange reaction ions in the Bentonite are replace by alkali ions. During this process, the crystal structure of the Bentonite is altered by the leaching of Na^+ , Mg^{+2} , and Ca^+ ions. And the specific surface area and porosity are increased^[13].

The standard quality of cooking oil is free fatty acid: 0.3% max. Natural clay has a normal pH of 4.0-7.0, and activated clay 2.5-4.0. Chlorophyll-rich oils such as soybean oil require a low pH, i.e. substantial acidity, for optimum adsorptive capacity. While a low pH with substantial acidity is desirable in the clay for bleaching the chlorophyll- type oil, low pH also has a detrimental effect ^[23].

There is an inverse ratio between clay pH and free fatty acid increase in the oil during bleaching. For this reason an optimum balance must be observed by the clay manufacture between a low pH for maximum adsorptive capacity on the chlorophyll type oils, and a high pH for minimum hydrolytic effect on any fat and oil ^[18].

In apparent bulk density, apparent bulk density means the (wt/unit vol) of clay when it has been tamped to constant volume in granulated cylinder. The apparent bulk density of clay is one of its most informative properties. The apparent bulk density is inversely proportional to the adsorption capacity and to the clays filtration rate expressed in sec. or some time unit. The apparent bulk density depends upon the air void space in the clay, which in turn measures directly the amount of oil the clay will retain as filter cake. It can be readily seen that the lighter the clay the more oil it will soak up; thus the apparent bulk density is inversely proportional to oil retention ^[24].

Bialy ^[25] recorded that the crude cottonseed oil contain free fatty acids, glycosides, phosphatides, sterols, tocopherols, hydrocarbons, pigments (gossypol and chlorophyll), sterolucosides, and protein fragments, as well as resinous and mucilaginous materials .

There are three major types of color in vegetable oil: organic color pigments of known composition, organic degradation products, and color formed by oxidation of colorless precursors. Pigments in the most common vegetable oils are ^[18] :

- Alpha, Beta Carotene ($C_{40} H_{56}$). The carotenes are yellow to red, and structurally consist of high unsaturated hydrocarbon chains arranged in various cyclic configurations. An important characteristic of the carotenoid pigments from the standpoint of bleaching is that they are unstable to heat and, as oxidation progress, they gradually fade practically to a colorless state.
- Xanthophyll ($C_{40} H_{56} O_2$). Xanthophyll is a colored yellow, and it is structurally similar to the carotenes except for extra oxygen in the cyclic ring at each end of the hydrocarbon chain.
- Chlorophyll A and B ($C_{55} H_{72} MgN_4 O_5$) and ($C_{56} H_{70} MgN_4 O_6$). The chlorophylls are green, and structurally are unsaturated magnesium-containing esters of unsaturated primary alcohol phytol. The carotenoid pigments and the chlorophylls don't fade appreciably on heating. They are more readily adsorbed by clay with low pH (2) because alkali tends to stabilize chlorophyll, whereas acid decomposes it.
- Gossypol Pigments. The gossypol is the complex system of red, yellow, etc. pigments in cottonseed oil. This type of color is usually difficult to remove by adsorption ^[22].

In "red" cottonseed oil and products of protein degradation combined with gossypol in dark cottonseed oils ^[23].

The ratio of the weight of coloring matter is very high and many of the coloring matters have chemical properties similar to dominant ones in the fats, so it is not surprising that is difficult to remove the whole of the coloring matter with a small amount of adsorbent or to find a chemical reaction with attacks the coloring matter and not the oil or fat itself ^[24, 25].

The usual material is fuller s earth, bleaching is carried out in two ways: firstly, the most important method in industry is decolorization by adsorption, in which materials with high surface activation, such as bleaching earth or

bleaching carbons, retain the coloring substances by adsorption. Secondly, bleaching fat by chemical action by which the coloring substances are destroyed by oxidation or change in to colorless compounds ^[26, 27].

2.2 ADSORPTION BLEACHING

The most important adsorption used in bleaching fats and oil is bleaching earth or clay. The mineralogical characteristic of these earths have been discussed by Kerr ^[28] and Nutting ^[29]. Within recent years natural bleaching earths for use with fat and oils have been supplanted to a considerable degree by acid activated clays. The raw materials used for manufacture of this type of bleaching clay consist for the most part of Bentonite or Montmorillonite, which have little in decolorization power in raw state. By treatments with sulfuric acid, the surface of the clay is so altered that its bleaching power will in most case considerable exceed that of natural clays ^[30]. The acid treatments extend the surface of the clay and probably also causes important change in its chemical and physical nature. acid activation clay retain more oil per unit weight of clay than do natural earths, but their use generally leads to a lower over all loss of oil because they are more active ^[31]. Certain types of color are extremely difficult to remove except by activated clay ^[32].

