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Preparation of Zeolite Type 13X from Locally Available Raw Materials

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Abstract

The aim of this work was to prepare zeolite type 13X from locally available kaolin and to study the effects of using some binding materials through the process of agglomeration of this zeolite. This study was focused on using kaolin binder in different weight percents (10,15,25,35 and 45%).Physical and mechanical properties of the agglomerates such as porosity , apparent density , pore volume, crushing strength , loss on attrition , surface area and finally the adsorption capacity had been measured and evaluated .The preparation step was achieved by mixing the reactants consisting of metakaolin , source of silica as (sodium trisilicate) and sodium hydroxide . The conditions was temperature of 70° C and time of mixing as 8, 10,24,34,50,65,75 and 80 hours .The zeolite –binder was shaped in the form of cylindrical particles of 2.5 mm in diameter and 4-8 mm long using a suitable experimental technique . It was found that the suitable binder kaolin clay with 25% by weight. This gave the best properties as crushing strength, adsorption capacity and density compared with standard properties of zeolite 13X.

***Keywords*:** zeolite 13X, kaolin binder, agglomeration process.

Introduction

Zeolites are crystalline, hydrated aluminosilicate with a negative charge framework structure containing holes occupied by large ions and water molecules that have substantial freedom of movement. This leads to possibities of ion exchange and reversible dehydration[1].

Two types (X) and (A) are most important. Their significance as commercial adsorbents depends on the fact that each crystal contains interconnecting cavities of uniform size , separated by narrow opening , or pores of three-dimensional framework structure. When formed, this crystalline network is full of water. This moisture can be driven from the cavities with moderate heating without changing the crystalline structure [2]. After dehydration, the zeolite is termed activated and the pores or channels may be filled with water or other materials [3]. The framework of X-type zeolite consists of a tetrahedral arrangement of sodalite units or truncated octahedron (each sodalite unite has six square faces of oxygen atoms and eight hexagonal faces or hexagonal faces by a hexagonal prism into a super structure to form X zeolite , [4]. The main cavities in the structure of X –zeolite are nearly spherical (elliptical) in shape and are about (13°A) diameter called supercages. These cavities are entered by way of channels (8-9 ° A) in diameter .The truncated octahedron has smaller cavities, the center being a bout (6.6°A) in diameter with entrance through the hexagonal face of about (2.2°A) [5]. Zeolites type 13X, in which the negative framework (high aluminum content) charge is balanced by the appropriate number of cations, electrostatic interactions.

This favors adsorption by this zeolite of substance with a large dipole moment (e.g. .H_2O, NH_3, H_2S, and SO_2) or quadruple moment (N_2, CO and CO_2) [6, 7]. Therefore if two molecules are capable of entering into a single zeolite system, the zeolite retains one preferentially to all other on the basis of some other zeolite interactions such as polarity, the molecule with strong degree of polarity being preferentially retained [8]. High purity zeolite crystals used in adsorption processing must be formed in agglomerates having high physical strength and attrition resistance. The crystalline powders are formed into agglomerates by the addition of an inorganic binder, generally clay, in wet mixture .The blended clay –zeolite mixture is extruded into cylindrical-type pellets, spherical or granulated [9]. Agglomeration is the process of making big particles from little ones. When fine particles, usually in a moist state, are brought into intimate contact through agitation, binding forces come into action to hold the particles together as agglomerate .Capillary binding caused by wetting with water or aqueous solutions is the most common binding mechanism [10].

Experimental Work

This study is aimed to prepare zeolite type 13Xwith different weight percent of kaolin binder (10, 15, 25, 35 and 45%wt) .The reaction time was also studied (10, 24,34,50,60 and 80 hours) .The experimental part of this work is consisted of two basic steps

1. Preparation of zeolite 13X from local materials (i.e.kaolin) and study the effect of mixing time on the preparation process at 70°C.
2. Agglomeration of the prepared samples using kaolin binder material and study the main properties of the agglomerates.

Materials

The used kaoline is available in Al–Dewekhala Quarry in Al-Anbar region.

Sodium silicate was supplied by Fluka Chemia, and sodium hydroxide was supplied from BDH (England).

