### Mineral Clays Bearing Montmorillonite Mineral, Studies of Physical and Structural Properties and Application in the Oil Industry

Dr. R. A. Buker Department of Chemistry College of Education / University of Mosul

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### **Abstract:**

Preparation and characterization of an adsorbent catalyst from natural mineral clay sample obtained from Kara Tappa area in the province of Diyala/ Iraq, in addition to its application in petroleum industries have been studied.

The solubility of the clay sample in some acidic and basic mediums was performed in order to get the more active and selective adsorbent catalyst, as a result, the sample which was treated progressively by three (25%) concentration acids (HCL,  $H_2SO_4$  and  $CH_3COOH$ ) was the best from the adsorbent view. Physical properties as well as chemical analysis of these samples were investigated. The mineralogical properties of those samples, powder x-ray diffraction, x-ray fluorescence, thermal analysis and infrared spectra.

Results indicated that such materials bear montmorillonite mineral in their composition in addition to others which vacillate them to be an adsorbent catalysts applied in chromatographic fractionation of Qaiyarah petrolene using five eluants increased in their polaritie. Infrared, nuclear magnetic resonanc (<sup>1</sup>H&<sup>13</sup>C NMR) techniques were utilized to determine the chemical composition of the separated fractions.

احتواء الطين المعدني على معدن المونتمور يلونايت ، دراسة صفاته الفيزيائية والتركيبية واستخداماته في الصناعات النفطية د.رجب عواد م.م. زينة مشعل قسم الكيمياء ملخص البحث: ملخص البحث دراسة تحضير وتشخيص حفاز طيني معدني كفوء من حيث الفعالية والانتقائية كعامل مساعد ماز في عمليات الفصل الكروماتوغرافي من اطيان معدنية طبيعية متواجدة في منطقة قرة تبه في محافظة ديالى / العراق. من خلال دراسة ذوبانية هذه الاطيان المعدنية الطبيعية بعدة حوامض وقواعد مختلفة التراكيز تبين ان معاملتها بحوامض الهيدروكلوريك والكبريتيك والخليك بتراكيز 25% وعلى التوالي ينتج حفاز ماز كفوء من وجهة نظر عمليات الفصل الكروموتو غرافي. تم دراسة الصفات الفيزيائية والتحاليل الكيميائية فصلاً عن دراسة الصفات المعدنية باستخدام تقنيات حيود الاشعة السينية وفلورة الاشعة السينية والتحاليل الحرارية وطيف الاشعة تحت الحمراء لنموذجي الطين الخام والمعالج لمعرفة المحتوى الكيميائي لهما ما

نتائج الدراسة اكدت الحصول على حفاز كفوء يحتوي على نسبة عالية من معدن المونتموريلونايت فضلاً عن بعض المعادن الطينية الاخرى جعلت منه مادة مازة ليتم استخدامها في عمود فصل كروماتوغرافي لفصل بترولين نفط القيارة الثقيل الى خمس مستخلصات باستخدام خمسة مذيبات متدرجة في القطبية، وتم استخدام تقنيات الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي لمعرفة الصيغ الكيميائية لهذه الاجزاء المفصولة.

### Introduction:

Mineral clays considered to be one of the interest subjects for the scientist nowadays. There are so many publications in this field that is difficult to mention some of them here. However, montmorillonite, betonies, bauxite, kaolin, feldspar, in addition to amorphous silica and alumina seemed to be the famous minerals to deal with since they are naturally occurring in many places in the world, in addition to their industrial applications<sup>(1-4)</sup>. One of the most such applications look to be in upgrading processes of heavy crude oil components. For example, it was reported that Fuller's earth has been used in chromatographic application of asphaltic–base crude oil to be separated into lubricating oil and resin using heptane and chloroform eluants, respectively<sup>(5)</sup>.

It is well known that our country contains very large amounts of heavy crude oils in addition to asphalt and bitumen's materials<sup>(6)</sup>. These are located beside so many deposits of rocks and clay minerals. As a results, it was our interest as researchers to investigate these fields. Ninivite silica rocks have been used as adsorbent materials in chromatographic application processes of Hammam Al-Alil bitumen's<sup>(7)</sup>. Mineral clays bearing feldspar have been applied to fractionate Iraqi heavy crude oil into its simple and useful components<sup>(8)</sup>. Moreover, recently it was reported that doping of Ninivite silica rocks by chromium oxides gel yields active and selective adsorbent catalysts which applied in solid phase extraction fractionation of Iraqi virgin olive oil<sup>(9)</sup>. Accordingly, and in order to continue searching in this field ,many subjects have been tabulated in our laboratories including the present one which is investigating natural mineral clays bearing montmorillonite as a

major mineral in their composition. Such material has to be characterized physically and chemically via several instrumental techniques and applied in petroleum refining .

