Chemistry Research Journal, 2019, 4(6):80-86

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Effect of Acid Treatment on the Properties of Syrian Natural Zeolites

Ibraheem Saied[1], Dr. Akel Roumie[2], Dr. Husam Al-dien Kawass[3]

[1]Student at Chemical Department, Faculty of Science, Tishreen University
[2]Professor at Chemical Department, Faculty of Science, Tishreen University
[3]Professor at Chemical Department, Faculty of Science, Tishreen University

Abstract The effect of particle size on the zeolite content of natural Syrian zeolite from TahAlsis has been studied which has name TS-14 according to the general Establishment of geology , the different sizes were named according to their sizes (<0.125mm, TS-14-1).(TS-14-2 0.125-0.3mm)**.**(TS-14-3 0.3-0.6) ،(TS-14-4 0.85-1.4mm).
In this work, the effect of acid treatment on previously studied samples was studied .some of the original samples were treated with HCL solution at PH=5 for 4 h , the samples were dried at 110 c for 24h and named the treated samples (<0.125mm ،TSH-14-1) **.**((TSH-14-2 0.125-0.3mm) **.**(TSH-14-3 0.3-0.6) ،(TSA-14-4 0.85-1.4mm)**.**
The texture properties were studied. We used the differential thermal analysis between 20-900 c field in Aragon, with a heating rate of 10 c/min for the raw and treated samples. It was found that the calcite was eliminated by a large percentage, which explains the increase in the specific surface area of the treated samples comparing by the raw samples.

Keywords natural zeolite, particle size, acid treatment, Adsorption, BET

1. Introduction

The zeolites are containing of crystalline aluminum silicate with uniform vacuum structure. The structure consist of the tetrahedron bonding (sio_4) and (ALO_4) which are the basic building unite of zeolite. The zeolitic structure has a negative charge modified by one of the Alkaline or Alkaline earth elements, the basic building unit of zeolite can be expressed as:

$$M_{x/n}\,[(AlO_2)_y(SiO_2)_x].wH_2O$$

Which: x/y >1, n Equal cation
The zeolites are characterized by the presence of (pores) channels and gaps which play the main role in many physiochemical processes, and pending on the type of crystallization of these quadrilaterals from many types of zeolitic structures and there are more than forty types of zeolitic structures, which differ mainly in the size of pores and diameter of the opening of their channels, of these types :*Phillipsite* , Mordinite , Clinoptilolite … and others

Zeolites are classified into
1- natural zeolites, which are not pure materials containing different ratios of these types of the former in addition to impurities such oxides, clay, calcite etc. the different component of natural zeolites vary according to their location.
2- synthesis zeolites, where each of these types are synthesis in special condition, we get a pure material with specifications that meet the desired purpose in terms of crystallization and pore size.

The natural zeolites are characterized by the availability , inexpensive and pure natural materials , the synthesis and natural zeolites have many common properties , the most important of which is ion exchange, tetrahedron [AL_2O_4] in their structure has a negative charge which is modified by the Alkaline and Alkaline earth elements these positive elements are easy to move and can be replaced by other cations, which gives zeolites that important as ion exchange as well as their high adsorption and chemical catalysis.

Natural zeolites are not pure as it is mixed in most cases with some other metals and acid treatment improves the zeolite properties, the zeolitic structure is destroyed in strong acid acidic milieu, but treatment with an acidic solution at pH=5 does not affect the structure of the zeolite. The dilute solution purifies ores of some materials, especially calcite, and help open pores within the zeolite structure.

Differential thermal analysis is used to study the properties of solid compound, especially the thermal stability of these compounds. It gives the associated phase changes when heating these compounds in a wide rage of temperatures a range of phase changes and transformation in the structure of compounds can occur while exposed to different temperatures these compounds lose water molecules within their porous structure and at higher temperature surface hydroxyl groups may be partially or completely lost, which contribute effectively to many processes using solid compounds, high temperatures can damage and cause thermal sintering, these compounds lose their effectiveness in most processes because the porous structure is a primary factor in the properties of these compounds. The phase and structural changes associated with the heating of solid compounds are heat absorbent or diffuser. This is reflected in the TG-DTA differential curves in the form of peaks upward and downward for the X axis representing temperature variation. Through the resulting peaks, it is possible to know the nature of changes in the structure of changes in the structure and judge the thermal stability of the studied structure.