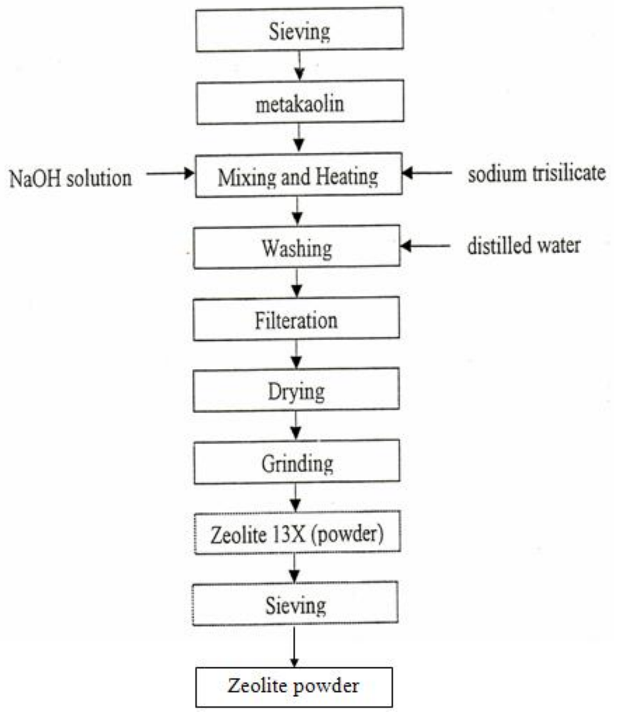
Preparations of zeolite 13X

The preparation of sodium type zeolite 13X was carried out by the addition of (9%wt) sodium hydroxide solution to the metakaolin and sodium trisilicate mixture. The reactant mixture has a composition expressed in terms of oxide mole ratio of:

SiO_2/Al_2O_3	Na_2O/SiO_2	H_2O/Na_2O
4	1	40

The temperature of reaction 70° C and mixing time ranged from 8 to 80 hours. In each experiment, metakaolin and sodium trisilicate were mixed together with sodium hydroxide solution in a two-necked round bottom flask. The agitation was achieved using a variable speed stainless steel paddle type mixer with a relatively medium revolution driven motor (Voss Instrument Ltd .Type SG/PA/ST). Heating the flask was achieved using an electrical mantle heater, while the temperature of the mixture in the heated flask was controlled using variable input voltage. The next steps were, decantation, washing several times with distilled water until the pH value reachs to 10, pH value was measured by a pH meter (METROHM 605). The product then was filtered in Bukhner funnel with the aid of a vacuum pump (type Edward vacuum pump model EiM5, serial 0146g) and dried at 120°C for 12 hours (11) using an electric oven (Tecnoformal Ltd., Max .Temp. 250° C) .

After drying zeolite was converted to a fine divided powder using centrifuge ball mill (Type RETCH, S2) provided with seven steel balls. The general steps in the preparation process are summarized in the following Fig..



Schematic diagram for the preparation of zeolite 13X

Agglomeration procedure

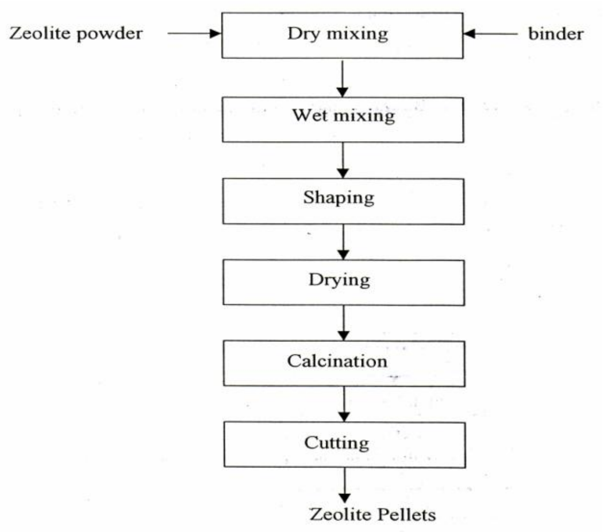
The general steps for the preparation of zeolite- binder agglomerates are illustrated in following Fig..

Dry zeolite powder was added to the binding material. It has a size of 45 micron. This particle size was found optimum and offered better porosity, adsorption capacity, strength and reasonable loss on attrition for the shaped bodies [12-14]. Different amount (10, 15, 25, 35 and 45 wt %) of kaolin binder are mixed mechanically with the corresponding amounts (90, 85, 75, 65 and 55 wt) of the zeolite powder. Samples prepared are shown in Table 1.

Table 1 Samples Identification

	Binder Content wt %				
Binder type	10	15	25	35	45
Kaolin	1*	2	3	4	5

* Sample no.1



Block diagram for the preparation of zeolite-binder agglomerates

Mixing of wet powders was carried out manually using the spatula after the addition of the appropriate amount (28-42 wt %) of water, as a binder plasticizer to the dry mixture in order to assist the mixing .If water content was low, the material would agglomerate poorly or would not agglomerate at all .On the other hand, if water content was high, the particles would not stick together.