### The Experimental Part A- Sources and Collection of Samples:

Natural mineral clays, obtained from the area around Kara Tappa at Diyala governorate / Iraq, were used as a natural clay samples. These samples were pale yellow in color have (120-150 mesh ASTM). Individual samples weighed from 1.0 to 3.0 kg ; and were thoroughly mixed to obtain representative samples. At each sampling site, parent rock, samples were also collected. The solubility of the clay samples in some acidic and basic mediums was performed in order to get the more active and selective adsorbent catalys, as a result, the sample which was treated progressively by three (25%) concentrated HCl, H<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COOH acids was the best from the adsorbent view. For X-ray diffraction analysis and bulk mineralogy, the raw and the treated samples were powdered by agate mortar and agate tama mill. Finally, Qaiyarah Petrolane (QP)<sup>(10)</sup> was used as a starting material to be fractionated into its useful and simple components.

### **B- Methods of Study:**

The identification of clay minerals and their alteration products was carried out by using X-ray powder diffraction method, which carried out Shimadzu X-ray Diffraction 7000. 2009 equipment using with monochromatic, Cu-radiation ( $\lambda$ =1.54178 Å<sup>o</sup>) at 40 k.v., 30 m.A. and scanning speed 0.02 °/sec. The reflection peaks between  $2\theta = 2^{\circ}$  and 60 °, corresponding spacing (d)A<sup>o</sup> and relative intensities (I/I<sup>o</sup>) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files. Meanwhile X-ray fluorescence(XRF) spectrophotometer was employed for the clay samples on Minipal 4 from Panalytical Holland analysis, atomic absorption spectroscopy (AAS) was measured by analytic jena, novaa 350, and the absorption spectra were recorded on FTIR 4100 JASCO spectrophotometer using KBr disk<sup>(11)</sup>.

The thermal analysis was preformed made by means of LINSEIS SAT PT-1600 DTA-50H, and TGA-50H. Each powdered sample was heated by  $10^{\circ}$ C/min. up to  $1100^{\circ}$ C with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a reference material. Temperature, weight ,change in wt., and the thermal behavior of the sample is recorded on the chart. Physical properties measurements were carried out applying abstracted methods<sup>(8)</sup>.

The above technical studies were performed at Aleppo university, central laboratory sector/ Syria. On the other hand, specific surface area measurements were carried out on SOROTOMER equipment model 1042

"Kelvin" in Italy, and on Micromerities Gemini III 2375 model in Syria. Finally, <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance spectroscopic measurements were performed on Bruker, Ultra Shield 300MHz equipment at Al- Al-Baiyt university / Jordon.

## **Results & Discussion** A- Chemical Analysis:

The results of chemical analysis provide information on the mineralogical and the treatment processes of the mineral clays using different acidic and basic laboratory and industrially available mediums. It seems that each of those acids and bases has its activity and selectivity in removal of one or more of the clay chemical components. This occur even the fact that those components are physically and chemically bonded together naturally during a very long period<sup>(12)</sup>. Therefore, it is the interest of our research to treat clay materials using 25% conc. HCl, H<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COOH progressively. It was noted that the prepared sample losses 32.7% from its original weight. Data of instrumental and classical chemical analysis in addition to that obtained from XRF & AAS, Table (1), clarifies the fact that all carbonates and most of sulfate compounds in addition to those compounds which present already in few amounts in the clay sample, were removed. The removal of the above components seemed to enrich the prepared clay sample with clay minerals, which is to be discussed later on, since it is so interest in chromatographic adsorption processes<sup>(8)</sup>.

## **B-** The Study of Physical and Structural Properties:

Physical properties for both clay samples presented in Table (2). pH measurement of the prepared sample was acidic in nature compared with that obtained from the natural one. It seems that removing all carbonate and sulphate compounds replaced the alkaline metals by hydrogen ions and leaving the sample containing so many vacancies. Bulk density, porosity, and pore size data, Table (2), seemed to point out the characterization of the above pores and cavities which are to be well connected by each others through a very narrow channels<sup>(7)</sup>. Such observation approved from the determination of specific surface area, Table (3), in addition to the capillary action of both samples, Figure (1), which show the rapid rise of water in the first few minutes in cases of the prepared sample to demonstrate the fact that such sample consist of large number of fine cavities well connected by easily through the clay sample <sup>(8)</sup>.

