PREPARATION AND AGGLOMERATION OF ZEOLITE 5A FROM LOCALLY AVAILABLE RAW MATERIALS

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ABSTRACT

The aim of the present work was directed to prepare zeolite 5A from a process of ion exchange from zeolite 4A and calcium chloride solution.The most affecting parameters on the synthesis process (i.e., temperature, time, and concentration of salt solution) were studied. It was found that a temperature of 94 °C, mixing time of 8 hours and concentration of 1M for the chloride salt solution are the most suitable conditions to get an extent of exchange of 90%. Kaolin clay was used as a binder in the process of agglomeration at different weight percents,then the important physical and mechanical properties of the agglomerates such as; porosity, bulk density, pore volume, crushing strength, loss on attrition and eventually the adsorption capacity had been measured and evaluated. It was concluded that the agglomerates made of (20-25) wt% kaolin had the optimum properties.

INTRODUCTION

Zeolites are crystalline hydrated aluminosilicates of group I and II elements, inparticular, sodium, potassium, magnesium, calcium, strontium.and barium. Structurally the zeolites are "framework" aluminosilicates, which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedral linked to each other by sharing all of the oxygen. They are represented by the empirical formula: $M_{2/n}.O.Al_2O_3.xSiO_2.yH_2O$.

In this oxide formula, x is generally equal to or greater than 2 since tetrahedral AlO_4 are joined only to tetrahedral Si04, and n is the cation valency. The framework contains channel and interconnected voids. The cations are quite mobile and usually are exchanged to varying degrees by other cations. Intracrystalline "zeolitic" water in many zeolites is removed continuously and reversibly. In many other zeolites, mineral and synthetic, cation exchange or dehydration may produce structural changes (Berck, 1974). Zeolite type A possesses the characteristic of being able to undergo dehydration with little, if any, change in crystal structure (Haden *etal,* 1963*)*.

Zeolite A, is the sodium form of the type A, also designated 4A. Calcium form refer to as 5A . Both zeolites have the same crystalline structure and being readily interchangeable by simple-exchange procedures. The numerical positions of the type designations refer to approximate pore dimensions in Angstrom units. The sodium form of zeolite A may be considered the parent of the other members of the same type (Haden *et al,* 1962).

Replacement of 1/3 of sodium ions by calcium ions increases the effective pore diameter to about 5A°, and if potassium ions are exchanged, the pore diameter decreases to about 3A°. These phenomenal and other structural analysis are explained on the basis of X-Ray diffraction method (Breck, 1956).

The zeolite family adsorbents are high capacity and selective because they separate molecules based upon size and configuration of the molecules relative to the size and geometry of the main apertures of the structures with a selectivity that is not found in other solid adsorbents. So that, separation can be made based on molecular-size differences (Othmer, 1981; Vanghan, 1988). Zeolites have high affinity for water and other polar molecules (e.g. NH_3, H_2S, SO_2, and CO_2) and can in general be used for removing water from gases and liquids and for general drying (Othmer, 1978).

Zeolite 5A is used in two major separation processes. The first is the separation of linear and isoparaffins by allowing the former to pass through the channels and the latter is not. It adsorbs n-decane from mixture containing cyclohexane, phBu and phEt solutions (Caro *et al,* 1981), also hexane adsorbed on the 5A zeolite from mixture containing hexane and benzene (Neimark et al 1963).The second process is air separation because the equilibrium loading of nitrogen on the 5A zeolite is much greater than that of oxygen and argon (Pererra and Crittenden 1998).

EXPERIMENTAL WORK

Zeolite 4A used ,was the Iraqi type synthesized in the Factory of Catalysts of Al-Basil Company, while the kaolin clay was brought from Al-Ga'ara area of western Iraq. Chemical analysis for zeolite 4A and kaolin clay were made in the Ibn-Sinaa Company. Calcium chloride was of analar type. Work was done in two stages. Each stage, concentration of salt solution was fixed with the other two parameters being varied. The extent of exchange was determined by analyzing for Na_2O (residual or left) in the prepared zeolite, compared with the original percentage of Na_2O present in zeolite 4A. The comparison was based on weight percent (wt %). This analysis was made in the Geological Survey and Mining Company .Each experiment, 25 g of zeolite 4A were mixed with 200 ml of $CaCl_2$ solution in a round bottom flask and placed in a shaker water bath (Type GFL, F.G. BODE & Co. Hamburg 60) which provides an excellent control on temperature during the experiment time. Zeolite 5A prepared.was agglomerated in a cylindrical pellets 2.5 in diameter and 4-8 mm. long by pressing the zeolite-binder paste manually into a cylindrical cavity .The next steps were , drying (at 120 °C for two hours)(Minachave 1973 and Bashir 1997); and calcination (at 650 °C for two hours)(Drost 1966 and Mahdi 1997).Then the characterization of the new adsorbent was made by the measurement of the important physical and mechanical properties.