Shaping

Shaping process was done after the paste was formed. The paste was placed in a cylindrical cavity of 2 cm inside diameter and 10 cm long and it ended with a die of 2.5 mm diameter. Pellets were obtained when the paste was compressed manually. Very uniform spaghetti shaped paste was ejected and put in a porcelain crucible at room temperature overnight.

Drying

Pellets were dried in an electrical oven (Tecnoformal Ltd., Max. Temp. 250° C) at 120° C for 2 hours [12,14]. This allowed the removal of water from the whole surface of pellets.

Calcination

The cylindrical pellets were calcined using a programmable electrical furnace (Model N2O /H, Max .Temp.1340° C) at 650° C for 2 hours [12, 13, 15], then the calcined pellets were cut into pieces (4-8) mm long.

Physical Properties:

Porosity, Density, and Pore volume

The porosity of the pellet adsorbent particles is determined by using the water impregnation method. The apparent or bulk density can be also determined by using the water impregnation method [16].

The pore volume of voids for the pellet adsorbent particles are calculated in the present work from the amount of absorbed water on the assumption that the water is present as the normal liquid , by using the following equation [17]:

$$V_p = \frac{X_s}{da} \qquad (1)$$

Where: Vp is the pore volume, Xs is the quantity of adsorbed water per unit mass of adsorbent, and da is the density of water.

Adsorption capacity measurement

Adsorption capacity of the prepared samples was tested using the gravimetric Method, which measures the amount of gas or vapor adsorbed by weighing the sample in the system on a balance [9, 18]. The test was carried out in the Al- Basil Company.

The procedure was as follows; an amount of the sample under testing was dried at 100° C using a mantle heater, cooled and weighed. The system was first evacuated then compressed air was allowed to pass through trap 1 containing water inside .Then humid air was passed over the tested sample , present in trap 2 .

Mechanical properties

Crashing Strength

The radial crashing strength of the pellets was done by using a compression force within (0- 220) Newton. The value of the force exerted on the pellet until it crushed was recorded. Ten pellets of each sample were tested and an average value was taken [19].

Attrition Test

The most widely used test for measuring losses by attrition is the ball mill test [16, 20]. The attrition value for each sample is calculated as the percentage loss by the attrition as follows [21]:

$$\text{Weight loss by attrition (\%)} = \frac{\text{Weight of fines (g)}}{\text{Weight of sample (g)}} \times 100 \qquad (2)$$

Results and Discussion

Chemical analysis of zeolite

The chemical composition of zeolite 13X prepared in the present work is given in Table (2) (the analysis was conducted in the Company of Geological Survey and mining). The ratio of SiO_2 to $Al2O_3$ was calculated as mole ratio and was equal to 2.48 .Breck [9], Rabo [22] and Howell [23] had reported that this ratio lies between (2-3) for the same type zeolite 13X .Hence the obtained results were in good agreement with those reported by Breck [9]. Also, there appeared that there were small amounts of impurities like anatase (TiO_2), hematite (Fe_2O_3) periclas (MgO) and CaO.

Table 2 Chemical Analysis of Prepared Zeolite Type 13X

Constituent	Weight (%)
SiO_2	38.54
Al_2O_3	26.42
Na_2O	14.8
CaO	0.636
Fe_2O_3	1.74
MgO	0.083
TiO_2	3.02
K_2O	0.07
L.O.I	12.45

Effect of mixing time and reaction temperature on the synthesis of zeolite 13X content

Fig. 1 shows the effect of 70° C reaction temperature and the mixing time on the preparation of zeolite 13X .At 70° C, the zeolite formation started after 34 hours from the beginning of the reaction, and the content of zeolite 13X increased with increasing time.

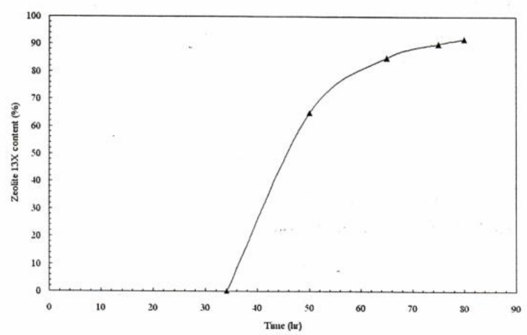


Fig. 1 the Effect of Mixing Time and Reaction Temperature on the Content of Zeolite 13X

The effect of binder content on the optimum H_2O content

The optimum amount of water added to each amount of binder used is so important to control the formation of the pellet particles since water facilitates the cohesion between solid particles. The best amount of added water was obtained by visual inspection of the paste. Fig. 2 shows that the optimal water ratio added to the mixture of zeolite- binder decreases with increasing of kaolin binder. It seemed that this material was saturated with less amount of water .The ability of kaolin to adsorb water is due to its crystals that consists of one dimension and single layer of silicon sheet .

