Local Mineral Clays, Characterization and Application in Petroleum Refining

R. A. Buker & M. Z. Hamoodat

Department of Chemistry / College Of Education

University of Mosul

الملخص:

تتضمن الدراسة تحضير ودراسة حفاز طيني معدني من معادن طينية محلية أخذت من مناطق قريبة من مدينة الموصل /العراق. وقد استخدمت هذه الحفازات في فصل وتنقية النفوط الثقيلة.

تم دراسة الصفات الفيزيائية للنماذج قيد الدرس فضلاً عن قابلية ذوبانها في عدة حوامض، كما تم دراسة التكوين الكيميائي والتركيب البلوري للمعادن الطينية المحلية والمحضرة من خلال استخدام طرق التحليل الكيميائية الكلاسيكية وتقنيات فلورة وحيود الأشعة السينية والتحاليل الحرارية فضلاً عن أطياف الأشعة تحت الحمراء.

سلطت نتائج الدراسة الضوء على المعدن الطيني المحضر كونه حفاز كفوء في فصل مشتقات نفط القيارة الثقيل إلى مكونات ابسط تم التعرف عليها وتشخيصها باستخدام تقنية طيف الأشعة تحت الحمراء.

Abstract

The study includes preparation and characterization of Mineral clay catalysts from local and natural mineral clays, which have been applied in purification and fractionation of heavy crude oils.

The studied samples were collected from area around Mosul city /Iraq. Physical properties were investigated to characterize the clay samples in addition to their solubility in many acids. Meanwhile, classical chemical analysis and X-Ray fluorescence were applied to determine their chemical composition.

Moreover, X-Ray diffraction, thermal analysis, and infrared spectroscopy have been used to study their structural properties. Such

investigations spot the light on the prepared sample to be active and selective in term of the adsorption chromatography. Qaiyarah heavy crude oil was fractionated into its simple and useful components which have been characterized via infrared spectroscopy.

Introduction :

Mineral clays are among several naturally occurring materials used in adsorption chromatography for the separation of complex mixtures of substances like heavy crude oils, into their simple and useful components[1-3]. The idea of adsorption and fractionation might be explained in term of the structure of the catalyst materials. They are porous in nature so they can hold water molecules as adsorbed, interlayer or lattice-OH water. The adsorbed water at relatively low temperature is driven off by heating to about 450°C [4]. Organic molecules are dipoles and act in the same manner as water molecules when they are in contact with the catalysts[5].

In general clays contain one or more of clay mineral components, in addition to relative amounts of non-clay mineral such as quartz, calcite, dolomite, gypsum, pyrite……etc[6]. Treatment of such materials was constructed by several diluted and concentrated acids and hydroxides to obtain good adsorbent catalysts[7]. It is obviously noted that almost carbonate and sulphate compounds, which are non-clay minerals, eliminated during the treatment leading to the formation of clay minerals rich adsorption catalysts.

It is well known that Hammam Al-Alil bitumen and Qaiyarah heavy crude oil fields which are located north of Iraq have not been used till recently[8-9]. Such materials are important in the energy sources, and the future promises further substantial increase in demand. Accordingly, some workers investigated the evaluation and fractionation of such crude oils to light fuels and petrochemical[10-12]. In general, zeolite, clay, alumina and silica gel were used as adsorbents to perform the above processes. However, clay materials seemed to be the most widely used adsorbents in this field since they are available in high purity with moderate cost, can be made with a range of physical properties, and they are chemically inert. Natural Iraqi Fuller's Earth[13] were employed and investigated in fractionation processes as adsorbent materials by many workers[7,14].

In order to continue researching for our raw materials and investigating their benefit uses, the present study is undertaken to extend the investigation via the treatment of clay mineral by multi acids. The prepared catalyst is to be characterized and employed in adsorption chromatography.