RESULTS AND DISCUSSOIN

Preparation step

The object of this study was to prepare zeolite 5A with an exchange of 75%. It was found that increasing the temperature of and time of mixing had a slight effect on the exchange, and this is represented by figures 1 and 2 as plotted at constant concentration of 0.2N and constant time of 8 hours for Fig.(l) and at constant concentration and constant temperature of 77°C for Fig. (2). Obviously, there is an increase in the extent of exchange as both parameters were increased, but this increase was small. Increasing the concentration of the salt solution in the second set (Table 1) had a pronounced effect within the range of temperature and time studied and the occlusion of calcium ions occurred to an extent higher than what was objected .A temperature of 94°C and time 8 hours with 1M of $CaCl_2$. According to these results ,the structure formula is identified as:

$$0.9\ CaO.0.1\ Na_2O.Al_2O_3.1.96SiO_2.yH_2O$$

An X-Ray structural analysis was made to the prepared zeolite and its pattern is given by Fig. (11), and by comparing it with the standard one (Fig. (12)), it was concluded that the preparation step had produced this zeolite with good crystallanity except for slight changes attributed to that the standard pattern was recorded for samples with 100% exchange.

Agglomeration step

It was found by examining Fig. (3) that the optimum water content to form a moldable paste decreases with increasing the amount of kaolin.

Physical properties

The addition of kaolin clay was found to decrease the porosity Fig. (4), pore volume Fig.(5) and, the adsorption capacity for water vapor Fig.(6). Binders are well known to offer mechanical strength to the agglomerates which causes a decrease in the physical properties (Haden 1963), and this was also concluded in the present work and all the above properties were decreased as the amount of kaolin increased This is attributed to the decrease in the porous media and in the amount of micropores originally present in the zeolite .therefore the internal area would be decreased .This may be due to the blockage of the micropores resulting from the sintering of fines and the combination of semi-molten impurities during thermal treatment of the clays. Sintering occurs when many crystal forms increase markedly in size without any change in crystallographic type. This crystal growth takes place at temperatures below the point of liquid formation and is usually acknowledged to start at the Tammann temperatures which is about 0.55 to 0.6 that of the melting point of the component (Searle and Grimshaw 1959). So each initial particle merges with its neighbors and the spaces between the particles progressively decrease and finally disappear. Then, the void spaces between the sintering crystallites vanish and an increase in the density of the impact is predicted .The addition of kaolin clay leads to increase particle (bulk) densities (Fig.7), by making solid bridges and interlocking bonds of different mechanisms. The change in the physical properties is greatly affected by the shrinkage that occurs in clays during drying and calcination. Reduction in the volume of the structure occurs because of the loss of large amounts of surface water through evaporation; and shrinkage is greatly increased in the initial rate of drying when the moisture content is high Fig.(8) demonstrates that the adsorption isotherm for water vapor is of type I classification that is favorable to adsorption (as do most zeolites) and posses a saturation limit corresponding to complete filling.

Mechanical properties

Prepared adsorbents of different catalysts gain a sufficient mechanical strength when mixed with an inert binder. The increase of this property is obvious by examining (Fig.9and 10), for the diametrical (radial) crushing strength is increased and the weight lost by attrition is decreased as more binder is added .Zeolite particles are held together by strong bonds resulting from sintering of the minor clay particles and the dissolution of solid material which becomes concentrated during the course of drying forming solid bridges and held the parent particles together forming a dense packing. However, high values for the mechanical properties contribute the physical ones for a pellet at a given condition. This means that the pellets will have low porosity, pore volume, and eventually low adsorption capacity, which is the most effective property for the prepared adsorbents in the present work. Thus, one must compromise the results.

