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NATURAL MINERAL CLAYS BEARING FELDSPAR, PHYSICAL AND STRUCTURAL STUDIES AND APPLICATION IN PETROLEUM FRACTIONATION

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الخلاصة

تشمل الدراسة على معاملة الطين المعدني العراقي الخام بالحوامض والقواعد ومن ثم معاملتها حراريا للحصول على حفاز طيني من خامات محلية . اكدت الدراسة التي اجريت بتقنيات حيود وفلورة الاشعة السينية والمعاملات الحرارية وطيف الاشعة تحت الحمراء والتحليل الالي الكيميائي على ان الطين الخام والطين المعالج يحتويان على كمية لا بأس بها من معدن الفلسبار ومن الممكن استخدامها كمواد مازة في مجال الفصل الكروموتوغرافي وقد استخدمت في فصل المشتقات النفطية الثقيلة حيث تم تحويلها الى مكونات ابسط تم التعرف على تركيبها الكيميائي من خلال الدراسة بطيف الاشعة تحت الحمراء.

ABSTRACT

Natural Iraqi mineral clays, treated chemically by acids and bases and activated physically, have been investigated using powder x-ray diffraction , x-ray fluorescence, thermal analysis, infrared spectra, and technical instrumental analysis. Results indicate that those samples contain a considerable amount of feldspar mineral and have physical and structural properties evaluated their scientific and economic utilization to be applied in fractionation processes as adsorbent to separate Iraqi heavy crude oils into their simple components. Infrared spectra has been applied to study the chemical composition of the separated fractions.

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 a 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 amounts of feldspar, caolinite, calcite, dolomite...etc[2]. The water molecules which can be held by clay materials is either

adsorbed, interlayer , or lattic (-HO) water. The above initially adsorbed water molecules was explained on the basis of the dipole character of the water formula. Since the surface of the clay particle is normally negatively 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 in contact with clay materials.

The idea of adsorption and desorption of organic compounds over mineral clays was the interest of many workers in the field of fractionation processes. The demand for all kinds of fossil fuel sources, such as heavy crude oils, as alternative energy sources to light petroleum has been the subject for many workers[4-6]. Such studies deal with the application of clay materials to fractionate heavy crude oils and bitumens into their simple components . Recently, adsorption of a considerable number of Iraq heavy crude oils on natural Iraqi clay and rock materials have been reported[7,8]. On the other hand, Al-Juboury[9] in his investigation, reported that numerous showings of clay materials around Mosul city bearing a considerable amount of feldspar minerals have been described .

Accordingly and in continuation of investigating the application of the Iraqi raw materials in petroleum refinery, the present study is considered. It deals with the treating of the naturally occurring clay minerals by acids and bases in order to concentrate their feldspar mineral. Such treated clays will be used in fractionation columns as adsorbents to separate Iraqi heavy crude oil (Qayarah petrolene, QP) into simple and useful components.

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 pale green in colour has (120-150mesh) chromatographic grade, bearing suitable amount of feldspar 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 acidic and basic mediums. A know weights of natural clay samples were left overnight under each of (several concentrations of HCl, HNO_3, H_2SO_4, CH_3COOH, NaOH, KOH, and Na_2CO_3), washed by distilled water and then dried at 110C°. The differences in weights before and after the treatment was recorded.

b. Chemical and Physiochemical Analysis

Minerals content and their chemical compositions of the natural and 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[10] followed by dissolving the content 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 ethylene glycol method[11].

c. Thermal Analysis

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

d. Infrared Spectra

Absorption spectra of natural and treated clay samples were recorded on Pye-Unicam 1100 infrared spectrophotometer using KBr disk. Meanwhile, the spectra of the eluted fraction in the study was obtained using NaCl cell[12].

e. X-Ray Diffraction and Fluorescence

Powder x-ray diffraction analysis carried out using Wave Length Dispersant X-Ray Diffraction (WLDXRD) Philips Type (PW-2400) at Aramco Oil Company/ Saudi Arabia Kingdom. On the other hands, and to support the results of wet chemical analysis, x-ray fluorescence spectophotometer was employed for natural and treated clays on Phillips/PW 1600 analysis.

