Natural Mineral Clays Bearing Bentonite , Grafting by Chromium Tri Oxide Studies and Application In Petroleum Fraction

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Abstract

Natural Iraqi mineral clays treated chemically by base using sodium hydroxide and grafting with chromium trioxide by using thermal analysis, infrared ,ultraviolet and high performance liquid chromatography .Result indicate that this sample have physical and structural properties evaluated their scientific and economic utilization to be applied in fraction processes as adsorbent to separate Iraqi heavy crude oils into their simple component

الخلاصة

شملت الدراسة على معاملة الطين المعدني الطبيعي العراقي(البنتونايت) بهيدروكسيد الصوديوم ومن ثم تطعيمها باوكسيد الكروم الثلاثي.كما أكدت الدراسة التي اجريت بتقنيات المعاملات الحراريه وطيف الاشعه تحت الحمراء وفوق البنفسجيه فضلا عن كروماتوغراف السائل ذات االكفاءه العاليه على ان الطين المنشط بالامكان استخدامه كماده مازه في مجال الفصل الكروماتوغرافي وقد استخدمت المشتقات النفطيه الثقيله من نفط القياره في العمود لغرض تحويلها الى مكونات ابسط تم التعرف على تركيبها الكيميائي.

Introduction

Mineral clays are occurred naturally in massive quantities in the world and especially around Mosul City/ Iraq(1).In general ,the term clay implies natural , earthy, fine grained material which develops plasticity when mixed with a limited amount of water .Chemical composition of such material mainly consist of silica ,alumina in addition to relative amount of feldspar , kaolinite ,calcite ,dolomite…etc(2).The water molecules which can be held by clay material is either adsorbed ,interlayer, or lattice hydroxyl group of water. The above initially adsorbed water molecu-les was explained on the base of dipole character of the water formula. Since the surface clay particle is normally negative charged ,the positive ends of the water molecule are considered to lie toward the clay surface (3).

Organic molecules are dipoles as a result of the lack of symmetry of electron distribution within individual molecule and act in the same manner as water molecules when they are contact with clay material .The demand for all kinds of fossil fuel sources ,such as heavy crude oil as alternative energy sources to light petroleum has been subject for many workers**(4-6).**Recently ,adsorption of a considerable number of Iraqi heavy crude oils on natural Iraqi clay and rock material have been reported(7 ,8).On the other hand ,Al-Juboury (9)in his investigation ,reported that numerous showings of clay material around mosul city .Accordingly and in continuation of investigating the application of the Iraqi raw materials in petroleum refinery, the present study is consider to deal with the treating of the naturally occurring clay minerals by bases in order to be activation

Experimental

a. Sources and Collections of Samples*:*

Natural minerals clay, obtained from area around Mosul City/Iraq , was used as a natural clay sample. The sample was yellow in colour has (120-150mesh)chromatographic grade, bearing suitable amount of Montmorill-onite minerals as reported recently(9). It was used as starting materials for preparation of activated natural and treated clay samples. The treated clay samples were obtained from the solubility in basic medium. A known weights of natural clay samples were left overnight under 10 % sodium hydroxid , washed by distilled water and then dried at 110C°. The differences in weights before and after the treatment was recorded.

b. Preparation of chromium trioxide samples:

Black brownish gelatinous precipitate of chromium trioxide was prepared by oxidation reduction reaction between chromic oxide and ethanol according to the equation below**:** (10)

$$2CrO_3 + 3C_2H_5OH_{aq} \text{---} Cr_2O_{3aq} + CH_3COH + 3H_2O$$

Note: *It similar that reaction between sodium hydroxide and chromic trioxide to produce sodium chromate which enhancement the activity clay properties* .