Sample optimization was made by selecting a sample of appreciable porosity and pore volume, maximum adsorption capacity, maximum strength and, minimum loss on attrition. Thus, Samples containing (20-25) wt.% kaolin were found to have the most preferable properties.

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Table (1) Design of experiments for the preparation step

Set I	0.2N $CaCl_2$		
Temperature °C	**Time h**	**Na_2O % in 5A**	**% Exchange 5A**
77	8	10.10	19.0
77	16	9.90	21.4
77	24	9.73	22.8
85	8	10.10	19.8
94	8	9.90	21.4
Set II	**2N $CaCl_2$**		
77	24	0.26	98
94	8	1.26	90

Table (2) Chemical analysis of zeolite and kaolin

Constituent	Weight (%)zeolite 4A	Weight (%) kaolin
SiO_2	35.90	50.1
Al_2O_3	31.19	32.8
Na_2O	12.60	0.27
K_2O	0.40	0.66
MgO	0.23	0.24
CaO	0.21	0.28
TiO_2	2.01	1.27
Fe_2O_3	1.13	1.24
L.O.I	15.20	12.3

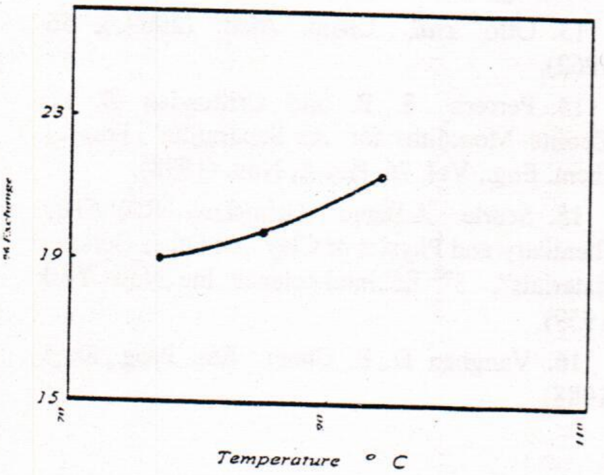

Fig. (1) The effect of temperature on the ion exchange process for zeolite 5A at 0.2N and 8 hr

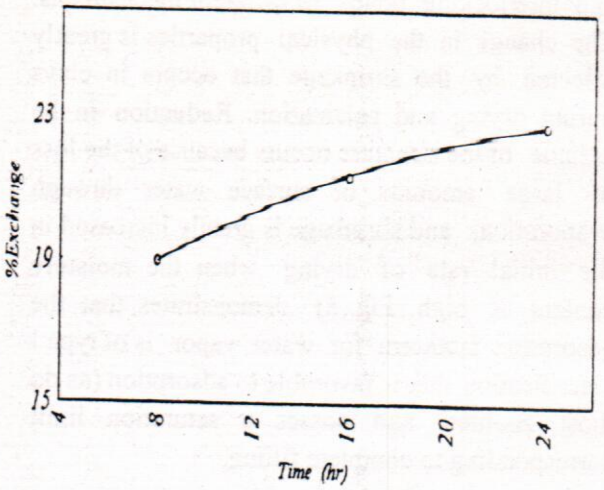

Fig. (2) The effect of time on the ion exchange process for zeolite 5A at 0.2N and 77°C