f. Application

Two fractionation columns packed with (120-150mesh) chromotographic grade natural and treated clay samples were employed in the processes. A known weight (~2g) of QP[5] was 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. The Solubility in Acidic and Basic Mediums

Natural mineral clay, which is supposed to bear a recognizable amount of feldspar, treated by different acids and bases in this study . It is well known[13] that treatment of rocks and clays by alkaline mediums and especially NaOH, amorphous silica was removed from the sample and that is what happened in our investigation. The results presented in table (1) which reflect the differences in weights before and after the basic treatment. Moreover, the results of treatment be concentrated and diluted acidic mediums, table(2), indicate that 25% HCl produced the best result in term of losing 38% during the solubility. The later condition seems to be related to the elimination of carbonate and sulphate compounds from clay sample under investigation[14]. Such treatment might result in concentration of clay minerals via the elimination or at least decreasing the amount of non clay minerals and at the end an activated catalyst in adsorption was obtained.

B. Chemical Analysis

The mean results obtained by wet chemical analysis and x-ray fluorescence for both natural and treated samples are shown in table (3). 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[11]. Moreover, the observed results show a notable differences in the clay sample composition before and after HCl treatment; i.e there is a decrease in percentage amounts of CaO and MgO in addition to SO_3^{2-} and an increase in the results of the rest oxides. Such results indicate that treatment of the clay by acid resulted in complete elimination of calcite and dolomite minerals accompanied with traces amounts of sulphate compounds .

C. *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[15].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(4).

It seems that treated clay sample shows low density, low porosity , low permeability low pore size and 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, Table(4), reflect the fact that treating the clay sample by HCl might produce so many fractures on its surface and hence increasing the percentage amount of water absorption. In conclusion, 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[16].

D. *Structural Investigation*

Many sedimentary clay and rocks are composed of more than one minerals that are mixed in several ways. The most satisfactory techniques for studying them however are by means of powder x-ray diffraction, thermal analysis and infrared absorption[2]. Therefore, such techniques have been applied for the natural and treated clay samples under investigation. Powder x-ray diffraction pattern of natural sample which is shown on Figure(2) reflect the presence of feldspar mineral in addition to quartz, hemetite, caolinite, illite, palygroskite , chlorite, calcite, and dolomite minerals. Meanwhile, Figure(3) shows the treated sample pattern which contains reflections of the above minerals in different intensities except clacite and dolomite since they are carbonate compounds and disappeared as a result of the acid effect. Such mixed unites of clay minerals are presented in Table (5) via their interplanar spacings[17] . On the other hands, it is reported that

[2], in general, clay minerals like the micas in the atomic structures; they consist of silica tetrahedron and two sheets of closely packed oxygen or hydroxyl in which metal atoms are embedded in octahedral coordination.

Under the proposed experimental observations of chemical analysis, x-ray fluorescence, x-ray diffraction and referring to the literature [2,11,17,18]it is of interest to mention here that the investigated feldspar minerals has the chemical formula of the potas group (orthoclase) and might be represented by $KalSi_3O_8$ has monoclinic symmetry with unit cell values; $\alpha = 90^0$, $\beta = 116.01^0$ *and* $\delta = 90^0$.

Moreover, 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[10] and the results were presented in Figures (4 and 5). In general, it is noted that three DTA endothermic peaks were found for both samples, Figure (4), 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(5). 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[3,8,13,15,16].

Finally, it is of interest to investigate the migration and elimination of the above mentioned water molecules from clay in addition to the clay minerology by infrared absorption. 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 (-OH) group[12].Such bands show a significance variation in the position and sharpness of the vibration upon heating the samples in the range of 120-500C° which is related to the dehydration phenomena. Moreover, the spectra reveal several structural absorption bands including those between 1000-1100, 515-470, 460-472, and 1434-1445 cm^{-1} which are attributed to the Si-O, Fe-O, Al-O, and $-CO_3^{2-}$ stretching vibrations respectively[12].

E. Adsorption Activity

The above physical and structural properties noted for the clay samples under study, and 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[19].

