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Synthesis of zeolite 4A via acid–base activation of metakaolinite and its use for water hardness treatment

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ABSTRACT

The synthesis of zeolite 4A from raw kaolinite has been studied using acid–base activation method. The raw kaolinite was first converted to metakaolinite and then dealuminated via acid treatment. Dissolution of the silicate in the unreacted solid was affected with base. The acid solution was blended with aluminum and then mixed with the silicate solution to form gel that allowed to crystallize in hot water bath. The crystallized zeolite 4A formed was separated, washed thoroughly with distilled water, characterized via XRF, XRD, scanning electron microscopy, and tested for water softening.

Keywords: Zeolite 4A; Kaolinite; Metakaolinite; Water softening; Water hardness

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1. Introduction

Zeolites are porous materials with pores within the range of small molecules, and thus are commonly used as molecular sieves to select molecules on the basis of their size [1]. Due to their porosity and open network structures, zeolites are widely used as catalysts, ion-exchangers, and adsorption agents. Zeolite 4A is a low-silica zeolite and widely accepted as a water softening agent in laundry detergents to substitute tripolyphosphate as a binder [2,3].

Zeolite 4A was first synthesized from pure chemicals by fresh precipitation of aluminosilicate gels [4]. This important development inspires many research groups to synthesize other zeolites, to study the complex equilibrium involved in their synthesis, and to optimize synthetic methods for industrial production [5]. However, the growing need for zeolites necessitates further work to utilize cheap materials for their synthesis. Kaolinite is a clay mineral composed of silicate sheets bonded to aluminum oxide/hydroxide layer called gibbsite. It belongs to the sheet aluminosilicate subgroup, the most widely spread mineral of the kaolinite group. With its composition ($Al_2Si_2O_5(OH)_4$) and the ratio of Si-to-Al which is similar to that in zeolite 4A, kaolinite is considered an appropriate source for the preparation of zeolite 4A [6–12]. In Jordan, kaolinite is considered one of the important industrial rocks with almost unlimited estimated reserves. Unfortunately, the Jordanian raw kaolinite is high-silica mineral with Si/Al ratio of about 2. The industrial rocks available in Jordan, as well as, their distribution have been well documented [13].

Herein, we present a new experimental protocol to utilize high-silica raw kaolinite for the production of high quality zeolite 4A. The proposed acid–base

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technique for the zeolite synthesis (which is different from related published protocols that involve direct hydrothermal treatment of metakaolinite) could be applied on purified kaolinite, but it is necessary for the utilization of high-silica raw kaolinite. The synthesized zeolite was characterized via XRD, chemical analysis, scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA).

2. Experimental

The raw kaolinite used in the synthesis of zeolite 4A was obtained from Batn El-Ghoul area, south of Jordan. Pure sodium hydroxide (AppliChem, Germany), analytical grade 98% sulfuric acid (GCC, UK), $Al(OH)_3$, 99% (Vickers, England), and pure triethanolamine (Siegfried, Switzerland) were used as purchased. Calcium standard solution was purchased from Riedel-deHaen. X-ray powder diffraction spectra were measured using a Shimadzu-XRD-6000 with nickel filter and copper X-ray radiation (Cu-Kα, $\lambda = 1.5406$ Å) at a scan rate of 2˚/min. TGA was conducted using a Netzsch Sta 409 PC instrument under N_2 gas purging and at a heating rate of 20˚C per minute upto 1,000˚C. The morphologies of the solid samples were monitored by SEM using an FEI-FEG INSPEC F50 instrument with secondary electron detector. Chemical analyses were determined using x-ray fluorescence spectrometer (Shimadzu-XRF-1800). The calcium ion concentrations were determined via atomic absorption spectrometer (Varian spectrAA 250 plus).

2.1. Metakaolinite

The kaolinite was crushed, dried at 110˚C, ground, and sieved. The fraction of particles less than 75 μm in size was collected and stored in a dry place. Samples of kaolinite were placed in nickel crucibles and calcined at 600˚C for 4 h to transform kaolinite to metakaolinite.