Research Importance

The importance of the research comes from the fact that it studies one the natural raw materials available in Syria and the possibility of using them in certain applied field and these materials can be obtained cheaply, making them of great economic importance.

Research Aims

The aim of this research is to study the effect of acid treatment on the properties of the tissue structure of natural materials containing zeolite that studied at work [8]

Research Methods and Materials

Preparation of samples

Depending on the hardness of the basic components of the TS-14 raw zeolitic samples as shown in table 1 According to Moss scale of hardness

Table 1: Moss ladder for the hardness of basic components in the studied samples

Content	feldspar	analcime	clay	calcite
Mohs scale hardness	6-6.5	5-5.5	2-3	2-2.5

The natural zeolitic sample was subjected to a constant grinding process of 5kg/m^2 and then completed sifted by sieves of different sizes and divided the product into four samples according to different sizes and labels were given according to these sizes as shown in the table

Table 2: Raw sample names according to their sizes

TS-14-4	TS-14-3	TS-14-2	TS-14-1	sample
0.85-1.4mm	0.3-0.6mm	0.125-0.3mm	< 0.125mm	Particle size

A section of the original samples was treated with HCl solution at pH=5 for 4h with continuous shaking in a mechanical shaker , then we filtered and washed with distilled water several times to get rid of the chloride ions and dried the samples at 110 ºC for 24h the treated samples were named as follows

Table 3: Treated sample names according to their sizes

TSA-14-5	TSA-14-4	TSA-14-3	TSA-14-2	TSA-14-1	sample
0.85-1.4mm	0.6-0.85mm	0.3-0.6mm	0.125-0.3mm	< 0.125mm	Particle size

Methods of Study

The adsorption curves for a raw and treated samples were determined by nitrogen gas adsorption at temperature 77K using a Gimini 2375 programmed automated device after discharge of samples into vacuum attached to the apparatus at low pressure at 250 ºC, the other tissue structure characteristic of the raw and treated samples (specific surface area, average pore radius, micro porous size, etc) were determined by processing the resulting adsorption data.

Results and Discussion

Using the resulting adsorption data for the raw samples, the specific surface area determined by applying a linear BET relationship [9]

$$\frac{X}{V(1-X)} = \frac{1}{C.}V_m + \frac{C-1}{C.V_m}X \quad (1)$$

where V the relative pressure value , V_m volume of adsorbed gas systemic condition , C_{BET} constant BET , the tissue structure was studied from analysis of adsorption data resulting from adsorption of nitrogen gas at 77K , using a Gimini device

figure 1 shows the adsorption curves of the studied samples and shows that all curves belong to type IV according to the classification of Sing and his associates [10]

a knee also appears on the adsorption curves at low pressure values up to 0.1 indicating of micro porous , we calculated the S_{BET} surface area from analysis of adsorption data by the linear shape of BET relationship

from linear BTE'S , to calculate the value of C_{BET} constant , the volume of single layer V_m , which is used to calculate the specific surface area , by the slope and intersection values of the relationship :

$$S_{BET} = 4.37 \times V_m \quad (2)$$

BET drawing show clear linearity in the relative pressure field (0.05-0.2) and the total pore volume V_P is calculated in 1mg/g by converting the adsorbed volume at relative pressure p/p_0=0.95 to the liquid state and considering that the nitrogen density at the degree 77K is 0.808 g/cm^3 after multiplying by the constant 15.4.

$$\bar{r} = \left(\frac{2V_P}{S_{BET}} \right) \times 10^3 nm \quad (3)$$

We determined the exact pore volumes using the Dubinin- Radushkevich DR [11], applying the following relationship:

$$\log V = \log V_o - D\left(\log {P_o}/{P} \right) \quad (4)$$

Where we V_0 represents the size of micro porous, D constant Dubinin, is observed as shown in figure 3, by the curves that the linear field falls in the of low relative pressure up to 0.04 and the begins to deviate upward and note that the linear field of the samples almost identical, which indicates on the similarity of these samples in that they contain micro porous. Trough linear relationship (4) we calculated the value of D and V_0 from intersection and inclination, as well as the characteristic energy value of adsorption E_o relationship:

$E_o = 2.8574/(D)^{1/2}$ (5)