Experimental

A- Sampling methods :

The samples used in this research were obtained from area around Mosul city/Iraq. They were pale green in color has (120-150 mesh) chromatographic grade, bearing suitable amounts of clay minerals like feldspar, caolinite montmorolinite and playgroskite as reported recently[7]. Such samples were used as starting materials for preparation of activated natural and treated clay samples. The latter was obtained by refluxing a known weight of natural clay with a suitable amount of 25% hydrochloric acid for two hours[15]. The result material after filtration and washing by distilled water was dried at 115°C. The differences in weights before and after the treatment was recorded for this sample which was then used for further treatment processes. 25% in concentration of HNO_3, H_2SO_4, H_3PO_4 and CH_3COOH were used progressively and in the same procedure mentioned above in case of 25% HCl to obtain the treated clay sample.

B- Chemical and physical properties:

Chemical compositions of the natural and prepared clay samples were determined via several chemical and physical processes started by sodium fusion technique[16], which followed by dissolving the content in 6M HCl in order to prepare stock solution for a full instrumental and classical chemical analysis. Such analysis was reinforced by X-Ray fluorescence method[17]. Moreover, physicochemical properties also were measured like PH, density, porosity and specific surface area[15].

C- Thermal analysis :

Thermogravimetric(TG) and differential thermal analysis (DTA) were obtained simultaneously on a Stan Redcroft STA-780 Analyzer at heating rate of 5°C /min., and α -Al_2O_3 was used as a standard reference.

D- Infrared spectra :

Absorption spectra of natural and prepared clay samples were recorded on FT-IR 27-BRUKER infrared spectrophotometer using KBr disk, meanwhile, the spectra of the eluted fractions in the study was obtained using NaCl cell[18].

E- X-Ray Diffraction and Fluorescence :

X-Ray powder diffraction studies were carried out in Geological Mining State/ Baghdad/ Iraq, using CuKα radiation,and the diffraction patterns were recorded using Philips/pw/ 1720 powder X-Ray diffractometer filled with a vertical goniometer. The phase contributing to the X-Ray diffraction patterns were identified by reference to the Joint

Committee on Powder Diffraction Standards powder diffraction file. Meanwhile, X-Ray fluorescence data were obtained from Ministry of science and technology/ Baghdad, using Philips PW 1450/10 Fluorescence Analysis.

F- Application :

Chromatographic fractionation technique of Qaiyarah heavy crude oil was applied in order to separate such material into its simple components. Three fractionation columns containing clay samples were employed in the processes. These samples were prepared and activated as mentioned previously by heating in an oven at the required temperature.

A known weight (2)g of Qaiyrah petrolene (QP) [10] was fractionated into four fractions using four eluants of different gradually increasing polarities in order to evaluate the adsorption capacities of clay samples.

Results and Discussion :
A- Solubility in 25% conc. acids

It is clear on referring to the previous studies related to the treatment of Iraqi natural mineral clays using basic solutions that such action subjected to the removal of amorphous silica minerals[15]. Meanwhile, it seemed that treatment of such materials by different laboratory and industrially available acids specified that each of those acids has its activity and selectivity in removal of one or more of their chemical components.This occur even the fact that those components are physically and chemically bonded together naturally during a very long period. Therefore it is the interest of our research to treat clay materials using 25% conc. HCl, HNO_3, H_2SO_4, H_3PO_4, and CH_3COOH progressively. It was noted that the prepared sample losses 59.8% from its original weight. Data of instrument and classical chemical analysis in addition to that obtained from X-Ray fluorescence, Table (1), clarify 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 to be discussed later on,since it is so interest in chromatographic adsorption processes.

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. Such observation approved from the determination of capillary action of both samples. Figure(1) show the rapid rise of water in the first few minutes in cases of the prepared sample, which demonstrate the fact that such sample consist of large number of fine cavities well connected by extremely very narrow channels and hence allowing the water to move up easily through the clay sample.