To do our best in investigating the structural properties of our samples we managed them by applying powder X-Ray diffraction, thermal analysis and infrared spectroscopy techniques. Figure (2) represents the pattern of natural clay sample which reflect the presence of amorphous silica mineral as a broad hump between  $2\theta$  (12 and 22)<sup>(13)</sup>. The pattern also contain reflection typical of montmorillonite, quartz, feldspar, calcite, dolomite, illite, caolinite, chlorite, hematite and gypsum.

Meanwhile, pattern of the prepared sample, Figure (3), reflect the presence of the above minerals in different intensities except calcite and dolomite since they are carbonate compounds and disappeared as a result of the acid effect. Such mixed units of clay minerals are presented in Table (4) via their interplanar spacings<sup>(14)</sup>. Under the proposed experimental observation and referring to the literature<sup>(13,14,9)</sup>, montmorillonite mineral seems to be present in acceptable abundance in our sample and might represented by Na(Al<sub>3</sub>.Mg)Si<sub>8</sub>O<sub>20</sub>(OH)<sub>4</sub>.nH<sub>2</sub>O formula has monoclinic symmetry with (C2/m) space group and unit cell values : a = 5.17, b = 8.94, c = 9.95 A° and  $\alpha = \gamma = 90^\circ$ ,  $\beta = 99.54^\circ$ .

In general all the clay mineral phases held water molecules in their surfaces and bulk pores and cavities and such water molecules might be classified into many kinds according to their departure and removing from the clay sample<sup>(15)</sup>. Therefore, DTA were performed for both samples to study such hydration phenomenon in addition to their structural properties as shown in Figures (4&5). It seems that endothermic peak was found at 128.4°C corresponding to the removal of hydroscopic and zeolitic water molecules. Meanwhile ,the peak at 179°C represent the conversion of gypsum to anhydrite mineral, and the peak at 660°C related to the calcinations of calcite to CaO. Finally ,it looks that the peaks at 852.3 and 901.4°C identify the transformation of  $\beta$ -quartz to  $\beta$ -termite and removal of sulfite compounds from the material<sup>(15)</sup>. It is clear that some variation is noted in comparison between the observed results before and after the acidic treatment. To interpret such foundation TG of the clay samples were preformed and represented in Figures (6&7). It is clear that some percentage values were noted from the original weight which characterize the compositional formula (16)

Finally, it is of insert to investigate the clay mineralogy in addition to the migration and elimination of water molecules by infrared absorption. Therefore, a range of 400-4000 cm<sup>-1</sup> in frequency was applied and the spectra revealed structural absorption bands including those at 467.22 cm<sup>-1</sup> and 523.10 cm<sup>-1</sup> which are attributed to the Al-O and Fe-O stretching and vibrations<sup>(17)</sup>. Also there are bands at 914.23 and 2387.60 cm<sup>-1</sup> which are related to the functional group Si-O in montmorillonite and quartz minerals, whereas the absorptions at 1403.88 and 796.62 cm<sup>-1</sup> are typical of CO<sub>3</sub> groups. Finally, the spectra between 3628-3443 cm<sup>-1</sup> characterize the structural(OH) groups<sup>(17)</sup>. However, on studying such absorptions for the prepared sample a significance variation was noted to support the above mentioned information which does not include, for example, absorption bands for CO<sub>3</sub> groups.

## **C-** Chromatographic Adsorption:

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The observed results mentioned above for both clay samples high light. even in different degrees, the fact that such materials are good adsorbents in fractionation processes. They are suitable for the separation of complex into groups of compounds<sup>(18)</sup>. As a result, they employed in mixture fractionation of QP into five groups of hydrocarbons. These groups have different adsorption polarities to the clay sample and therefore they were separated by using five eluants increased gradually in their polarities. Table (5) revealed the percentages of the fractions eluted on packing the columns with chromatographic grade  $(212 - 300 \ \mu m)$  natural and prepared clay samples which have been activated at 400°C. In general the observed results show a notable variation between the separated groups, but there is no doubt that adsorption and desorption processes of QP was occurred and in high degrees of activity and selectivity. Data of the prepared sample seemed to be better than others but indeed such fact has to be conformed by studying the chemical characteristic nature of the eluted fractions. It was adopted from the previous studies<sup>(8,9)</sup> and relaying on the infrared data of QP, Figure (8), and the separated fractions which are presented in Table (6). It is obvious that the results reflect the fact that all the eluted fractions contain straight aliphatic hydrocarbons via the adsorption bands at 2924 and 1462 cm<sup>-1</sup> which are attributed to the stretching and bending vibrations of methylene groups<sup>(19)</sup>. Interference of branched aliphatic, naphthenic and aromatic compounds was happened and represented in the table by absorption bands at 2954, 1377 cm<sup>-1</sup>, 2853 cm<sup>-1</sup> and 1603 cm<sup>-1</sup> which are related to CH<sub>3</sub>, naphthenic –CH<sub>2</sub> and aromatic (C-C) groups respectively<sup>(19)</sup>. However, on comparison between the shown data through their positions and intensities, it seems that noted interference occurred between the above hydrocarbon compounds in each eluted fraction, but diffidently this shown to be less in case of using the treated clay sample. Activity and selectivity of such sample reflected from the appearance of straight aliphatic hydrocarbons in second fraction, whereas, large percentage of naphthenic compounds seemed to be eluted in fourth and fifth fractions.