In water bath , CrO_3 (40 gram) was mixed with 500 ml water and 20 ml ethanol , stelling 4 hr. reflux for 16 hr. until black brownish colour appeared , filtered and dried at 110 Č for 24 hr.

c-Preparation of Impregnation Clay:

(171.6) g activated clay was mixed with (16 g) chromium trioxide and (200ml) water in traces of ethanol),for six hours stirring , filtered and dried at (110 Č) ,then calcined at 760 Č for 3 hours .

d- Chemical and Physiochemical Analysis:

Minerals content and their chemical compositions of the treated clay samples were obtained by x-ray fluorescence and classical chemical analysis. Stock solution for the later analysis was obtained by sodium fusion technique(11) followed by disso-lving the contents in (6M) HCl. Moreover, physicochemical properties also were determined like pH, which was 8.3 (solid: distilled water, 1:1w/v), density, porosity, and specific surface area, which was determined by ethy-lene glycol method(12).

e-Thermal Analysis

Thermo gravimetric (TG)and differential thermal analysis (DTA) were recorded between(25 and 700 Č)on a Stan Redcroft STA-780 Analyzer at heating rate of 5Ċ/min., and α-Al_2O_3 was used as standard reference.

f-Infrared Spectra

Absorption spectra of clay samples were recorded on Pye-Unicam 1100 infrared spectrophotometer using KBr disk. Meanwhile, the spectra of the eluted fractions in the study was obtained using NaCl cell(12).

g- UV.VIS Spectra

Absorption spectra of activated clay samples were recorded on SHIMADZU double beam UV-VIS Spectrophotometer type 160 A , the spectra of the eluted fractions in the study were obtained using quartz cell with scan wavelength 200-800 nm.

h- High Performance liquid chromatography

The spectra of the eluted fractions in the study were obtained using SHIMADZU HPLC Analyzer with optimum condition(flow rate, type of column ,mobile phase,temperatur injection volume, wavelength, retention time), these condition are:

Type of instrumental : LC—2010 A SHIMADZU
Type of column :15 Cm * 4.6 mm TM Sulpelcosil LC-8
Mobile phase : 60/ 40 Methanol / Water
Flow rate : 1 ml /min
Temperature : Ambient
Pressure : 7 mm/Hg
Detector : U. V 254 n.m
Sample size : 10µl

i- Application

One fractionation column packed with (120-150mesh) chromatographic grade treated clay sample were employed in the processes. A known weight (~2g) of QP(5) were fractionated into four fractions using four eluants of different gradually increasing polarities in order to evaluate the adsorption activity and selectivity of clay samples.

Results and Discussion

A. Chemical Analysis

The chemical analysis of treated samples are shown in Table (1). It seems that clay samples compose of different oxides most of them related to mineral rocks and clays suggested to be used as adsorbed catalysts like silica, alumina, iron oxides, calcium, magnesium, and potassium oxides**(12).** Moreover, the observed results show a notable differences in the clay sample composition before and after NaOH treatment .

B. Physical Properties

Minerals rocks and clays should have certain physical properties in addition to their chemicals to be satisfactory adsorbent materials and used in fractionation processes**(13)**.The major advantages of an adsorption system for petroleum refining are listed in terms of porosity, density, surface area, and water absorption. Accordingly, such physical properties for the clay samples under investigation are studied and presented in Table(2).

The treated clay sample wewr shown low density, porosity, and permeability pore size but high surface area on comparison with the natural one. In order to interpret such results, the capillary action was measured also and the rising water level observed in the clay samples as monitored with the time is taken as the measurement of the capillary action. It seems from the data shown on Figure (1), which demonstrate the rapid rise of water in the first few minutes in case of treated sample, that such sample consist of a large number of fine cavities well connected by extremely very narrow channels and hence allowing the water to move up easily though the clay sample. However, the observed result in case of surface water absorption, reflect the fact that treating the clay sample by NaOH might produce so many fractures on its surface and hence increasing the percentage amount of water absorption. In conc-lusion, it is obvious that treatment the minerals clay in the above mentioned procedure might alter its whole physical properties in the direction of adsorption application**(14).**

Table (1): Chemical Composition of Treated Mineral clay

Sample	%SiO_2	%SO_3	%Fe_2O_3	%Al_2O_3	%MgO	%CaO	%K_2O	%Na_2O
Natural Mineral Clay	39.0	1.2	31.6	6.8	0.8	11.9	4.0	0.4

Table(2):Physical Properties of Natural and Treated samples

Sample	Density gm/cm^3	Porosity %	Surface Area cm^2/gm	Water Absorption %	Pore Size cm^3/g	Surface Water Absorption %
Natural Mineral Clay	2.3	143	155	126	8.58	203
Treated Mineral Clay	2.11	131	176	115	6.58	210