2.3 CHEMICAL BLEACHING

In earth bleaching pigments are removed from oil. In chemical bleaching the pigments are allowed to remain but are oxidized to a colorless or less colored form. When an oxidizing agent is added to oil, anything that can oxidize under the conditions used will oxidize. Moreover, a slight oxidation could be serious in term of flavor stability, since the concentration of materials in parts per million can markedly affect the flavor of oil and fat ^[33]. The effect on flavor stability of edible oil naturally varies with the oil and the condition used but is generally regarded as undesirable. Consequently, edible oils and fats are never bleached chemically ^[34]. Besides bleaching clay, the only adsorbent used to any extent on fatty oils is activated carbon. Because of its retention, carbon is rarely used alone on most vegetable oils, but oil refiners frequently employ it in admixture with bleaching clay in a ratio of about (10-20) part by weight of clay to 1 part of carbon. Carbon is also a superior adsorbent for traces of soap in refined oils. It is particularly effective in removing the red, blue, and green pigments of coconut and palm kernel oils and the better grades of animal fats and popular ^[30]. Small amounts of activated carbon may be added to the bleaching clay, where chlorophyll pigments impart a greenish color to the oil ^[32].

2.4 THEORY OF ADSORPTION BLEACHING

Bleaching of oils by adsorption involves the removal of pigments that are either dissolved in the oil or present in the form of colloidal dispersed particles. The most important adsorbent used in bleaching fats and oils is bleaching earth or clay.

Bleaching clay performs not only color removal, but also the removal of trace metals, adsorption of phospholipids and soaps and decomposition of oxidation products such as peroxides [11], [35].

Two main types of adsorption, in the first type, the forces are of a physical nature and the adsorption is relatively weak [36]. The forces in this type of adsorption are known as van der Waals forces and this type of adsorption is called van der Waals adsorption, physical adsorption or physisorption. The heat evolved during van der Waals adsorption is usually small, less than 20 KJ mol⁻¹. In the second type of adsorption, first considered in 1916 by Langmuir, the adsorbed molecules are held to the surface by covalent forces of the same general type as those occurring between bound atoms in molecules. The heat evolved during this type of adsorption, known as chemisorption's; is usually comparable to that evolved during chemical bonding, 300-500 KJ mol⁻¹ [11].

Langmuir [37] considered adsorption to distribute molecules over the surface of the adsorbent in the form of a monomolecular layer and for the dynamic equilibrium between adsorbed and free molecules, he proposed the following relation:

$$\frac{P}{X/m} = \frac{1}{a} + \left(\frac{b}{a}\right)P \dots\dots\dots (2 - 1)$$

Where P: is the equilibrium pressure for a given amount of substance adsorbed.

X: is the amount of substance adsorbed.

m: is the amount of adsorbent.

a, b: are constants.

$$P = \frac{P}{P_0} = \frac{Pt}{P_0} = \frac{At}{A_0} + Xe \dots\dots\dots (2 - 2)$$

Where P_o : is saturation vapor pressure .

P_t : is pressure at time t .

P is equilibrium pressure.

The mathematical expression relating adsorption to residual solute concentration at single temperature was developed by Freundlich^[38]:

$$\frac{X}{m} = KC^n \dots\dots\dots (2 - 3)$$

Where C : is the amount of residual substance.

K, n : are constants.

Since the absorbance measurements are taken in all experiments for the bleaching process, the relative amount of pigment adsorbed (X) and the residual relative amount at equilibrium (X_e) are obtained from equation (2-3) and (2-4)^[39] .

:

$$X = \frac{A_o - A_t}{A_o} \dots\dots\dots (2 - 4)$$

$$X_e = \frac{A_t}{A_o} = 1 - X \dots\dots\dots (2 - 5)$$

Where A_o : is the absorbance of unbleached (crude) oil.

A_t : is the absorbance of bleaching oil at time t .

Thus, by means of equations (2-1) and (2-2)^[40] :

$$\frac{X_e}{X/m} = \frac{1}{a} + \frac{b}{a} X_e \dots\dots\dots (2 - 6)$$

$$\frac{X}{m} = KX_e^n \dots\dots\dots (2 - 7)$$

The equation can be written in the form:

$$\text{Log} \frac{X}{m} = \text{Log}K + n\text{Log}X_e \dots\dots\dots (2 - 8)$$