Table 4: The porous structure factors of the raw samples

sample	V_p ml/g	V_o ml/g	V_{meso} ml/g	v_o/v_p x 100	$\bar{r}$ nm	E_o kj/mol	D	C_{BET}	S_{BET}
TS-14-1	0.108	0.0293	0.079	27.13	2.84	16.2	0.031	192	75.8
TS-14-2	0.079	0.021	0.060	26.6	2.91	15.7	0.033	202	54.2
TS-14-3	0.080	0.0234	0.057	29.0	2.69	16.2	0.031	242	60.2
TS-14-4	0.091	0.0263	0.068	28.9	2.69	15.8	0.031	215	67.6

Using the aforementioned relationships, the porous structure factors for acid-treated samples were calculated

Table 5: The porous structure factors for acid-treated samples

sample	V_p ml/g	V_o ml/g	V_{meso} ml/g	v_o/v_p x 100	$\bar{r}$ nm	E_o kj/mol	D	C_{BET}	S_{BET}
TS-14-1	**0.108**	**0.0293**	**0.079**	**27.13**	**2.84**	**16.2**	**0.031**	**192**	**75.8**
TS-14-2	**0.079**	**0.021**	**0.060**	**26.6**	**2.91**	**15.7**	**0.033**	**202**	**54.2**
TS-14-3	**0.080**	**0.0234**	**0.057**	**29.0**	**2.69**	**16.2**	**0.031**	**242**	**60.2**
TS-14-4	**0.091**	**0.0263**	**0.068**	**28.9**	**2.69**	**15.8**	**0.031**	**215**	**67.6**

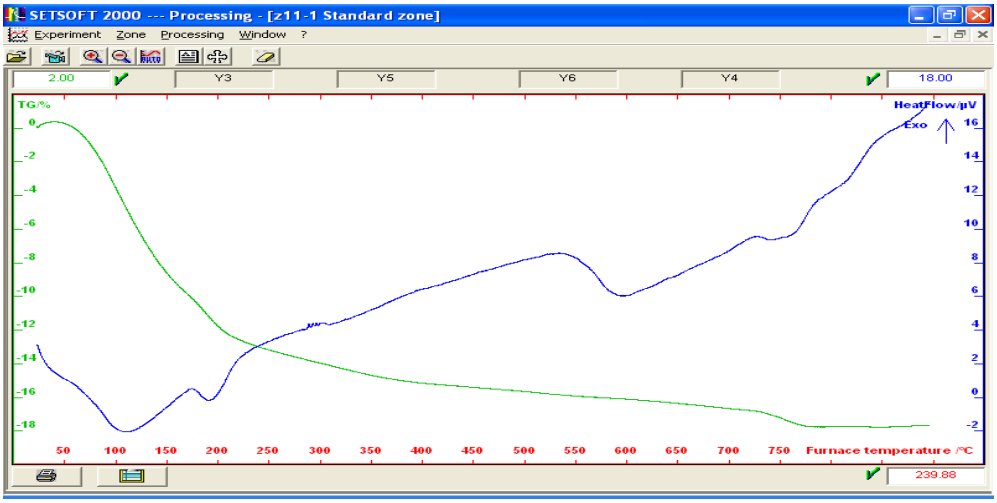
Note that the percentage increase in the surface area of the sample TSH-14-1 is 17.5%, TSH-14-2 is 19%, TSH-14-3 is 8.8% and TSH-14-4 is 7.7%