Accordingly, two fractionating columns were packed with chromatographic grade (120-150mesh) activated clay samples and compared with other related sedimentary rocks and clays in the area[3,6,8,13,15,16] in order to determine their adsorption activity and selectivity. They employed in fractionation of QP to its simple components using four eluants increased gradually in their polarity and the

observed results are shown in Table(6). 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 petrolene 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 study 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 hydrocarbons via the absorption bands at 2927 and 1463cm^{-1}which are attributed to the stretching and bending vibrations of methylene groups. Interference 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[20]. 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 hydrocarbons. Meanwhile, it was noted that ethanol fraction contains aromatic hydrocarbons accompanied with traces of naphthenics and the whole interference was low in using treated clay sample.

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.

Table (1): The Solubility in Different Basic Solutions

% Base	NaOH % Loss	KOH % Loss	Na_2CO_3 % Loss
5	8	6	5
15	13	15	6
20	19	18	4
25	20	18	3

Table (2): The Solubility in Different Acidic Mediums

HCl		HNO_3		H_2SO_4		CH_3COOH	
% Acid	Loss %	% Acid	Loss %	% Acid	Loss %	% Acid	Loss %
5	24	5	22	5	12	5	19
15	30	15	33	15	22	15	26
25	38	25	36	25	24	25	30
Conc.	38	Conc.	35	Conc.	20	Conc.	33

Table (3): Chemical Composition of Natural and Treated Mineral Clays

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
Treated Mineral Clay (25% HCl)	44.0	0.2	3.8	7.2	0.3	1.2	4.8	0.8

Table (4): Physical Properties of Natural and Treated Samples

Sample	Density gm/cm^3	Porosity %	Surface Area gm/cm^2	Water Absorption %	Pore Size cm^3/g	Surface Water Absorption %
Natural Mineral Clay	2.94	385.78	129.03	137.30	7.87	10.16
Treated Mineral Clay (25% HCl)	2.11	231.69	176.33	115.2	6.58	11.33

Table (5): Interplanar Spacings for Contributing Phases in Clay Sample

Crystaline Phase	hkl	$2\theta^0$	d values in Å
Quartz	100	21.0	4.221
	006	28.0	3.316
	110	36.3	2.741
Feldspar	002	29.5	3.181
	222	33.0	2.903
	241	34.9	2.705
	401	42.7	2.113
	113	43.2	2.088
	245	44.4	2.033
	422	47.5	1.909
Kaolinite	020	20.1	4.409
	022	24.3	3.737
	202	38.2	2.347
	221	45.8	1.978
Calcite	102	23.7	3.835
	132	30.7	3.018
	116	48.6	1.870
Palygroskite	201	22.2	3.993
Chlorite	202	39.5	2.273

Table (6): Chromatographic Fractions (%) of 2g QP* Using Different Adsorbents

Solvent	Polarity (Deby)	Natural Clay Sample	Treated Clay Sample (25% HCl)
n-hexane	31.0	55	46
Toluene	33.9	14	19
Chloroform	39.1	20	22
Ethanol	51.9	8	10
Loss	-	2.5	3

* QP Composition : Straight Aliphatic 38%, Branched Aliphatic 27%, Naphthenic 18%, and Aromatic Compounds 17%[5].