In the Langmuir isotherms for the bleaching of cottonseed oil with Bentonite, at a certain temperature, the constants (a and b) can be determined from the plot of $X_e/(X/m)$ versus X_e . Here, the slope gives $1/a$ and the intercepts is equal to b/a . Where a is a measured for maximum adsorption corresponding to complete monolayer converge and b is Langmuir constants related to bonding energy of adsorption and represents the quantity of adsorption to adsorbents for a unit equilibrium concentration. The Freundlich constants can be determined by plotting $\log (X/m)$ against $\log X_e$, the value of n can be evaluated from the slope, and the intercept gives $\log K$. Where K is a general measure of activity of decolonization power of the adsorbent, and n is an indication of its characteristic manner of adsorption ^[41]. The Freundlich equation is valid for any method of color measurement as long as the units of measurement are additive and proportional to the actual concentration of coloring materials in the oil. Results of a typical test to determine the bleach colors produced by different percentages of an adsorbent are shown in Figure 2.1. In this test the oil was refined cottonseed oil with an initial red Lovibond color of 8.0 units, and the adsorbent was acid-activated bleaching clay. The adsorption isotherm calculated from the results of the some test is shown in Figure 2.2 .The value of k for this particular test was 1.14 and the value of n was 0.84. From particle standard point, K is a general measure of the activity or decolonization power of the

adsorbent, whenever n is an indication of its characteristic manner of adsorption [42, 43].

The value of n determines the range of decolorization within which the adsorbent exhibits its greatest relative effect [44]. If n is high, the adsorbent will be relatively effective in removing the first portions of color from the oil but relatively inefficient as an agent for effecting a very high degree of decolorization. If n is low, the reverse is true. It is evident from the Freundlich equation that bleaching clay or carbon that has reached equilibrium with respect to the coloring matter in light oil will still have adsorptive capacity for the color in darker oil [45].

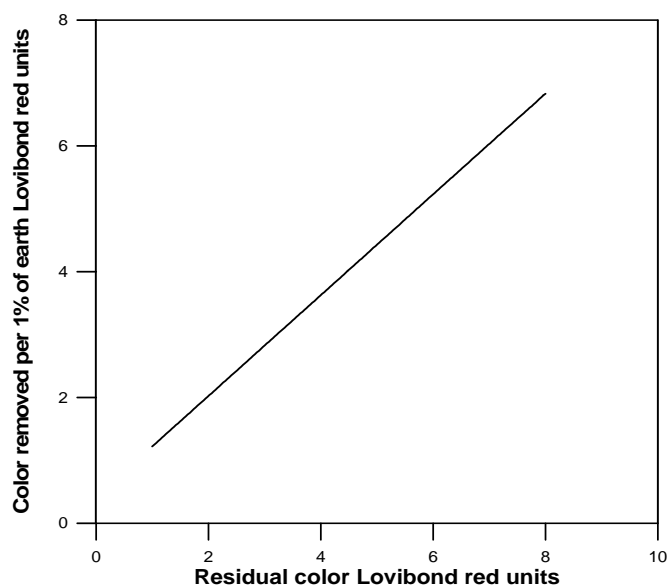


Figure 2.1 Typical bleaching tests on cottonseed oil [43].

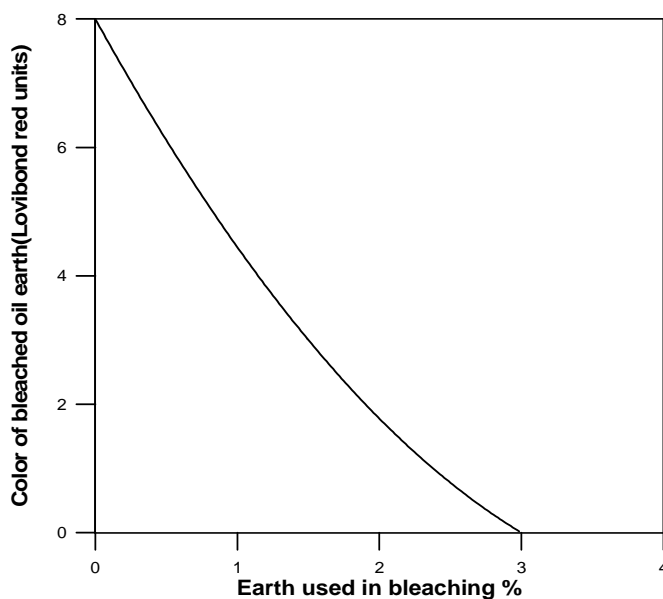


Figure 2.2 Typical adsorption isotherms for the bleaching of cottonseed oil ^[43].

2.5 SWELLING

The swelling of clays can be discussed in terms of particle interaction. Two stages of swelling should be distinguished. The first stage, up to four monolayer of water penetrate between layers of expanding clay, or between flat surfaces of adjoining particles. In the parting of the surfaces, three forces are operative – the van der Waals attraction, the electrostatic interaction of charged surfaces and cations, and the adsorption energy of the water ^[6].