It is of importance to report that infrared technique is not enough to reach the goal of the present study. Therefore, <sup>1</sup>H and <sup>13</sup>C NMR<sup>(19)</sup> techniques were utilized to determine the percentage and chemical composition of the whole components of the separated fractions. Table(7) indicates that methyl groups decrease gradually from fraction one until fraction three but there was an increase in the percentage values in both fraction four and five since methyl groups seemed to be conjugated with naphthenic and aromatic compounds. Moreover, it is clear that methylene groups are noted to be decreased in values from fraction one until fraction five. On the other hands, it was shown that naphthenic groups increased from fraction one until three where it should be eluted completely but since it is highly substituted similar to aromatics, it was shown to be appeared in fraction four and five. Finally,  $\alpha$ 

substituted hydrogen to the aromatic rings seemed to be increased gradually from fraction one until

fraction four, but there is a decrease in the value in case of fraction five due to the substitution of methyl groups on the aromatics.

<sup>13</sup>C NMR, Figure (9) show that methyl and methylene carbons have chemical shifts ( $\delta$  13.4) and ( $\delta$  22.4), respectively which increase in their percentage values in the fractions with increasing the polarity. Meanwhile, naphthenic ( $\delta$  29) noted to be increased from fraction one until fraction three, whereas aromatic ( $\delta$  125.7) seemed to be presented in large quantity in fraction four especially.

In conclusion, NMR studies show that straight and branched paraffinic compounds decrease gradually with increasing the polarity of the eluted solvents. On the other hands, naphthenics seemed to be presented in the middle of the polarity strengths. Finally, the aromatic hydrocarbons were eluted in the fourth and fifth fraction.

Table (1):- Percentage values of metal oxides in clay samples.

Samples	% oxides	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	SiO <sub>2</sub>
	Gravimetric analysis	5	4.1	25.2	5.1	2.21	13.56	0.01	35.4
Natural	XRF	6.3	4.21	25.66	3.7	2.83	11.81	0.1	37.6
	AAS	5.9	3.7	24	3.5	2.8			
	Gravimetric analysis	6.7	4.5	28	0.6	1.14	4.0	0.32	51.5
Treated	XRF	8.0	5.9	27.13	0.75	1.19	4.4	0.45	48.0
II cateu	AAS	7.1	4.6	27.4	0.5	1.1			•••••

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# Table (2):- Physical properties of natural and treated clay samples.

Samples	Density g/cm <sup>3</sup>	%Porosity	Water %absorption	Pore size g/cm <sup>3</sup>	РН	External water %
Natural	1.83	296	43.3	2.96	8.03	2.4
Treated	1.42	333	86.9	3.33	4.6	1.6

# Table (3):- Specific surface area data of natural and treated clay samples.

Data	Natural sample	Treated sample
BET Constant	743	90
BET Surface Area m <sup>2</sup> /g	111.55	311.75
Total Pore Volume ml/g	0.1009	0.5172
MicroPore Volume cc /g	2.13	5.45
Mean Pore Radius nm	1.81	3.32
Volume Adsorbed and not Desorbed cc /g	25.5	71.6

# Table (4):- Interplanar spacings for contributing phases in clay sample.

Crystalline phase	hkl	20	d-values(A <sup>o</sup> )
Montmorillonite	100	6.10	14.477
Montmorillonite	101	17.69	5.013
Montmorillonite	112	19.80	4.482
Montmorillonite	103	25.31	3.518
Montmorillonite	104	29.52	3.025
Illite	113,204	24.3	3.662
Illite	115	29.1	3.068
Illite	114	28.6	3.121