To do our best in investigating the structural properties of our samples we managed 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 2θ (16 and 28)[19]. The pattern also contain reflection typical of quartz, feldspar, calcite, dolomite, illite, caolinite, chlorite, 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 (3) via their interplanar spacings [20]. Under the proposed experimental observation and referring to the literature [17,19,20], feldsbar mineral seems to be present in acceptable abundance in our sample and classified into three chemical formula:

i- potas group (Orthoclase) and might represented by $KAlSI_3O_8$ has monoclinic symmetry with unit cell values: $\alpha = 90°$, $\beta = 116.01°$ and $\gamma = 90°$.

ii- Albite ($NaAlSI_3O_8$), triclinic, $\alpha = 94.16°$, $\beta = 116.35°$, and $\gamma = 87.40°$,

iii- Anorthite ($CaAl_2SI_2O_8$), triclinic, $\alpha = 91.13°$, $\beta = 115.51°$ and $\gamma = 93.10°$.

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[4]. Therefore DTA were performed for both samples and shown in Figure (4). It seems that endothermic peaks were found corresponding to the two classes of hydrations ; hydroscopic and zeolitic or coordination water molecules. It is clear that some variation is noted in comparison between the observed results before and after the acidic treatment. Such variation might be explained by the fact that treatment by acids might produce so many fractures on the clay surface and hence increasing the bond strength between water molecules and such defect surfaces. To interpret such foundation TG of the prepared sample was preformed and represented in Figure (5). It is clear that losses of 4.3% and 7.44% from the original weight were observed and correspond to the above hydration phenomena.

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^{-1} in frequency was applied and the spectra revealed structural absorption bands including those between 500-700 cm^{-1} which are attributed to the Si-O stretching and bending vibrations[21]. Also there is a band in the rang 3400-3625 cm^{-1} which is related to the structural(OH) group. Such absorption show a significance variation in the position and sharpness of the vibration upon heating the samples in the range of 120–450°C which is related to the dehydration phenomena.

C- Chromatographic Adsorption

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 mixture into groups of compounds[1-3]. As a result, they employed in fractionation of QP into four groups of hydrocarbons. These groups have different adsorption polarities to the clay sample and therefore they were separated by using four eluants increased gradually in their polarities. Table (4) revealed the percentages of the fractions eluted on packing three columns with chromatographic grade (120 – 150 mesh) natural, activated 450°C, and the prepared clay samples. 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[10,7] and relaying on their infrared data which are presented in Table (5). It is obvious that the results reflect the fact that all the eluted fractions contain straight aliphatic hydrocarbons via the adsorption bands at 2925 and 1461 cm^{-1} which are attributed to the stretching and bending vibrations of methylene groups. Interference of branched aliphatic, naphthenic and aromatic compounds was happened and represented in the table by absorption bands at 2825, 1377 cm^{-1}, 2842 cm^{-1} and 1604 cm^{-1} which are related to CH_3, naphthenic –CH_2 and aromatic (C—C) groups respectively[22].

It is of importance to report that infrared technique is not enough to reach the goal of the present study. However, on comparison between the shown data through their positions and intensities, it seems that first fraction contains mainly of straight aliphatics, while the second is branched aliphatics, the third is nahpthenics and finally the forth eluted fraction is riched with aromatic hydrocarbons. Interference between the

above groups in fact was occurred but in conclusion the results suggest that the whole interference was low in using the prepared clay sample which is assumed to be an activated adsorption catalyst and has a promising future.

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Table (1): Average data analysis of clay samples.

Sample	Oxides	Na$_2$O	K$_2$O	CaO	MgO	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	SiO$_3$
Natural	Wet analysis	0.33	5.70	14.70	1.90	7.3	28.00	2.30	36.41
	XRF	0.31	4.49	12.28	1.39	4.46	38.12	2.19	35.30
Prepared	Wet analysis	0.71	6.80	0.18	0.01	10.30	35.40	0.01	45.00
	XRF	0.33	8.03	1.20	0.13	4.95	40.82	0.43	44.11

Table(2): Physical properties of clay samples.

Sample	Density gm/cm^3	Porosity %	Surface area gm/cm^3	Pore size cm^3/mg	Water absorption%	PH
Natural	2.99	231.25	200.12	5.36	97.98	8.01
Prepared	2.03	255.82	257.37	6.01	147.53	3.99

Table(3): Interplanar spacing for contributing phases in clay sample.