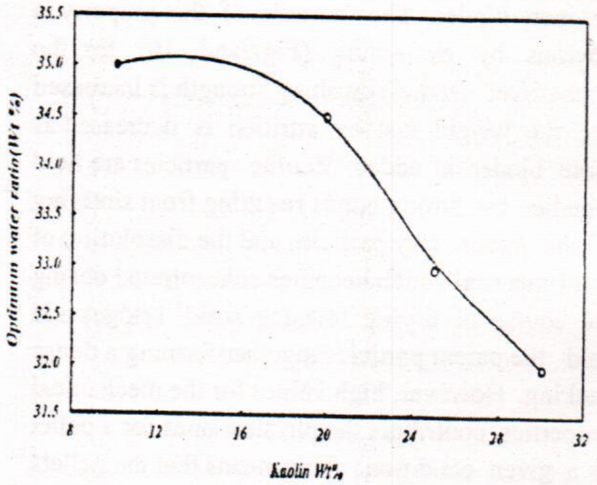

Fig. (3) Optimum water content for the agglomeration

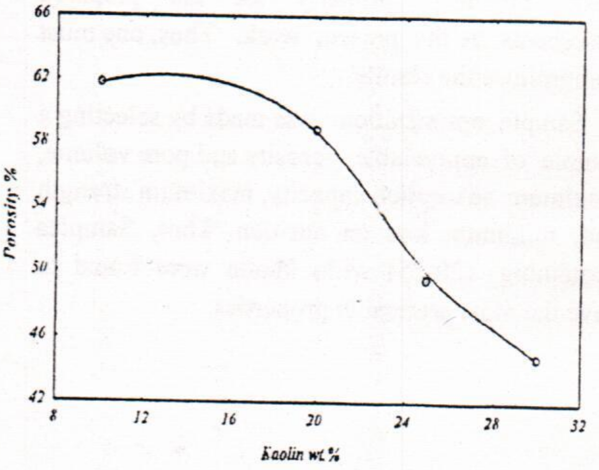

Fig. (4) The effect of kaolin porosity

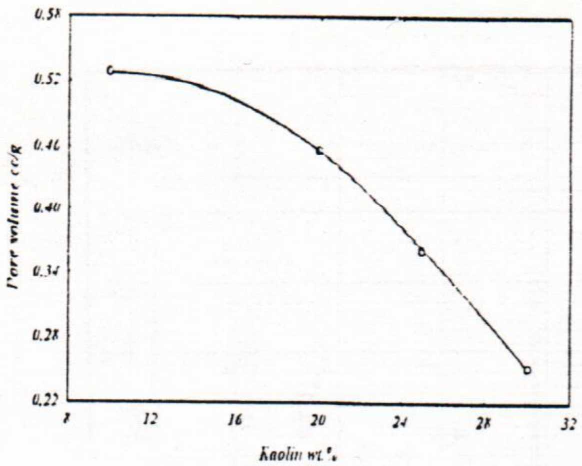

Fig. (5) The effect of kaolin on pore volume

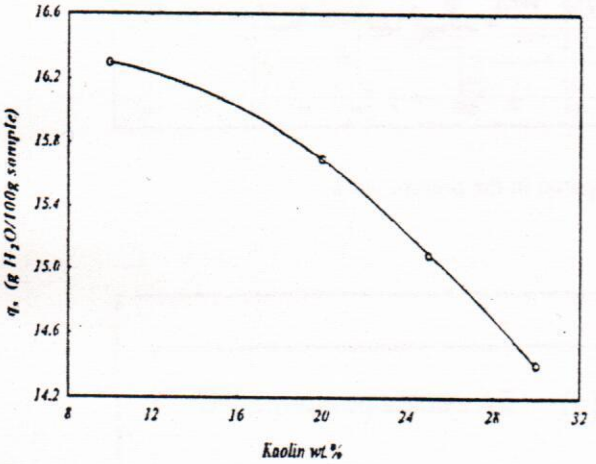