In the second stage of the swelling process in which the plates are separated to distances larger than equivalent with the thickness of four layers of waters, the swelling is now governed by double layer repulsion, which is identical with the “osmotic pressure” of the system ^[1]. When Montmorillonite clay is contacted with water or with water vapor, the water molecules

penetrate between the layers. This is called interlayer swelling or intracrystalline swelling of Montmorillonite as Figure 2.3. Interlayer swelling leads to at most a doubling of volume of the dry clay. The inherent swelling potential of aggregates of clay minerals is closely related to the total external and internal surface areas of clay-mineral particles. Clay minerals are capable of adsorbing water on their outer surfaces, and water adsorbed will cause a small amount of swelling related to enlargement of the capillary films. Some clay minerals, however, such as montmorillonite and beidellite of the Smectite group, are capable of absorbing appreciable amounts of water between the individual silicate layers of the structural lattice, which results in a high swelling potential [1,6]. The swelling potential of clay is dependent upon the amount and kind of clay minerals present, their exchangeable ions, the electrolyte content of the aqueous solution, particle-size distribution, void size and distribution, water content, superimposed load, and probably other factors [21].

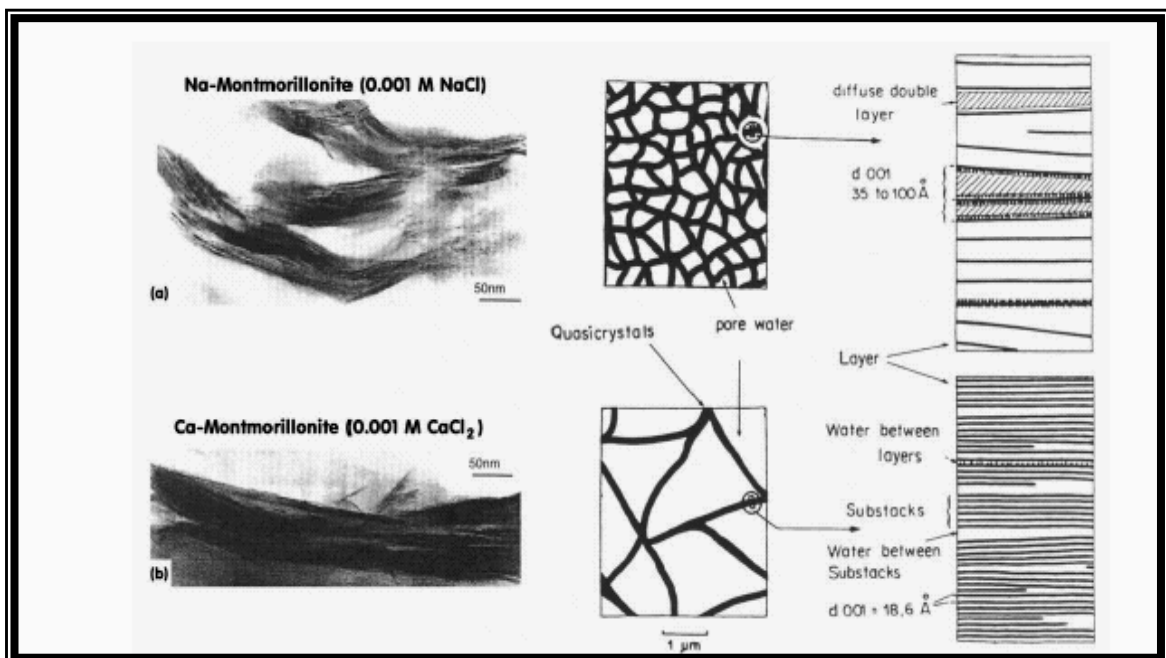


Figure 2.3 Clay fabric microstructure as affected by water solution composition [21].

2.6 ION EXCHANGE

Clay minerals have the property of sorbing certain anions and cations, retaining these in an exchangeable state; i.e. they are exchangeable for other anions or cations by treatment with such ions in a water solution (the exchange reaction also take place sometimes in an aqueous environment). The exchangeable ions are held around the outside of silica–alumina clay mineral structural units, and the exchange reaction generally does not affect the structure of silica–alumina clay packet. Exchange capacity are determined at pH=7 ^[46]. In clay minerals the common exchangeable cations are calcium, magnesium, hydrogen, potassium, and sodium, frequently in about that order of general relative abundance ^[6].

Broken bonds around the edges of the silica-aluminum units would give rise to unsatisfied charges which would balance by adsorbed cation. The number of broken bonds, the exchange capacity due to this case, would increase as the particle size decrease. In Montmorillonite broken bonds is responsible for relatively small portion (20 percent) of cation-exchange capacity ^[1].