Crystalline phases	hkl	2θ	d values A°
kaolinite	001	12.4	7.165
chlorite	002	12.4	7.150
Ab/ Feldsbar	020	13.8	6.443
kaolinite	021	19.9	4.460
Quartz	100	20.9	4.248
Gypsum	021	20.8	4.248
Ab/ Feldsbar	201	22.2	4.015
calcite	102	23.0	3.869
Illite	113	24.2	3.685
Or /Feldsbar	220	26.6	3.350
Quartz	101	26.6	3.343
An/ Feldsbar	204	27.9	3.203
calcite	104	29.4	3.036
Dolomite	104	31.0	2.887
Gypsum	200	31.0	2.887
Or /Feldsbar	132	32.4	2.766
Illite	116	34.9	2.583
Chlorite	203	36.1	2.491
Gypsum	202	36.9	2.436
Kaolinite	003	37.7	2.383
calcite	113	39.5	2.280
Or /Feldsbar	003	42.5	2.127
calcite	202	43.3	2.087
Kaolinite	132	45.6	1.990
calcite	018	47.6	1.911
calcite	116	48.7	1.870
Dolomite	018	50.2	1.818
Illite	311	53.9	1.699
Kaolinite	133	54.9	1.671
Dolomite	211	57.6	1.599
Chlorite	208	57.6	1.599
Chlorite	060	59.9	1.549

Table(4): Percentage fraction of QP* on using clay sample.

Solvent	Polarity(deby)	Natural	Natural 450 °C	Prepared
n- Hexane	31.0	58.5	56.5	45.0
Toluene	33.9	15.0	16.5	21.5
Dichloro methylene	39.1	11.0	15.5	15.0
Ethanol	51.9	12.5	9.5	15.5
Loss		3.0	2.0	3.0

QP* composition: straight aliphatic 38% branched aliphatic 27% naphthenic 18% and aromatic Compounds 17% [10].

Table (5): Infrared adsorption bands for aliphatic, naphthenic and aromatic hydrocarbons eluted on using clay sample.

| Sample	Solvent	Aliphatic (C-H) CH₃	Aliphatic (C-H) CH₂	Naphthenic (C-H) CH₂	Aromatic (C-H)	Aromatic C=C
Natural clay	Hexane	2955(s) 1377(m)	2925(s) 1461(s)	2854(s) 1461(s)	3080(w),1034(w) 875(w),814(w)	1603(vw)
	Toluene	2955(s) 1377(m)	2923(s) 1485(s)	2855(m) 1458(s)	3087(vw),1032(w) 864(w)	1601(w)
	Dichloro methylene	2953(m) 1379(m)	2926(s) 1462(s)	2856(s) 1462(s)	3080(w), 1039(s)	1600(w)
	Ethanol	2951(s) 1380(m)	2927(s) 1462(s)	2858(s) 1462(s)	3080(w),1072(s) 1040(s)	1600(m)
Natural clay 450°C	Hexane	2954(m) 1377(s)	2931(m) 1462(s)	2844(s) 1462(s)	3080(w),1034(w) 805(s)	1604(vw)
	Toluene	2953(s) 1378(m)	2926(s) 1460(m)	2856(s) 1460(m)	3060(vw)	1604(w)
	Dichloro methylene	2956(m) 1378(w)	2927(m) 1462(w)	2855(m) 1462(w)	3080(w),1005(m) 808(s)	1605(m)
	Ethanol	2956(w) 1377(w)	2927(w) 1459(vw)	2856(w) 1459(vw)	3080(m) 907(s)	1607(s)
Prepared clay	Hexan	2953(m) 1379(m)	2927(s) 1463(s)	2856(s) 1463(s)	3067(vw), 1036(vw) 875(w),813(w)	1604(vw)
	Toluene	2955(s) 1377(s)	2925(s) 1459(s)	2855(s) 1459(s)	3067(vw) 1033(vw) 864(w)	1600(vw)
	Dichloro methanol	2955(w) 1377(w)	2924(w) 1458(w)	2855(vw) 1458(w)	3080(w) 1004(s) 883(s)	1653(w)
	Ethanol	2955(vw) 1377(vw)	2927(vw)	2855(vw)	3080(m) 1007(s)	1634(s)