2.2. Synthesis of zeolite 4A

A sample of metakaolinite (25.0 g) was mixed with 3.0 M sulfuric acid (75 mL). The mixture was heated at 90˚C with stirring (magnetic stirrer) or shaking for 8 h. After the reaction time had elapsed, the mixture was allowed to cool and then filtered. The solid residue (dealuminated kaolinite) was washed with deionized water (2 × 30 mL) and dried at 110˚C. To the filtrate was added a sample of $Al(OH)_3$ (3.2 g) to compensate for the aluminum-to-silicon ratio in the starting raw kaolinite. Iron ions were complexed via the addition of triethanolamine (4.1 g). The solution was kept aside for further workup.

The solid dealuminated kaolinite was treated with 8.0 M sodium hydroxide solution (200 mL). The mixture was stirred at room temperature for 6 h, filtered, and the solid residue was washed with deionized water (2 × 30 mL). The solution containing the aluminum salt was slowly added to the solution containing silica salt with strong stirring. By the end of addition, the solution became turbid due to the formation of aluminosilicate gel. The mixture was placed in a water bath at 80˚C for 6 h. After the zeolitization time has elapsed, the white crystalline zeolite was washed with deionized water (5 × 100 mL) and dried at 110˚C for 2 h.

2.3. Cation exchange capacity of the prepared zeolite 4A

A sample of the synthesized zeolite (1.00 g) was mixed with 100 mL of 0.30 M solution of $CaCl_2$ in a polyethylene bottle and was stirred for 20 min. The mixture was centrifuged and the supernatant liquid was decanted. The procedure was repeated three times. The zeolite samples were then washed with isopropyl alcohol (3 × 30 mL) and dried at 110˚C. A sample of the Ca-exchanged zeolite (1.00 g) was mixed with 1.00 M ammonium chloride solution (100.0 mL) and was gently stirred for 20 min. The procedure was repeated three times. The supernatant ammonium chloride solution was collected and diluted to 500 mL and titrated with standard solution of EDTA.

2.4. Treatment of hard water

The water softening capacity of the synthesized zeolite was evaluated via its ability to remove Ca^{2+} ions from aqueous solutions under variable conditions that include Ca^{2+} concentration, time of contact, and mass of zeolite. A series of Ca^{2+} solutions with the concentrations of 10, 20, 40, 60, 80, 100, 120 ppm has been prepared from a 1,000 ppm stock solution. The concentration of calcium in the solutions (before and after treatment with zeolite) was determined by atomic absorption spectrophotometer.

3. Results and discussion

The chemical analysis of Butn Al-Ghoul kaolinite clay and synthesized zeolite 4A are given in Table 1. The results show a significant change in the ratio of SiO_2-to-Al_2O_3 between raw kaolinite and the

Table 1
Chemical analyses of raw kaolinite and synthesized zeolite 4A

Constituents	Raw kaolinite (wt.%)	Synthesized zeolite 4A (wt.%)
SiO_2	57.78	35.24
Al_2O_3	25.27	27.82
Fe_2O_3	1.82	0.07
TiO_2	1.58	<0.01
Na_2O	<0.01	18.75
K_2O	<0.01	0.05
MgO	<0.01	<0.01
CaO	<0.01	<0.01
P_2O_5	0.02	<0.01
LOI*	12.93	18.1

*Loss on ignition.

synthesized zeolite. It also shows the noticeable decrease of most impurity metal ions especially iron and titanium ions in the synthesized zeolite. The low iron content of the synthesized zeolite is reflected on its brightness which is an important parameter in detergent industry.

The transformation of kaolinite into zeolite was affected by a number of factors. An important factor is the calcination temperature of kaolinite which is necessary for its transformation into the metastable phase called metakaolinite. This transformation is clearly seen in the TGA/DTA of raw kaolinite (Fig. 1). The DTA curve shows a strong endothermic peak at about 550˚C due to dehydroxylation of kaolinite (loss of kaolinite structural water), which resulted in a mass loss of about 10%.

$$\underset{\text{kaolinite}}{2Al_2Si_2O_5(OH)_4} \rightarrow \underset{\text{metakaolinite}}{2Al_2Si_2O_7} + 4H_2O$$

The XRD patterns of the starting raw kaolinite and metakaolinite are shown in Fig. 2.