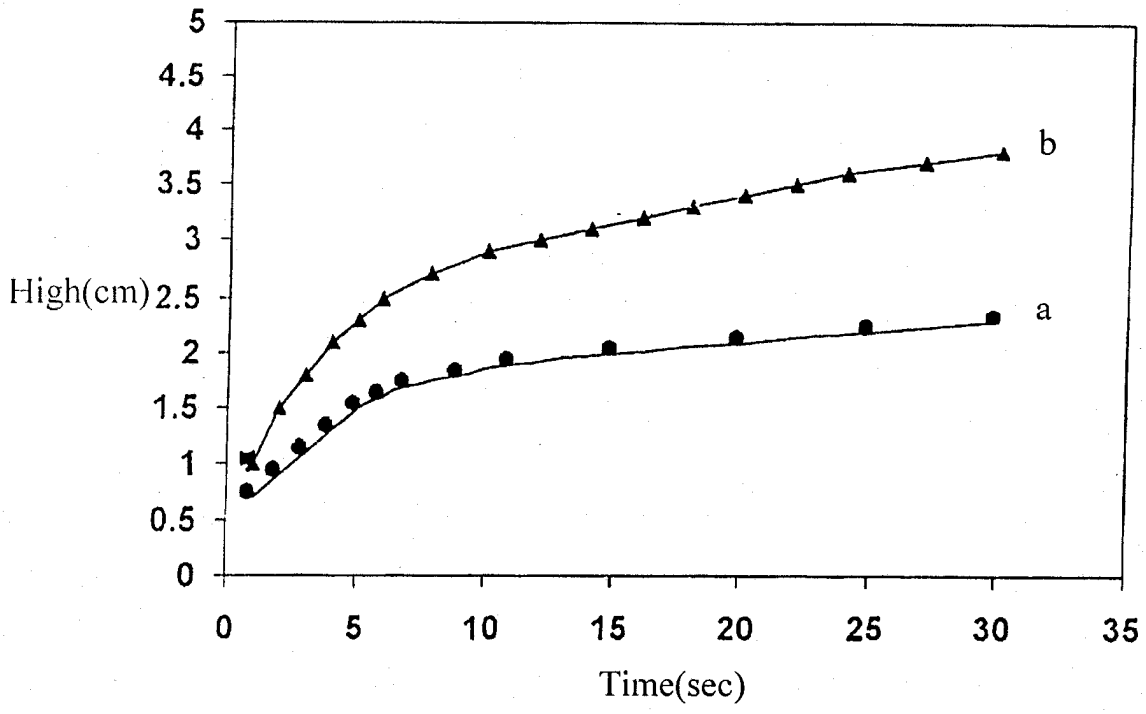

Figure (1): Capillary Action Curves of (a) Natural and (b) Treated Samples

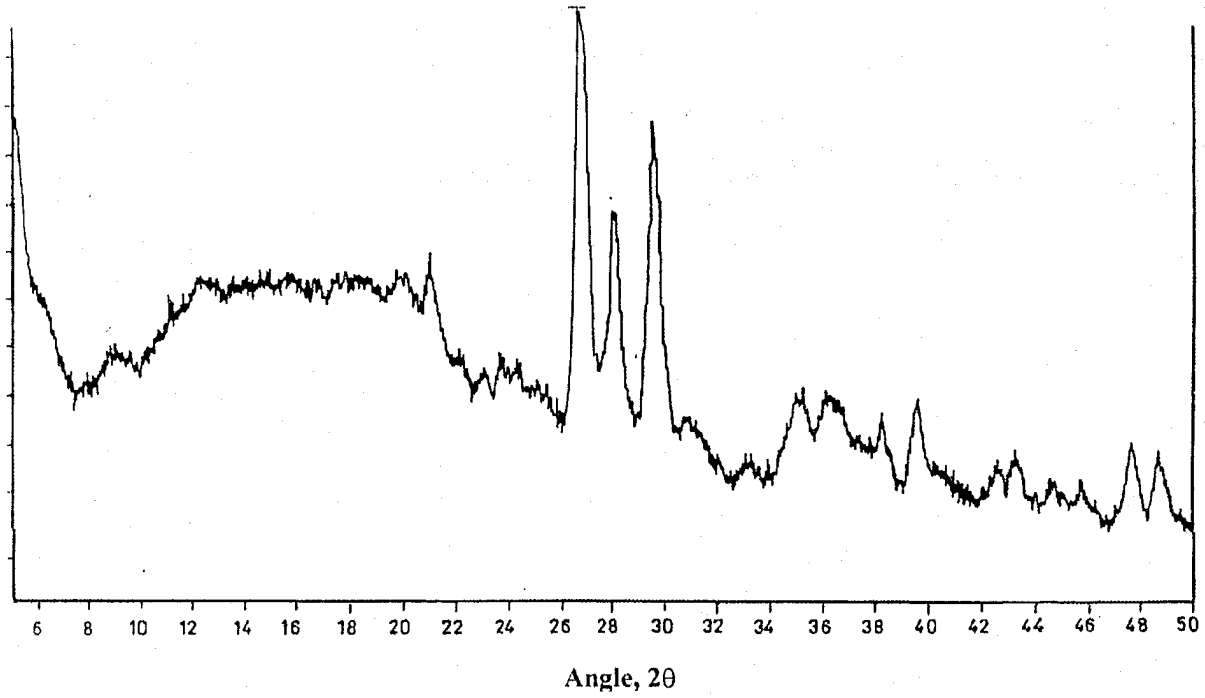

Figure (2): Powder X-Ray Diffraction Pattern of Natural Clay Sample