s: strong, m: medium, w: weak, vw: very weak.
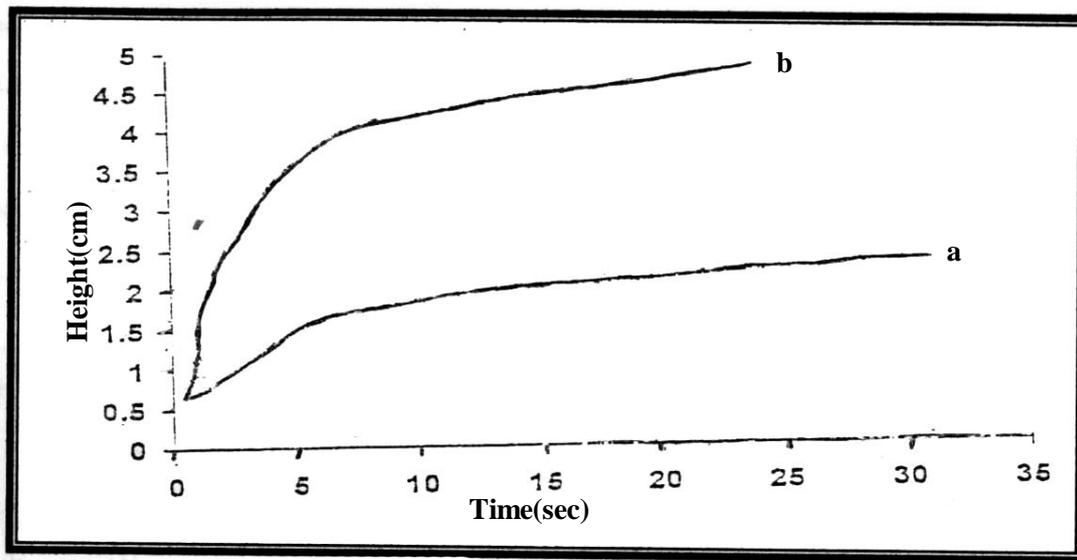
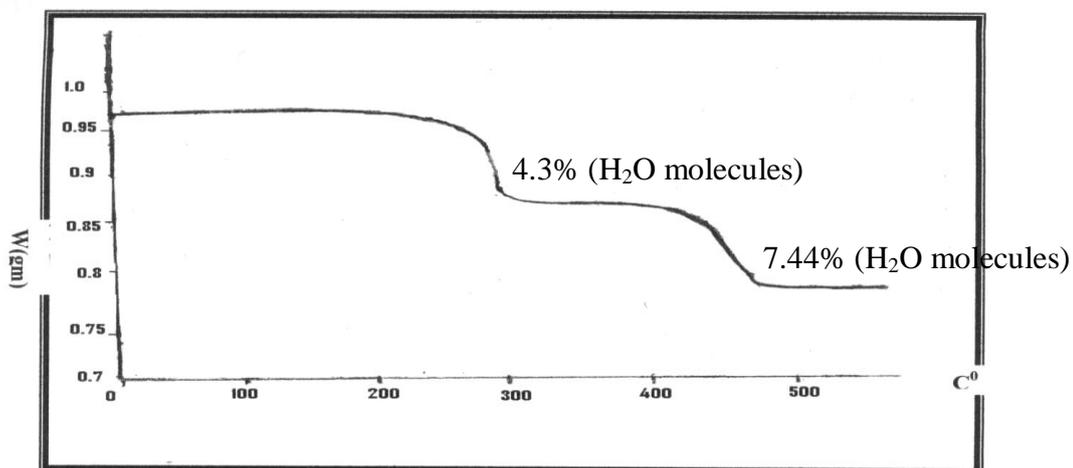**Figure(1): Capillary action curves