Substitutions within the lattice of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium, for trivalent aluminum in the octahedral sheet result in unbalance charges in the structure units of same of the clay minerals. In Montmorillonite substitution within the lattice cause about 80 percent of the total cation-exchange capacity. The hydrogen of exposed hydroxyl may be replaced by action which would be exchangeable. The percentage of the cation ionized depends on the particular clay mineral, the amount of water, the natural of the cation, and the relative concentration of the cations. Anion exchange capacity acts tiny little part compared with cation exchange capacity ^[1, 5]. The adsorption phenomena of anion surfactant SDS on Bentonite particles as a

function of concentration of the surfactant is schematically presented in Figure 2.4. When clays are added into water, colloidal clay particles being to swell and disperse in suspension. Clay particles move randomly in the dispersion, and the motion, called Brownian motion, causes partial- to-partial collision. When clay minerals approach a sufficient short distance, different interactions among clay partials will be, and columbic and van der Waals forces play in important role. Dispersion of clay particles flocculates in three possible modes of particle association: (i) association between flat oxygen planes of two parallel platelets (face to face), (ii) association between adage surface of neighboring particles (edge-to-edge), and (iii) association between edge surfaces and flat oxygen planar surface (edge to face) ^[5].

When anionic surfactant is slowly added into dispersion, negatively charged hydrophilic heads bond with positively charged edge of clay minerals (Figure 2.4b). This will decrease the electrostatic attraction between clay particles and Bentonite particles. At higher surfactant concentration, free hydrophilic edges come together to develop bridge flocculation; consequently, the viscosity values increase (Figure 2.4c). Then a decrease in viscosity with further addition of surfactant corresponds to the full coverage of the particles. This decrease of the viscosity is related to the steric push occurring between SDS covered clay particles (Figure 2.4d) ^[47].

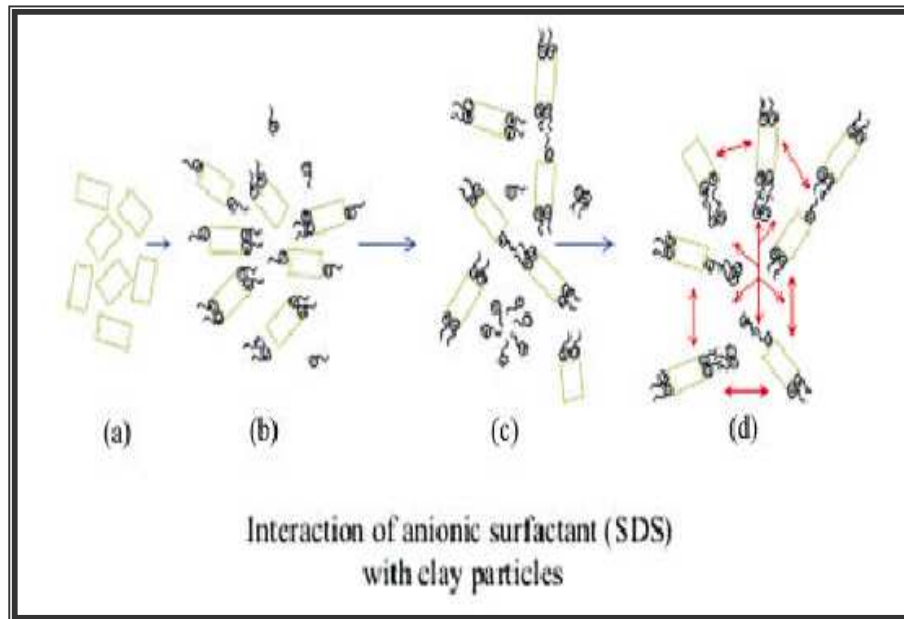


Figure 2.4 Schematic representation of adsorption of anionic surfactant on Bentonite particle as a function of the concentration of surfactant ^[47].

2.7 PLASTICITY

Plasticity may be defined as the property of a material which permits it to deform under stress without rupturing and to retain the shape produced after the stress is removed ^[2]. Clay materials develop plasticity when they are mixed with relatively small amount of water. In general, three ways to approach the measurement of plasticity can be used. One to determine the amount of water necessary to develop optimum plasticity or the range of water contents in which plasticity is demonstrated ^[1]. A second method is to determine the amount of penetration of a needle or some type of plunger into a plastic mass of clay under a given load or rate of loading. A third way is to determine the stress necessary to deform the clay, and the maximum deformation the clay will undergo before rupture at different moisture contents and with varying rate of stress application ^[48].

2.8 HYDRATION

Clay hydration may be occurs by three mechanisms. The first is the Surface hydration is the bonding of water molecules to oxygen atoms on the surface of the clay platelets. The second is the ionic hydration is the hydration of interlayer cations with surrounding shells of water molecules. The third is the osmotic hydration occurs in some clay after they are completely surface hydrated ^[49].