C. Structural Investigation

Clay materials are porous in character and should held water molecules as a hydration and geometrical water. Such materials, therefore, should be treated thermally in order to obtain a highly activated and selective adsorption catalysts. DTA and TG were employed to study the hydration phenomenon(11) and the results were presented in Figures (2and 3). In general, it is noted that three DTA endothermic peaks were found for both samples, Figure (2), corresponding to the three classes of hydrations; hydroscopic , zeolitic or coordination water molecules, and finally the structural hydroxy groups. To interpret such foundation, TG of the treated sample was performed and represented in Figure(3). It is clear that losses of 3.0%, 6.1%, and 7.3% from the original weight were observed which represent the dehydration of physical, interlayer adsorbed and structural water molecules respectively **(3,8,13,14)**.

Finally, it is of interest to investigate the migration and elimin-ation of the above mentioned water molecules from

clay in addition to the clay mineralogy by infrared absorp-tion. Therefore, a range of (400-4000cm^{-1}) in frequency was applied and the spectra shows an absorption bands at 1630cm^{-1} and in the range (3400-3600cm^{-1}) which are related to the structural of hydroxyl group(15).

D. Adsorption Activity

The above physical and structural properties noted for the clay samples under study, especially those for treated clay sample, evaluate them to be applied as a good adsorbents in fractionation processes. They are suitable for the separation of majority

of substances or for the separation of complex mixture into groups of compounds**(16)**.

Accordingly,two fractionating column were packed with chromato-graphic grade (120-150mesh) activated clay samples. They employed in fractionation of QP to its simple components using four eluants incre-ased gradually in their polarity and the observed results are shown in Table(3). Results in the above table revealed the percentages of the fractions eluted on using different polarities and the chemical characteristic nature of the eluted fractions was adopted from the previous studies(5) and relying on their infrared data. In general adsorption of petroleum materials on clay minerals strongly occurred and desorption also occurred on the same strength on using polar eluants. The eluted fraction on using low polar solvents were mainly saturated paraffinic hydrocarbons meanwhile, as the polarity of the eluted solvent increased naphthenic and finally aromatic hydrocarbon fractions were obtained. Usually, interference between the above compounds occurred but in our studies it seems that such interference is decreased on using treated clay sample. Data of infrared recorded for the eluted fractions support such observation. It is clear that the first fraction contains mainly of straight aliphatic hydro-carbons via the absorption bands at (2927)and (1463)cm^{-1} which are attri-buted to the stretching and bending vibra-tions of methylene groups. Inter-ference of branched aliphatic and naphthenic compounds was happened in this fraction and especially in natural clay sample compared with the treated one. This happened through the presence of absorption bands at (2857 ,1377cm^{-1})and (2842cm^{-1})which are related to –CH_3 and naphthenic –CH_2 group respectively(17). On studying the toluene fraction it was suggested that such fraction contain mostly of branched aliphatic compounds in addition to naphthenic once and little amounts of aromatics (C = C Stretching bands at 1604cm^{-1}). This aromatic appeared secondly in chloroform fraction which contains mainly of naphthenic hydro-carbons. Meanwhile, it was noted that ethanol fraction contains aromatic hydro-carbons accompanied with trac-es of naphthenics and the whole inter-ference was low in using treated clay sample.

Table (3):Chromatographic Fractions (%) of 2g QP* Using different adsorbents

Solvent	Polarity (Deby)	Treated Clay Sample	Natural Clay Sample
Petroleum ether	31.0	35	32
Toluene	33.9	30	29
Chloroform	39.1	10	8
Ethanol	51.9	25	21
Loss	-	-	10

- QP Composition : Straight Aliphatic 38%, Branched Aliphatic 27%, Naphthenic 18%, and Aromatic Compounds 17%(5).