of (a) Natural and (b) Prepared clay samples.**
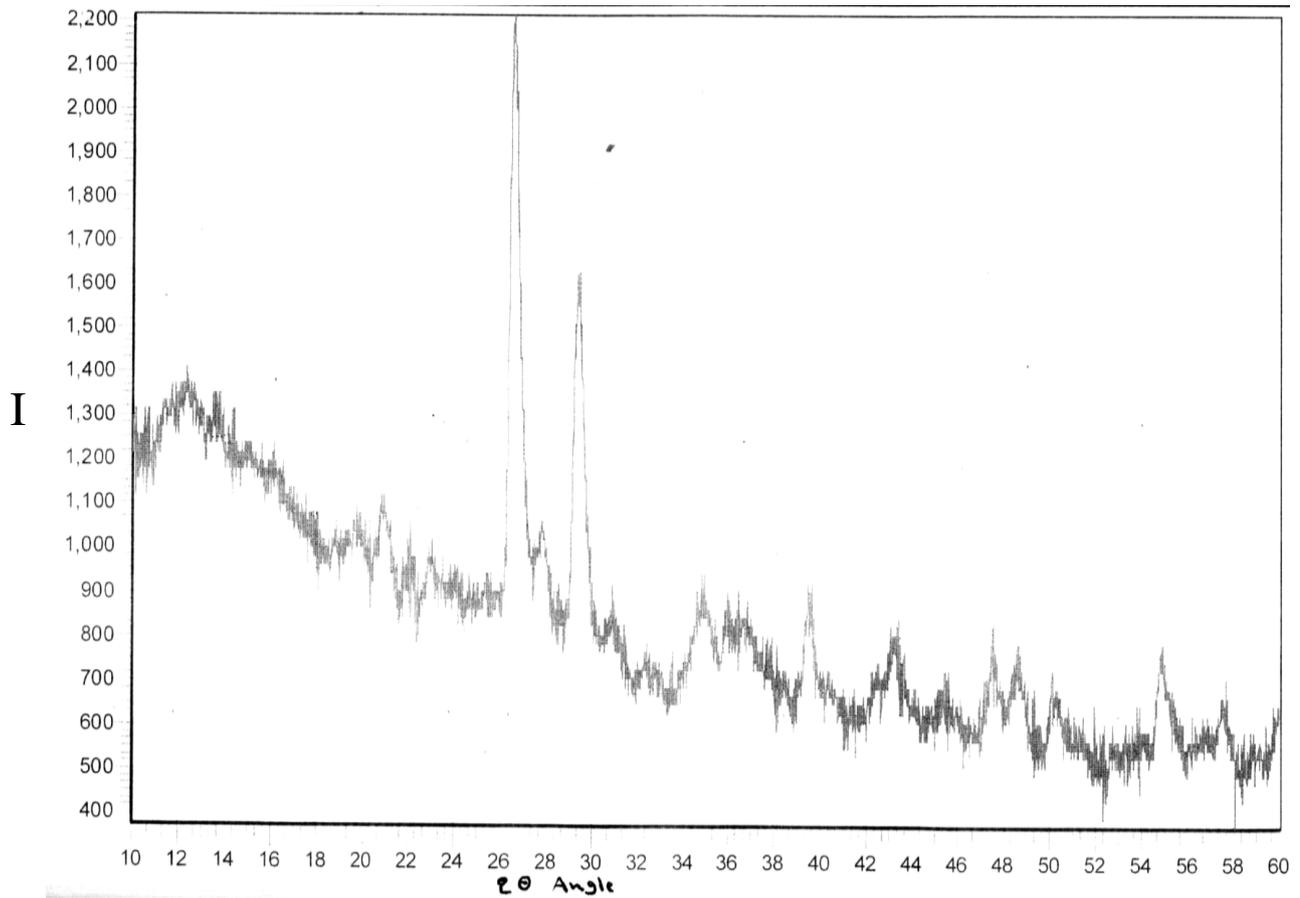
Figure(2): Powder X-Ray diffraction Pattern of natural clay sample.