Figure 2.5 depicts the concept of the micro-structure and the permeability of Na-Bentonite vs. Ca-Bentonite. As shown, hydrated Na-Bentonite consists of finely dispersed clay particles, or platelets, with lower flow-efficient pore spaces resulting in longer flow paths around the clay particles due to high water binding capacity. Conversely, the divalent Ca-Bentonite particles are subjected to higher surface tension and tightly bound clay platelets resulting in aggregate clay partiales, decreased swelling potential, and increasing interstitial flow ^[50].

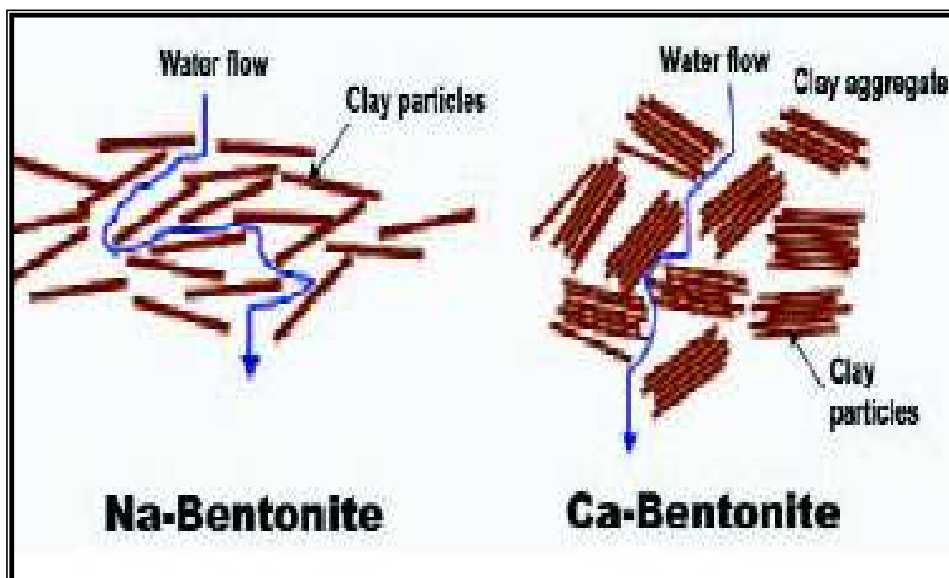


Fig 2.5 Micro-structure and permeability of Bentonite clay. Left: dispersed clay including sodium Bentonite .right: aggregated clay such as calcium Bentonite ^[50].

2.9 APPARATUS OF COLOR MEASUREMENTS

The refining of the colors of the lighter refined and bleaching oil was products by matching in a suitable tintometer a 5.12- in column of the method fat against red and yellow Lovibond color glasses (LOVIBOND, type AOSC, made by Tintometer L.T.O, SALISBNRY, ENGLAND) ^[51]. The red glass is standardized by national Bureau of standards in terms of the Priest Gibson N" color scale. The scale adopted by the manufactures of the glasses ^[52]; the latter varies slightly from one set off glasses to the other. Yellow glasses are not standardized since relatively large variation in yellow are imperceptible to the eye; in matching the color of a sample of oil ^[53]. It is necessary to only approximation the yellow color to obtain a satisfactory match with the red glasses. The depth of color of the fat or oil is satisfactorily expressed in term of red units according to the preceding scheme. The Lovibond system of color measurement is unsuitable, however, for oils that are excessively dark or that contain colored substances other than red and yellow in considerable concentration ^[54]. A Schematic diagram of the apparatus of the color was show in Figure 2.6.



Figure 2.6 Schematic diagrams of the apparatus of the color.

2.10 X-RAY DIFFRACTION MEASUREMENTS

X-rays are electromagnetic waves whose wavelength are in the neighborhood of 1\AA , which is the same order of magnitude as the lattice constants of crystals, and it is this which makes x-ray useful in the analysis of crystal structure ^[55].

The basic principle of the energy of the x-ray photon is given by the Einstein relation ($E=h\nu$), where h is plank's constant and ν is the frequency ($\nu=c/\lambda$); c is the velocity of light, λ is x-ray wavelength. When a monochromatic x-ray beam incident on the surface of a crystal, it is reflected. This reflected is well-defined by Bragg's law for constructive interference ^[56], which is:

$$2d \sin \theta = n\lambda \quad \text{..... (1.8)}$$

The angles determined by Bragg's law, for a given interplaner distance (d) and x-ray wavelength (λ), are the only angles at which reflection takes place. the maximum frequency of the continuous spectrum ν_0 is related to the accelerating potential by [$eV=h\nu_0$], since the maximum energy of a photon cannot exceed the kinetic energy of incident electron. The corresponding wavelength λ_0 is then given by $\lambda_0 (\text{\AA}) = 1.3/V$, where V is kilovolts ^[57, 58].