E. UV spectra:

It is well known that careful UV-VIS studies reveals the presence of multi component which will be eluted by many fraction. Figure(4)shows that sample which contain four fractions at optimum wavelength ,these Peak leads to be four transition ,which indicate that the electronic spectra of the compounds fraction in different solvent have been recorded .The maximum at about 260-280 nm in case of fraction may be assigned to π --π * (benzenoid).The spectra of the fraction show band at 228-233 nm related to n-- π * .

F. Infrared Spectra

The results of infrared studies , which are shown in Table (4) indicate that the sample which contain naphthenic and aromatic groups in addition to moisture ,the most of saturated aliphatic compounds were eluted in petroleum ether fraction. Meanwhile , it seems that in toluene and chloroform fraction most aromatic and carbonyl groups .Finally it is noted that in ethanol fraction the rest of phenolic compounds were eluted.

G. HPLC Spectra :

After measurement the four fractions in UV—VIS spectrophotometer ,HPLC data which are presented in Figure observation and (5)supported the above indicate the presence of saturated aliphatic compounds in addition of organic compounds ,such as aromatic rings branched with long aliphatic seem to be chains.

Table (4) : Infrared spectroscopic data for eluted fraction of QP.

Solvent	Type of band	Wave number (Cm $^{-1}$)	Transmittance (%)
Petroleum ether	moisture	3356(bw)	40
	υC-H:CH_3,CH_2,CH Naphthenic group	2927(w)	30
	υ C=C Aromatic group	1545(w)	35
	δ C-H:CH_2,CH Naphthenic group	1459(w)	33
	δ C-H:CH_3 Naphthenic group	1377(w)	33
	δ C-H Aromatic group	1006(w) 793(s)	40 5
Toluene	moisture	3356(bw)	40
	υC-H:CH_3,CH_2,CH Naphthenic group	2926(w)	42
	C=O group	1742 (w)	38
	υ C=C Aromatic group	1545(w)	38
	δ C-H:CH_2,CH Naphthenic group	1451(w)	33
	δ C-H:CH_3 Naphthenic group	1216(w)	33
	δ C-H Aromatic group	1136(w) 792(s)	40 5
Chloroform	moisture	3402(b)	2
	υC-H:CH_3,CH_2,CH Naphthenic group	2932(s)	1
	C=O group	1734 (s)	0
	υ C=C Aromatic group	1540(m)	15
	δ C-H:CH_2,CH Naphthenic group	1454(s)	3
	δ C-H:CH_3 Naphthenic group	1410(s)	3
	δ C-H Aromatic group	1148(s) 878(s) 793(s)	3 4 3
Ethanol	moisture	3402(b)	2
	υC-H:CH_3,CH_2,CH Naphthenic group	2932(s)	1
	C=O group	1734 (s)	0
	υ C=C Aromatic group	1540(m)	15
	δ C-H:CH_2,CH Naphthenic group	1454(s)	3
	δ C-H:CH_3 Naphthenic group	1410(s)	3
	δ C-H Aromatic group	1148(s) 878(s) 793(s)	3 4 3

In conclusion, such results suggest that treating the local natural mineral clays chemically and physically might yield an activated adsorption catalysts have a promising future.