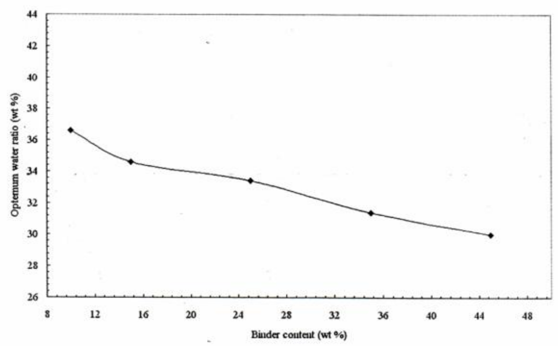


Fig. 2 Optimum Water Content for the Agglomeration of Zeolite 13X

Effect of binder content on porosity, pore volume and density

Fig.s 3 and 4 show the effect of the binder amount on the porosity and pore volume respectively.

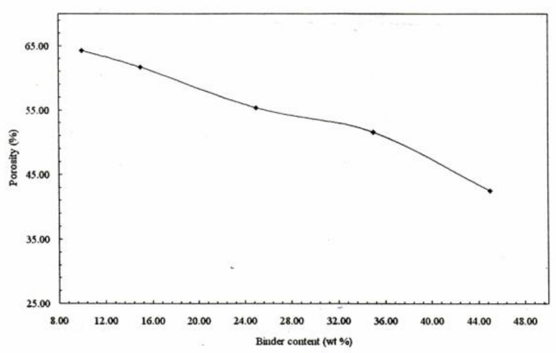


Fig. 3 the Effect of Binder Content on the Porosity of Pellets of Zeolite 13X

It is shown that with increasing the binder amount, the porosity and pore volume decreases .This is due to the decreasing in the porous media (i.e. ., decrease in the quantity of micropores). The decrease in the porous media resulted from the sintering of the fines and the combination of semi- molten impurities during thermal treatment of clay, which causes blockage of the micropores [9].

Fig. 5 shows the bulk density increased as the kaolin binder content increased. This behavior is attributed to the high binding power of binder because zeolite particles will adhere by the binder and arrange themselves to form a dense packing leading to an increase in the bulk density by solid bridges.

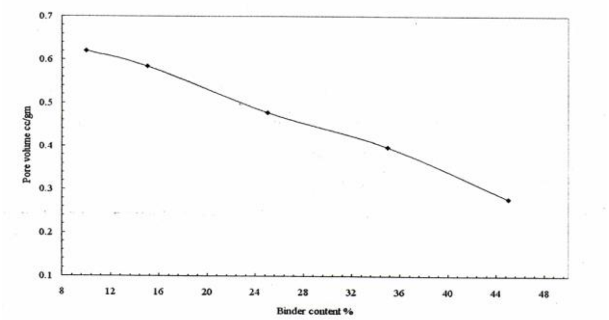


Fig. 4 the Effect of Binder Content on the Pore Volume of Pellets of Zeolite 13X

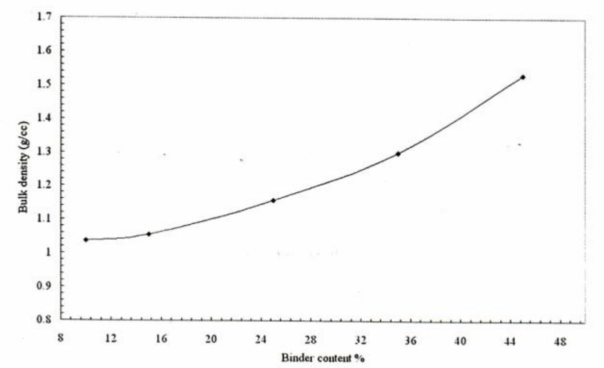


Fig. 5 The Effect of Binder Content on the Apparent Density of Zeolite 13X

Effect of binder content on adsorption capacity

Fig. 6 shows that the adsorption capacity decreased by increasing the binder content.