2.11 INFRARED ANALYTIC

Infrared spectroscopy can be described as the use of instrumentation in measuring a physical property of matter, and then relating the data to chemical composition. The instruments used are called infrared spectrophotometers,

and physical property measured is the ability of matter to absorb, transmitted, or reflect infrared radiation ^[59]. The basic principle of infrared instruments is to measure the vibration spectrum of a sample by passing infrared radiation through it, and recording which wavelengths have been absorbed and what extent. Since the amount of energy absorbed is a function of the number of molecules present. The source of infrared may be a glowing filament or hot silicon carbide rod, both of which emit radiation over a wide range of frequency. The infrared beam passes through a collimator to the specimen which should be in the form of a thin film. The transmitted rays then pass through a system of mirrors on the rock salt prism, which can be rotated, so vary the frequency of radiation received on the detector ^[60].

The analysis for these spectrums was carried out using two frequency regions. The details are as following:

1 –Wave number between 3500 and 3700 cm⁻¹:-

Ruswell and Dudenbostel ^[61] first showed that absorption in this range is due to hydroxyl group (O–H). In the structure of dioctahedral minerals, each pair of aluminum ions shares two hydroxyl groups, which are related by a center of symmetry between the aluminum ions. Sarasota ^[62] through that the absorption frequency of (O–H) bonds depends on the degree of association of these groups. The Bands in the region 3260-3950 cm⁻¹ can be assigned to [O–H] vibration in different environments. Thus, the bands at 3750 cm⁻¹ is assigned to terminal Si band –OH, the band at 3600 cm⁻¹ to bridge [Si-OH-Si(AL)], and the bands at 3570 cm⁻¹ and 3450 cm⁻¹ are due to hydrogen bonded [Si(AL)-OH] ^[62,63]. The bending vibration of H₂O is found at region 1650 to 1750 cm⁻¹ which has expected suffered shift to higher frequency as compared to molecular water.

In general, the layer–silicate structural OH groups that are comparatively slightly show absorption of high frequencies of 3600 to 3700 cm^{-1} , where as the absorbed water shows absorption at low frequencies 3400 cm^{-1} , and another band 1640 cm^{-1} corresponding to the deformation vibration of water ^[1]

2 Wave number between 1500 and 600 cm^{-1} .

The position and sharpness of the perpendicular vibration varied with physical state, thus, in the spectrum of Bentonite of large crystal size this node appears as abroad shoulder near 1089 cm^{-1} ^[64,65]. The bands at 526 cm^{-1} (Si-O-Al), 466 cm^{-1} (Si-O-Si), 1040 cm^{-1} (Si-O) ^[16].

The band intensities and shift to higher frequencies in the spectra of smaller crystals until in very finely ground material the band is at 1109 cm^{-1} smaller but distinct shifts in frequency, together with sharpening and intensification of bands as particle size decreases ^[66, 67].

Republic of IRAQ
Ministry of Higher Education
And Scientific Research
AL-Nahrain University
College of science
Physical Department



THE USE OF IRAQI RAW MATERIAL IN BLEACHING OF VEGETABLE OIL

A Thesis

Submitted to the College of Science

Al-Nahrain University

In Partial Fulfillment of the Requirements for the Degree of Master
of Science in
Physics

By

RASHA SHAKIB HAMEED MAKKIA

(B.Sc. 2003)

Supervised by

Dr. Azhar J. Dawod

**Rabi'a Al - Aw'wal
April**

**1427 A.H
2006 A.D.**

Examination Committee Certificate

We certify that we have read the thesis entitled
**“The Using of Iraqi Raw Material for Bleaching of Vegetable
Oils”**

And as Examining Committee, examined the student

RASHA SHAKIB HAMEED MAKKIA

In its contents and what is related to it, and that in our opinion it is
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In *Physics*

Signature:

Name: Dr. Emad Kh. AL-Shakarchi

Title: **Assist Professor**

Address: Dept.of Physics College of Science AL-Nahrain

Date: //2006

Signature:

Name: Dr. Fadhil A. Resan

Title: Assist Professor

Address: Babylon University

Date: //2006

Signature:

Name: : Dr. Fadhil Atia

Title: Scientific Researcher

Address: Ministry of Science and Technology

Date: //2006

Signature:

Name: Dr.Azhar J.Dawod

Title: Lecture (Supervisor)

Address: Dept.of Physics College of Science AL-Nahrain .

Date: //2006

Approved by the University Committee of Postgraduate studies

Signature:

Name: **Dr. Laith A.AL-Ani**

(Dean of the College of Science)

Date: //2006

Supervisor's Certification

We certify that this thesis was prepared under our supervision at the 'AL-Nahrain University' as a partial requirement for the degree of Master of Science in Physics.