Fig. (6) The effect of kaolin on the adsorption capacity

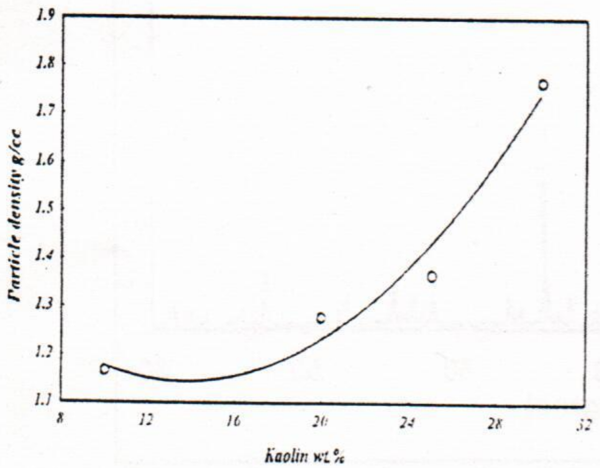

Fig. (7) The effect of kaolin on the particle density

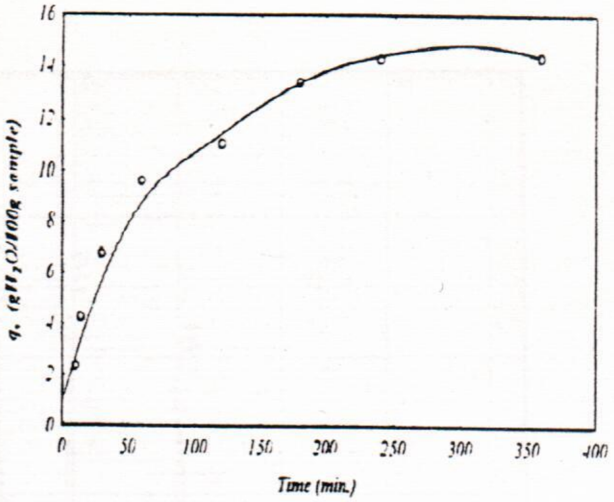

Fig. (8) Adsorption isotherm for sample containing 25% kaolin

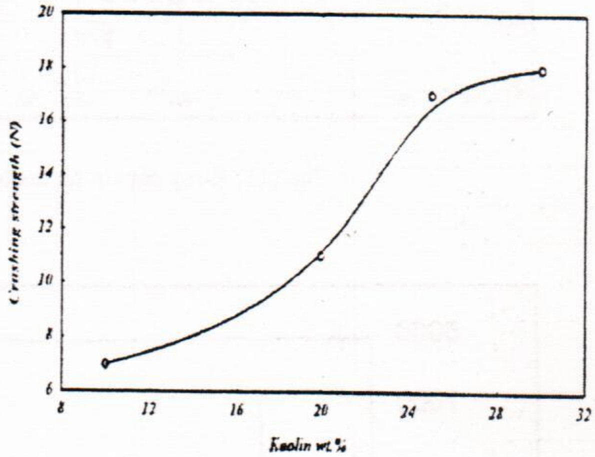

Fig. (9) The effect of kaolin on strength of the agglomeration