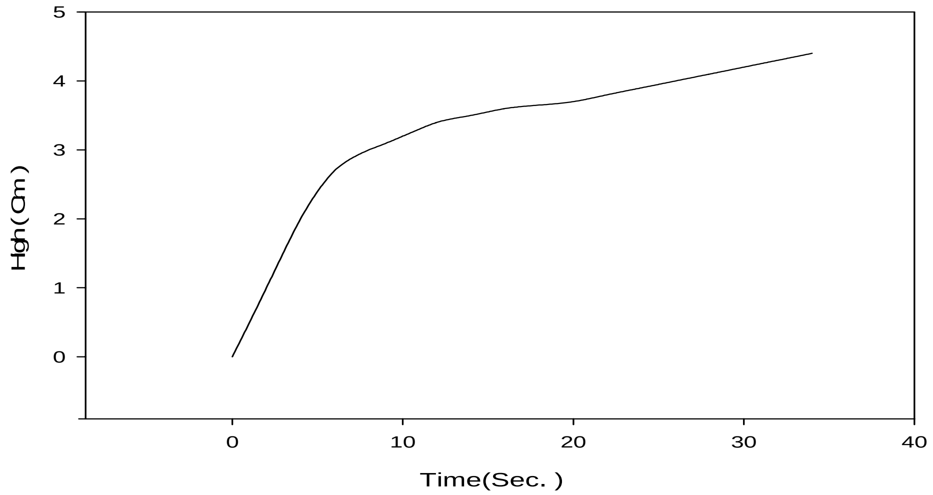

Figure (1): Capillary Action Curves of Treated Samples

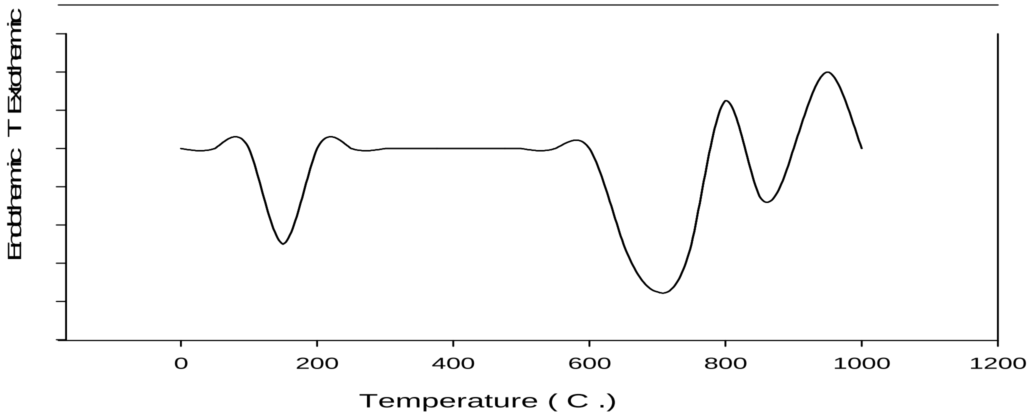

Figure (2): Differential Thermal Analysis Curve of Treated Clay Samples

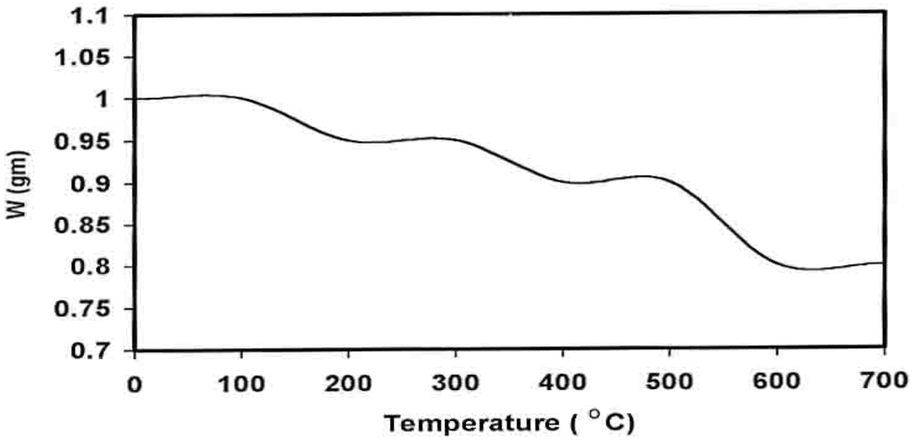

Figure (3): Thermogravimetric Curve of treated clay .sampe .