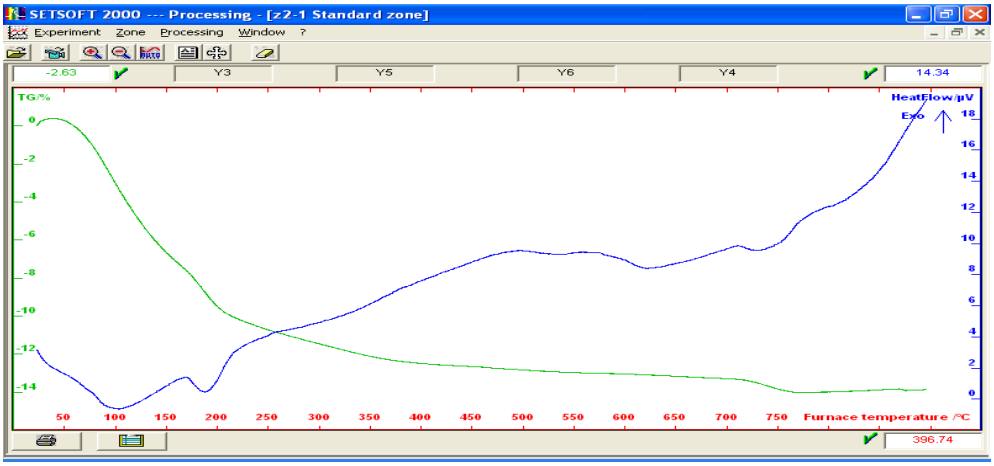
This confirms that calcite is highly concentrated in smoother samples due to its lower hardness, and concentrated in TSH-14-2 more than TSH-14-1 and significantly different from other samples where zeolite concentration is expected due to zeolite hardness.

C_{BET} values indicate weak affinity between the adsorbent and adsorbent, while low E_0 values show that the adsorption is of the physical type for both raw and treated.

Differential thermal analysis is used to determine the thermal effects and weight loss of solid when heated in specific thermal field and the presence of an inert gas.

Thermal heating in the 20-900 ºC range was performed in aragon, and at heating rate of 10 ºC/min, the differential analysis curves of the raw samples are shown in the following figure :





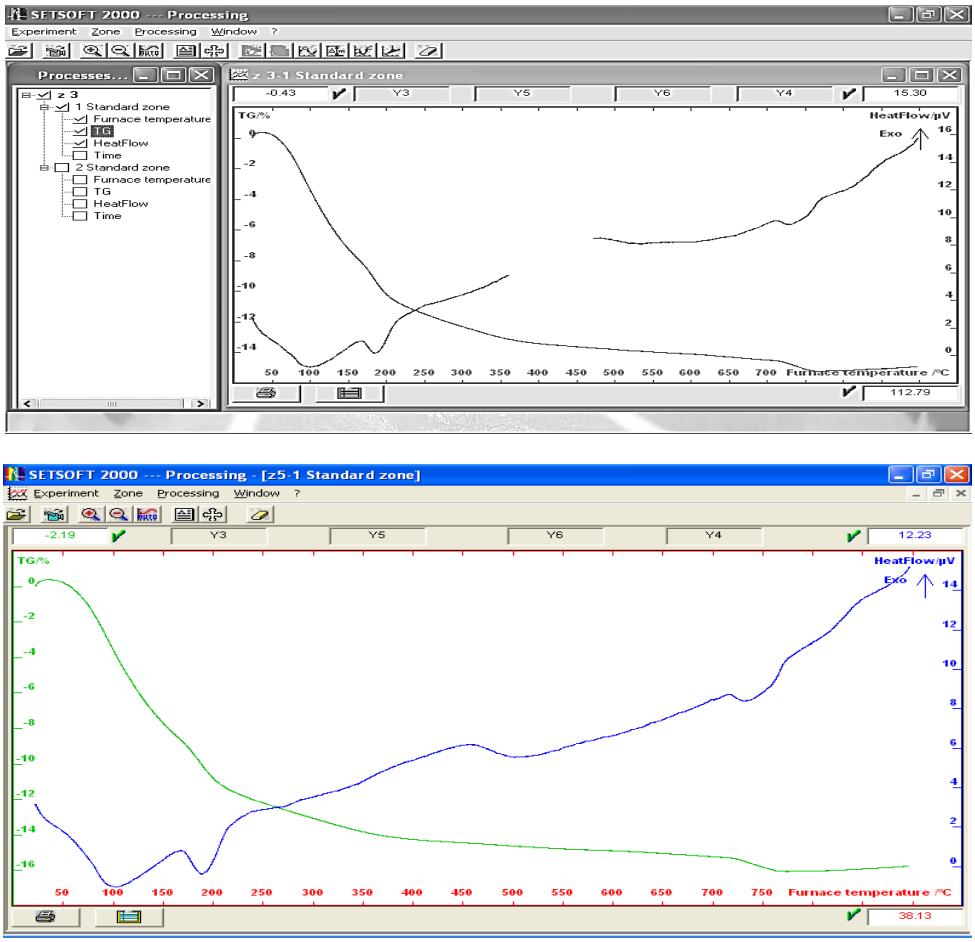
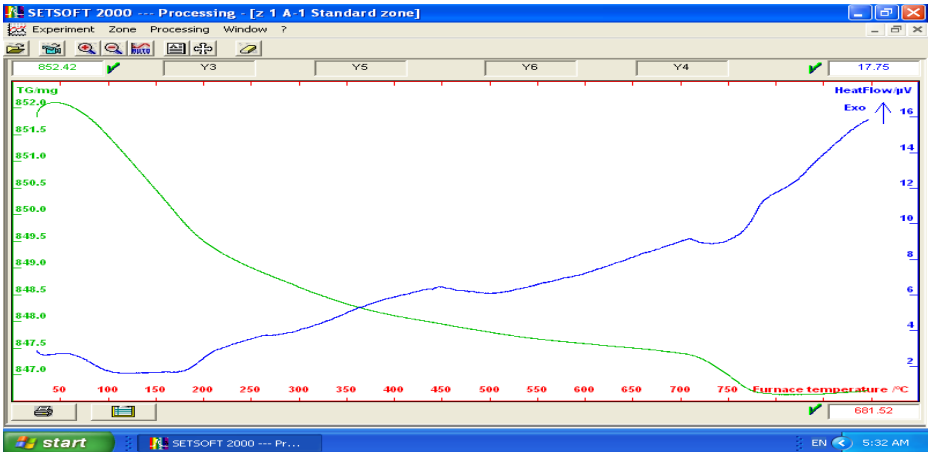