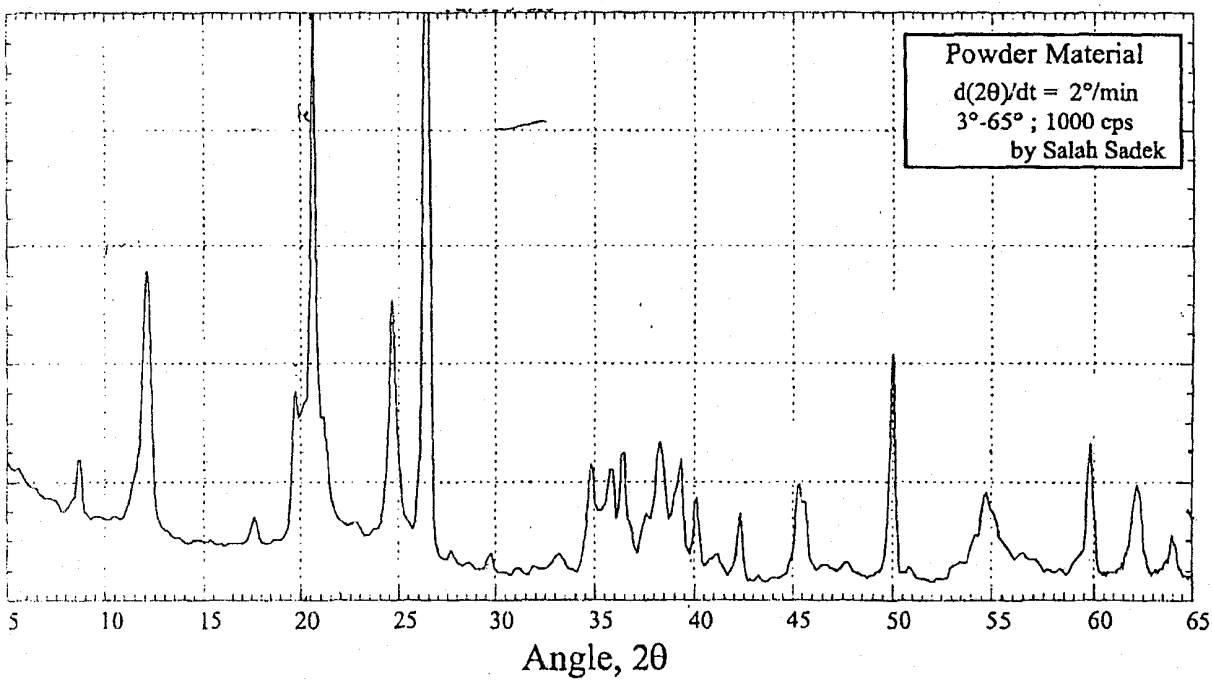

Figure (3): Powder X-Ray Diffraction Pattern of Treated Clay Sample

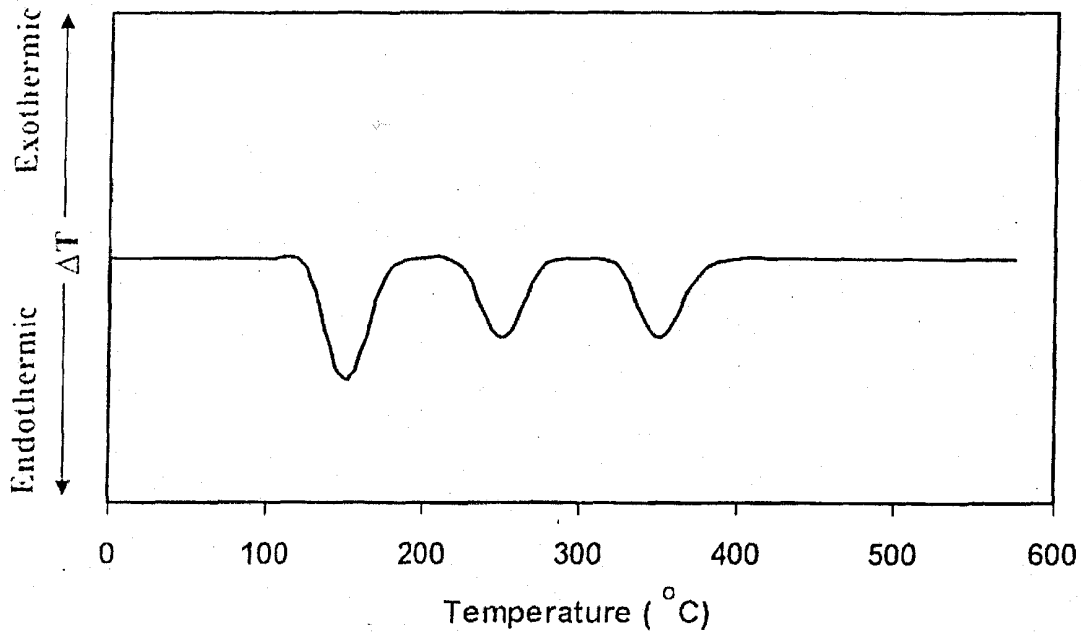

Figure (4): Differential Thermal