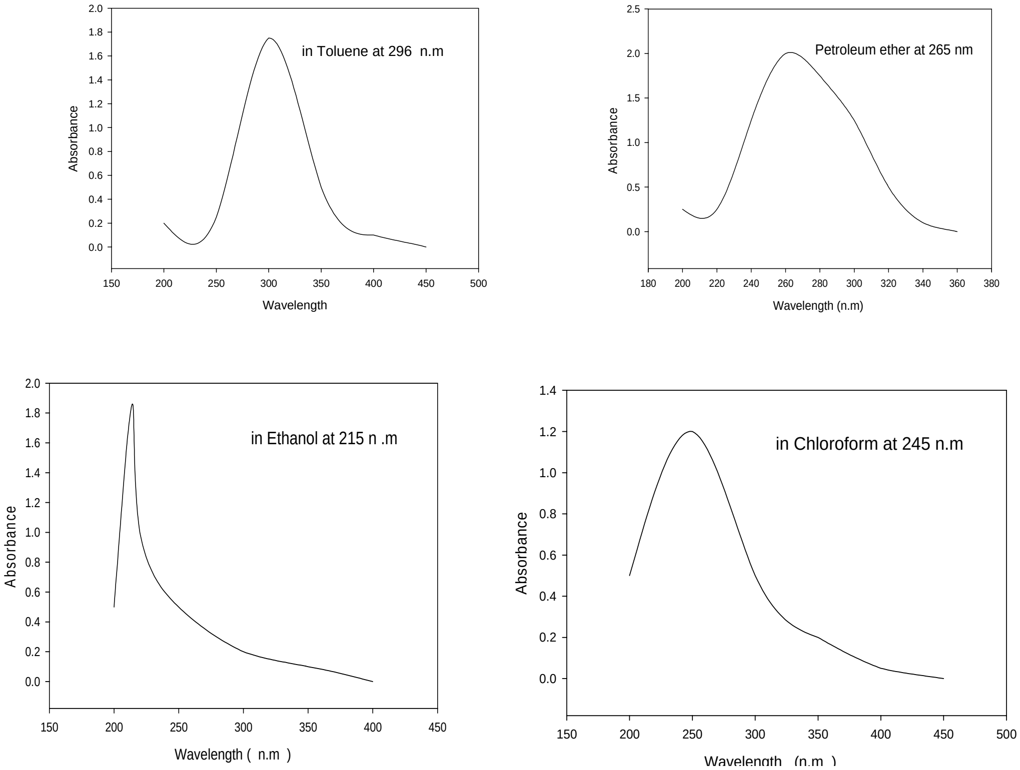

Fig 4: UV-VIS spectrophotometer for eluted of QP

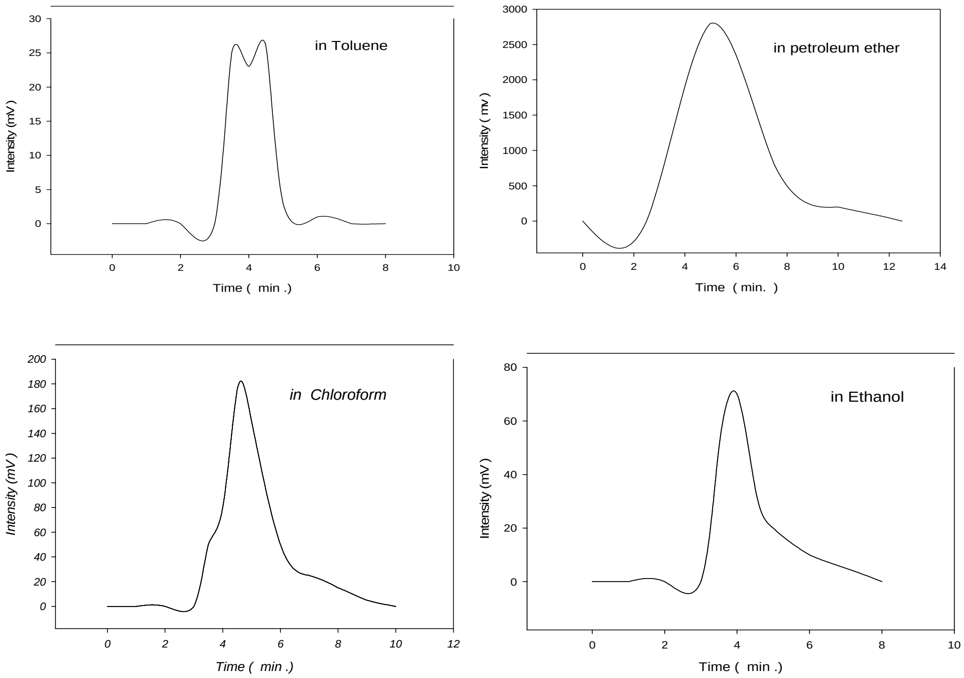

Fig5: HPLC spectroscopic for eluted fraction of QP .

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