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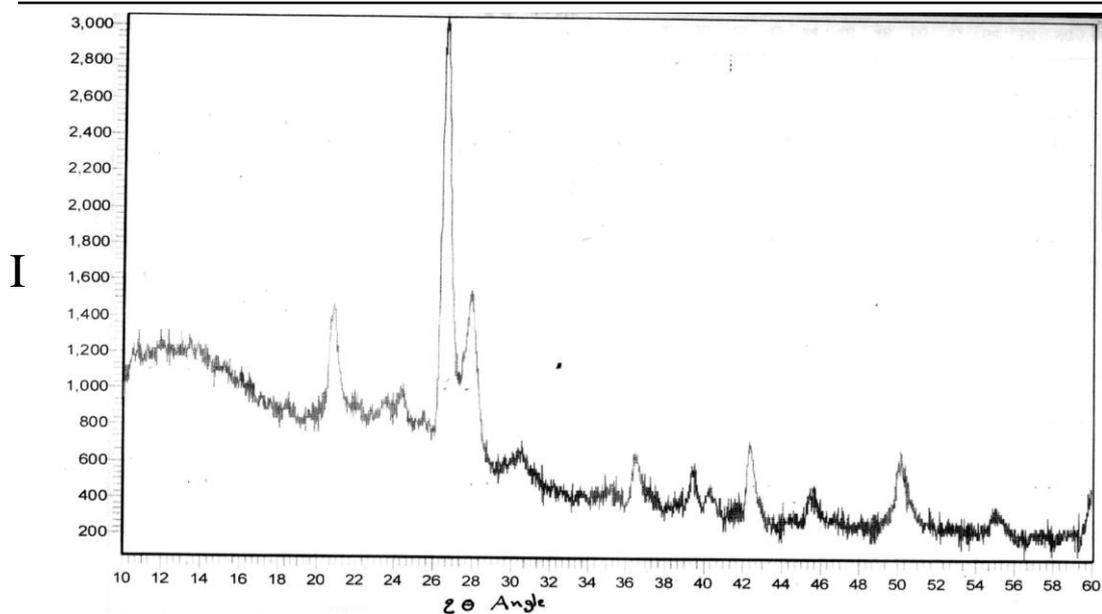
Figure(3): Powder X-Ray diffraction Pattern of the prepared clay sample.
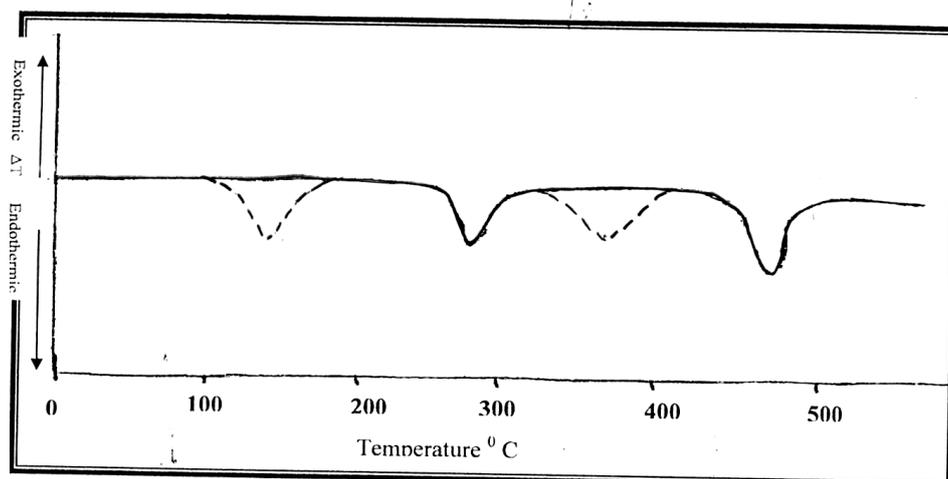
Figure(4): DTA curves of natural clay (…...) and prepared sample(⎯).

Figure(5): TG curve of the prepared clay sample.

4.3% (H_2O molecules)

7.44% (H_2O molecules)