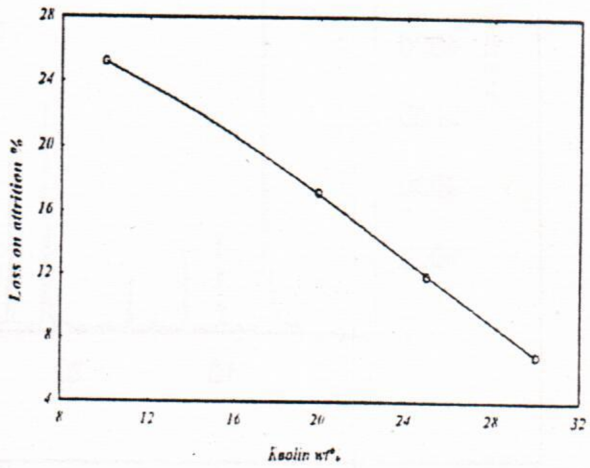

Fig. (10) The effect of kaolin on the attraction resistance

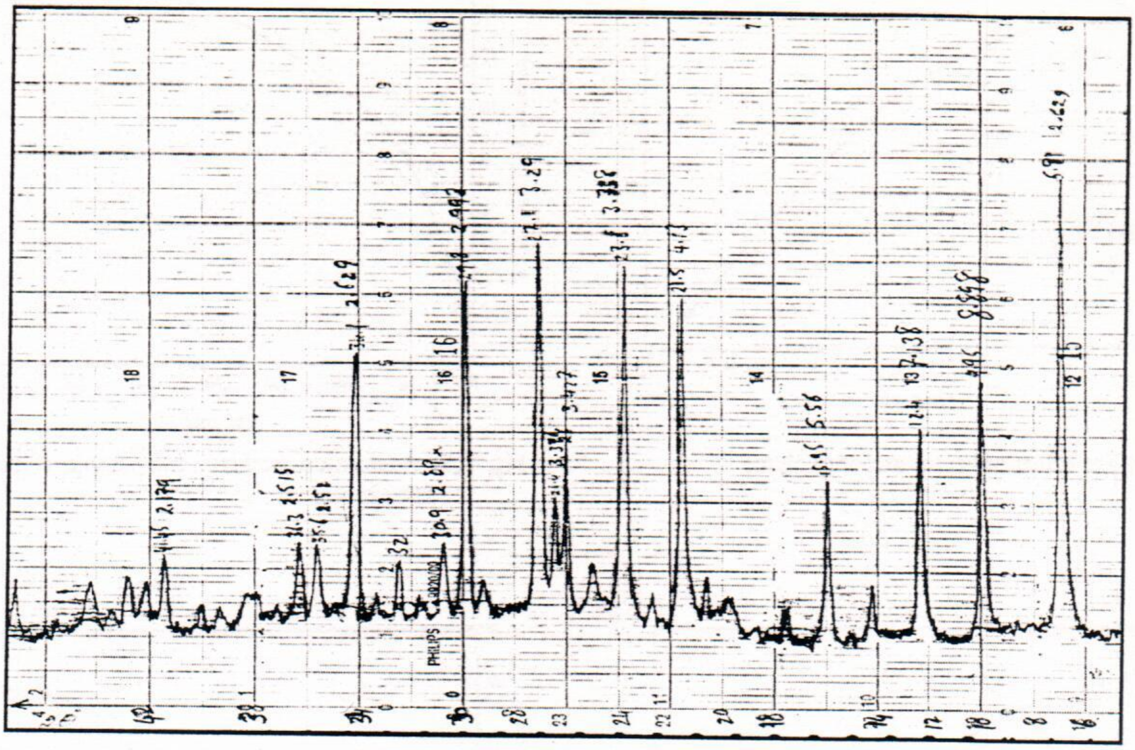

Fig. (11) X-ray pattern for zeolite 5A prepared in the present work

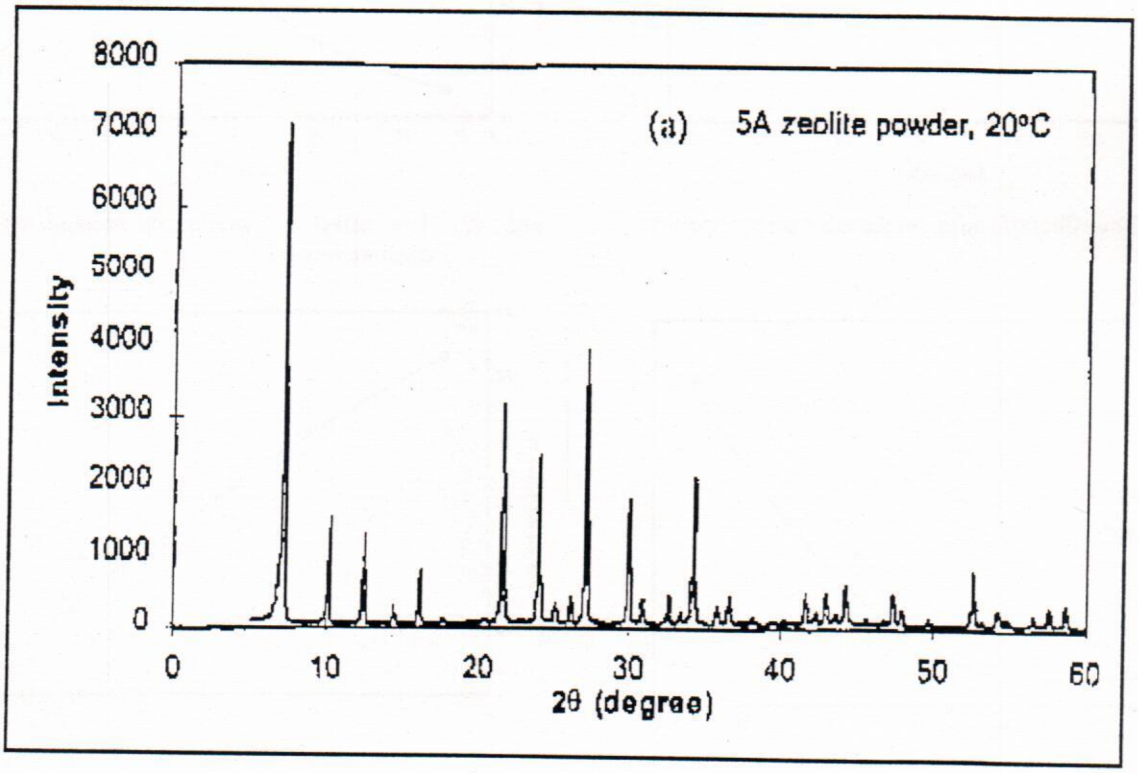

Fig. (12) X-ray pattern for standard type of zeolite 5A