Figure 1: TG-DTA differential thermal analysis curves for raw samples

The differential thermal analysis curves of the raw samples exhibit four endothermic effects , at 50-120 degrees indicating the loss of physically adsorbed water , the second effect between 180-210 degrees indicating the loss of chemically adsorbed water , third endothermic effect between 450-550 degrees indicating loss of some hydroxyl groups and the fourth and final effect between the 700-800 degrees indicates the dissolution of carbonates in the raw samples , and we preformed the previous process for treated samples and the differential thermal analysis curves were shown in figure 2.



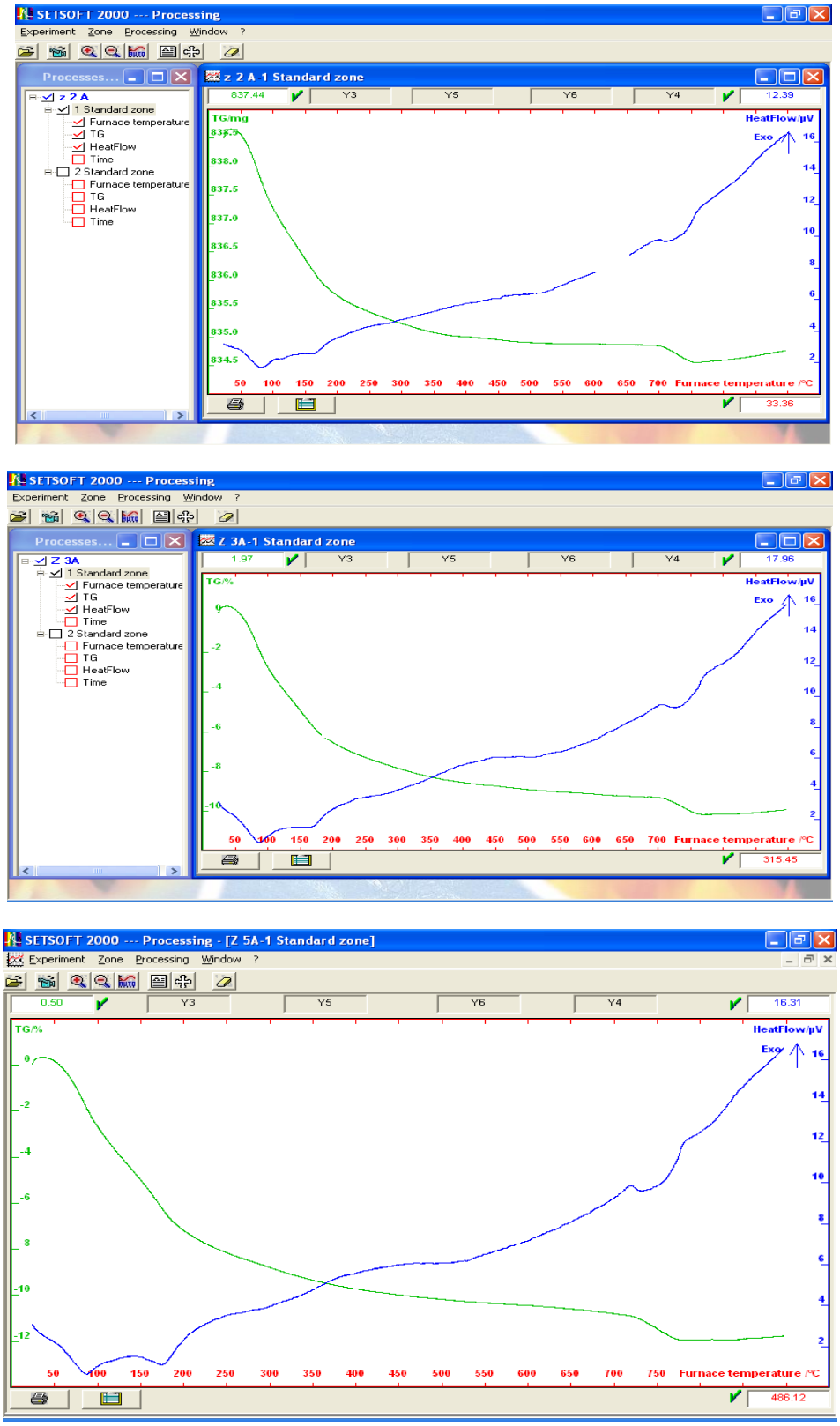


Figure 2: TG-DTA differential thermal analysis curves for treated samples

The differential thermal analysis curves of the treated samples show the same thermal effects compared to the raw samples but the weight loss at heat-absorbing peak resulting from dissolution of the carbonates is lower due to the elimination of the large proportion of carbonates by acid treatment, this confirms the reason for increase in the surface area between the samples before and after treated as well as increasing the volume of micro porous.

Conclusion and Recommendation

- The bulk of calcite were removed from the samples by acid treatment.
- Increased specific surface area if treated samples, and increased pore size.
- We recommend a XRD to further confirm what we have come to conclusion.
- We recommend to take advantage of this work marketing to support the national economy by gridding and sifting of natural of natural materials containing zeolite for sale and use it in various field, such as agriculture for soil enrichment.