Illite	206	31.3	2.857
Illite	113	22.9	3.883
Kaolinite	001	12.4	7.137
Kaolinite	202	38.47	2.339
Kaolinite	201	39.34	2.290
Kaolinite	002	28.6	3.121
Kaolinite	132	45.6	1.989
Chlorite	201	35.8	2.508
Chlorite	203	36.4	2.468
Chlorite	202	37.6	2.392
Chlorite	202	34.6	2.592
Chlorite	205	42.0	2.151
Feldspar	201	21.05	4.220
Feldspar	112	25.66	3.471
Feldspar	220	26.6	3.350
Feldspar	131	29.85	2.993
Feldspar	132	32.35	2.767
Quartz	101	26.67	3.342
Quartz	100	20.85	4.260
Quartz	110	36.541	2.458
Quartz	102	39.45	2.284
Quartz	200	42.46	2.129
Gypsum	200	31.2	2.866
Gypsum	021	20.8	4.270
Crystalline phase	hkl	20	d-values(A <sup>o</sup> )
Gypsum	220	33.5	2.674
Gypsum	100	11.7	7.563
Gypsum	113	29.1	3.068
Calcite	104	29.43	3.034
Calcite	102	23	3.866
Calcite	113	39.43	2.285
Calcite	202	43.18	2.095
Calcite	112	36	2.494
Dolomite	104	30.98	2.886
Dolomite	104	31	2.884
Dolomite	113	41.18	2.192
Dolomite	018	44.99	1.817

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Dolomite	116	37.39	1.787
Hematite	104	33.14	2.704
Hematite	110	35.8	2.508
Hematite	012	24.3	3.663
Hematite	113	41	2.201
Hematite	024	49.5	1.841

## Table (5):- Percentage values of fractions separated from QP\* using chromatographic columns.

<b>Polarity</b>		Solvents								
Samples	Petroleum ether 0.0	Toluene 2.38	Chloroform 4.81	Ethanol 24.6	Carbon tetra chloride 26.2	Loss %				
Natural at 400°C	59	13	6	16	3	3				
Treated at 400°C	0	51	8	17	15	9				

 $*~\rm QP^{(10)}$  contains, 38% straight aliphatic, 27% branched aliphatic, 18% naphthenic and 17% aromatic hydrocarbons.

## Table (6):- Infrared spectroscopy data of the eluted samples.

		Aliphatic co	ompounds	Naphthnic compds	Aromatic	compounds
Samples	Solvents	CH <sub>2</sub> (C-H) aliphatic cm <sup>-1</sup>	(C-H) CH <sub>3</sub> aliphatic cm <sup>-1</sup>	CH <sub>2</sub> (C-H) naphthnic cm <sup>-1</sup>	(C-H) aromatic cm <sup>-1</sup>	C····C aromatic cm <sup>·1</sup>
	Petroleum ether	2924.26 1462.20		2853.98	1032.72 869.70 811.49	1602.59

Natural	Toluene	2924.46 1463.02	2954.75 1377.21	2853.93	1033.14 871.28 848.58 811.03	1603.99
	Chloroform	2923.22 1462.22		2852.32	1032.80 868.45 812.09	1604.99
	Ethanol	2924.97 1456.22		2854.35	1019.26 813.06	1644.87
	Carbone tetrachlorid	2924.54 1456.09		2853.78	1072.41 1032.43 813.54	1606.51
	Petroleum ether					
	Toluene	2923.38 1462.84	 1376.97		1032.98 868.91 810.05	1603
Treated	Chloroform	2923.82 1462.65	 1377.09	2853.98	1056.77 1032.90 870.74 811.49	1602.60
	Ethanol	2924.50 1462.36		2854.07	1028.51 871.57 814.98	1608.79
	Carbone tetrachlorid	2925.54 1454.92		2855.59	1031.99	1606.74

# Table(7):- Proton percentage values for separated fractions from chromatographic columns.

Solvents	%Hme	%Hmy	%Hn	%Ha	%Ha
Petroleum ether	24.74	69.80	1.77	1.77	0.87
Toluene	15.07	59.70	3.50	14.32	1.83
Chloroform	12.50	55.00	12.50	17.90	2.10
Ethanol	15.70	37.30	5.11	37.30	3.93
Carbon tetra chloride	35.30	35.30	6.66	18.20	4.40



Figure (1):- Capillary action curves of (A)- Natural, and (B)- Treated clay samples.



Figure (2):- Powder x-ray diffraction pattern of natural clay sample.



Figure (3):- Powder x-ray diffraction pattern of treated clay sample.



Figure (4):- DTA graph of natural clay sample.



Figure (5):- DTA graph of treated clay sample.



Figure (6):- TG graph of natural clay sample.



Figure (7):- TG graph of treated clay sample.



Figure (8):- Infrared spectra of QP.



Figure (9):- <sup>13</sup>C NMR of toluene fraction by using natural clay sample.

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