The higher values of the adsorption capacity were obtained for the pellets of zeolite having the lowest weight percent of kaolin binder (10%). This is attributed to the three dimensional frameworks of zeolite that have high ability to adsorb polar molecules causing them to be high capacitance for water molecules. The decreasing of adsorption capacity with increasing the amount of kaolin binder is attributed to the increasing of sintering due to the increase in the proportions of kaolin, leading to occlude the microporous channels in the structure of pellets. It may be also attributed to the fine colloids of the kaolin, which adhere to the surface of zeolite crystals interrupting the adsorption process [9].

Effect of binder content on mechanical properties

Fig.s 7 and 8 illustrate the effect of kaolin binder amount (weight %) on the crushing strength and percentage weight loss by attrition, respectively. These figures show that with increasing the binder amount in the mixture, the crushing strength of the extrudate particles gradually increases and the percentage loss by attrition decreases.

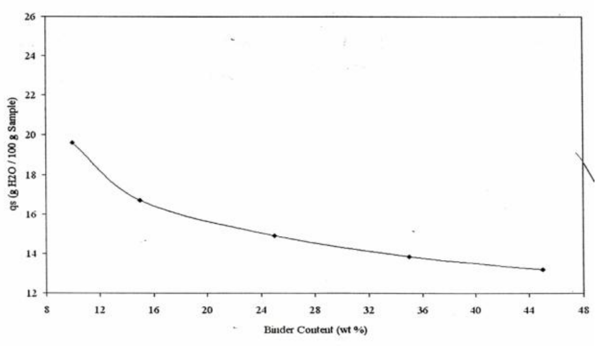


Fig. (6) the Effect of Binder Content on the Adsorption Capacity of Water Vapor on Zeolite 13X

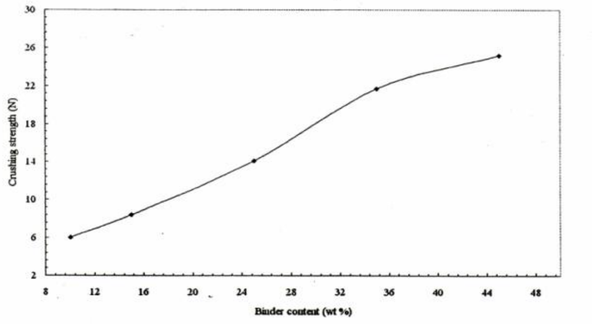


Fig. 7 the Effect of Binder Content on the Crushing Strength of Pellets of Zeolite 13X

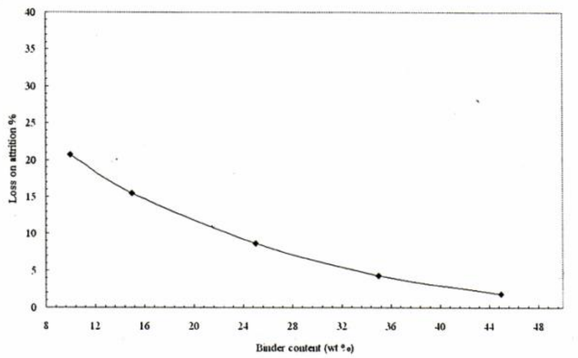


Fig. 8 the Effect of Binder Content on the Attrition Resistance of Pellets of Zeolite 13X

It is clear that kaolin as binders with 45% by weight have the highest strength and the smallest weight loss by attrition .This is attributed to the high binding power of this plastic clay and high cohesion when dried and calcined [18].The plasticity of the kaolin clay is attributed to the proportion of the colloidal gel matter present .It will concentrate the liquid bridges especially at the contact points and on the contact surfaces of the zeolite particles .During drying , the gel concentrated there dry up and form solid mortar bridges .This contributes to increasing the mechanical properties of the extrudates .Also, when the proportion of clay increases, the sintering increases, leading to an increase in the mechanical properties of extrudates because zeolite particles are held together by strong bonds resulting from sintering of the minor kaolin clay particles [10].

Effect of binder on surface area measurement

The surface area of pellets decreased with increasing the kaolin binder content. Table 3 shows the surface area for some selected samples of the prepared zeolite 13X .The surface area measurements were conducted by Ibn-Sina Company.

The increase in the binder content causes the grains to become closer, thus decreasing the surface area of the zeolite pellets.

Table 3 Surface area for some selected samples of prepared zeolite

Binder	Surface Area m^2/g
10%kaolin	530.2
25%kaolin	470.1
35%kaolin	370.0

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