Signature:

Name: Dr.Azhar J.Dawod

Title: Lectuer

Address: Dept.of Physics College of
Science AL-Nahrain University

Date / / 2006

In the view of the recommendation. I forward this thesis for debate by the examination committee.

Signature:

Name: *Dr. Ahmad K. Ahmad.*

Title: *Assist Professor*

Address: *Head of the Department of
Physics
College of Science
AL-Nahrain University.*

Date: / / 2006

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Rasha makia
April 2006.



CHAPTER ONE
INTRODUCTION



CHAPTER TWO
THEORETICAL PART



CHAPTER THREE

EXPERIMENTAL WORK



CHAPTER FOUR

RESULTS &

DISCUSSIONS

&

CONCLUSIONS

AND

FUTURE WORK

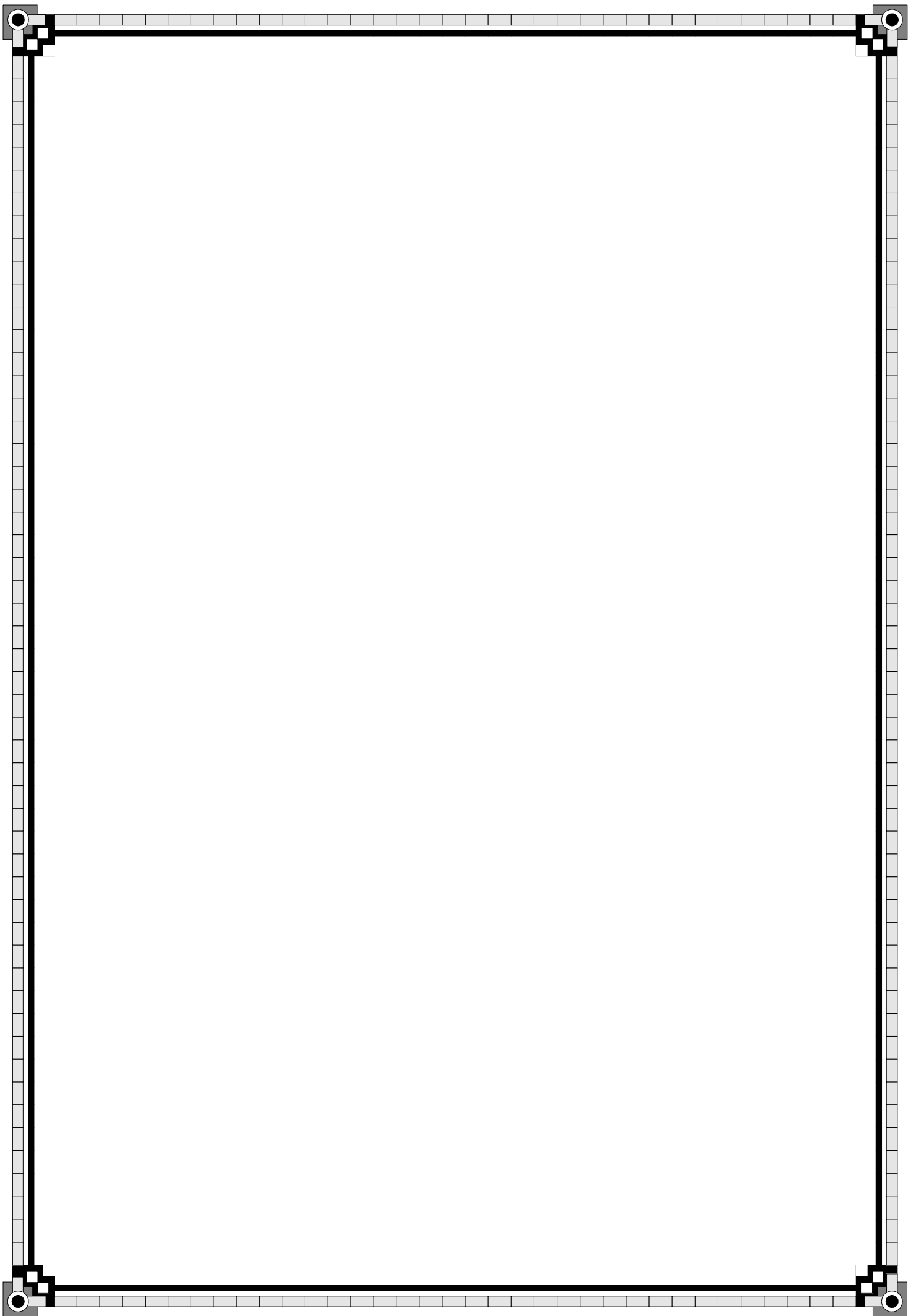


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DEDICATION

TO
MY FAMILY



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