References

[1]. Breck. D.W., Zeolite Molecular Sieves, Willy Interscience Pub New York, London, 771, (1974).
[2]. Lubomira T., Zeolite Macrostructures, Licentiate, 543, (1999).
[3]. Raheb. A, Kawass. H.AL, *Characterization of the Syrian Ores Containing Zeolite in Om'Ezen Area*, Tishreen University Journal for studies and Scientific Research – Basic Science Series Vol (27) No(1), (2005).
[4]. Raheb. A, *Preparation of zeolitic structure and a study of the influence of the thermal treatment in the porosity structure*, Tishreen University Journal for studies and scientific Research – Basic Science Series Vol. (29) No(1), (2007).
[5]. Raheb. A, *Influence of acidic treatment on the properties of Syrian Zeolites*, Tishreen University Journal for studies and scientific Research–Basic Science Series Vol. (26), No(3), (2004).
[6]. Romie. A, Raheb. I, Suleiman. S, *Removal of ammonium from Aqueous solutions by Syrian Natural Ores containing Zeolite* , Tishreen University Journal for studies and scientific Research – Basic Science Series Vol. (32) No(1), (2010).
[7]. Supance Chayabutra., Basicity of MgO by temperature programmed desorption of phynol., WWW.Journal.SU.ac.th/index.php/suij/article/view File/45/45.
[8]. Effect of the granular size on the zeolite content in the natural zeolite ores
[9]. Brunauer, S; Emmet, P, H; and Teller, E. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc, 60, 309-319, (1938).
[10]. Gregg, S, S, J; Sing, K, S, W; Adsorption, surface area and porosity, Academic press, London, New York,.15p, (1938).
[11]. Dubinin. M.M; progress in surface and membrane science, Ed. Cadenhead. D.A, Danielle. J.F and Rosen bur. G.M, Acad. Press, New York, p.1-70, (1975).