Analysis Curve of Natural orTreated Clay Samples

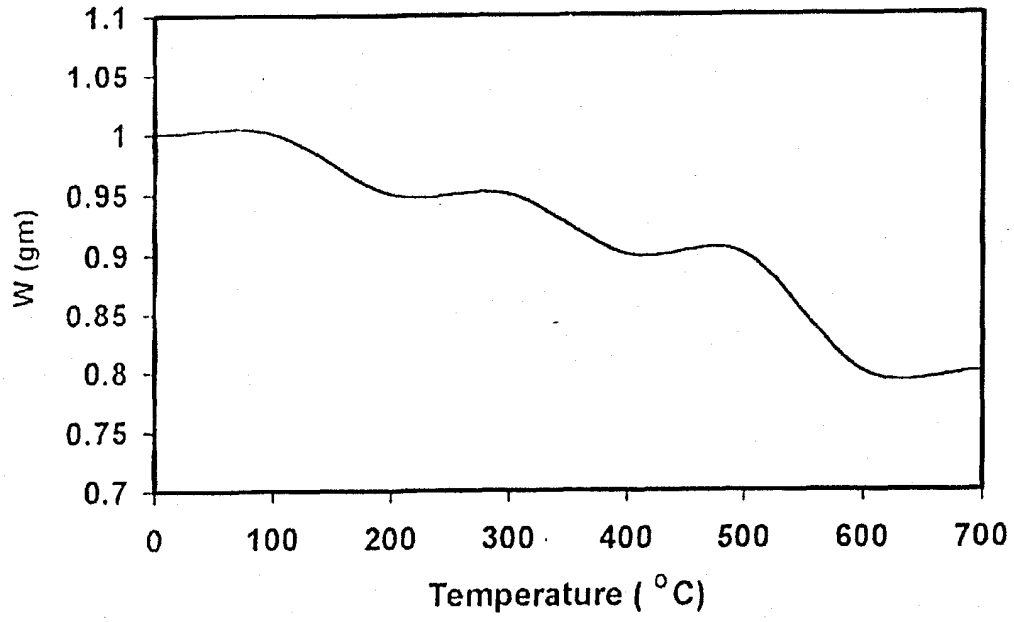

Figure (5): Thermogravimetric Curve of Treated Clay Sample

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