The formed metakaolinite phase is easily attacked by both acids and bases.

The effect of the calcination temperature and time of calcination on the yield of zeolite were studied and best results were attained when the kaolinite was heated at 600˚C for 4 h. Another important factor is the molar ratio of SiO_2/Al_2O_3 in the raw kaolinite investigated, which is about 3.9. This ratio is far from the ratio of 2.0 required for zeolite 4A synthesis. Therefore, the ratio was amended by the addition of appropriate amount of aluminum salt. Based on Si-to-Al ratio in raw kaolinite and the final unreacted residue (which is mainly quartz as shown by its XRD spectrum), aluminum hydroxide (0.13 g/g metakaolinite) or an equivalent amount of $Al_2(SO_4)_3 \cdot 16H_2O$ was added to compensate for low aluminum content.

Reactions of kaolinite with inorganic acids at elevated temperatures have been previously investigated [14–16]. Although the results indicate that sulfuric acid is the best among other inorganic acids tested, the reactivity of kaolinite towards sulfuric acid remains low. In this study, the dealumination was carried out

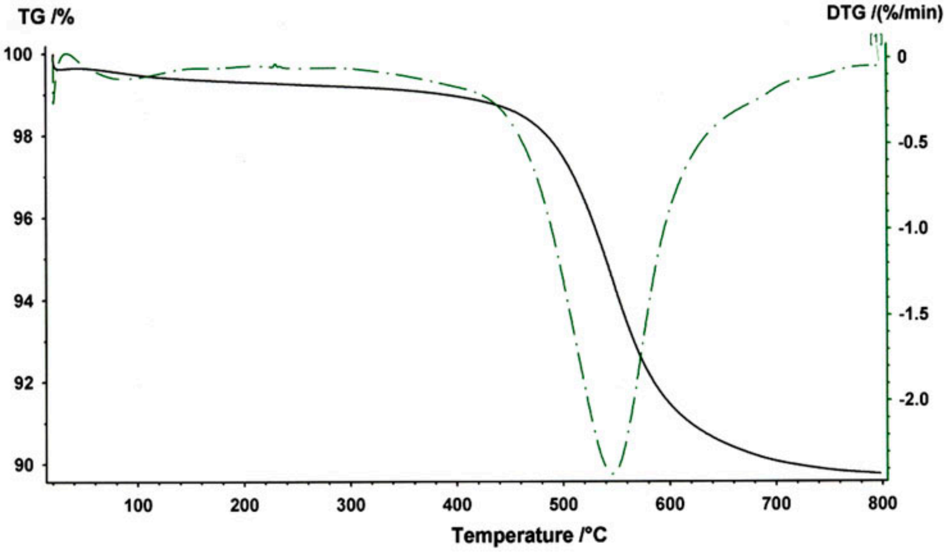

Fig. 1. TGA/DTA curve of raw kaolinite.

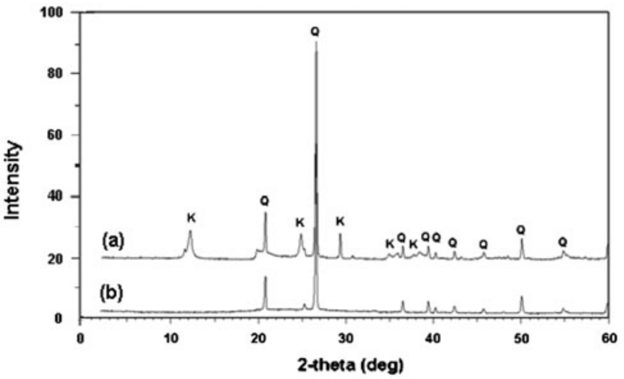

Fig. 2. XRD patterns of (a) raw kaolinite (b) metakaolinite (K = kaolinite, Q = quartz).

on the metakaolinite at 90°C. The reaction between metakaolinite and sulfuric acid could be viewed as:

$$2Al_2Si_2O_7 + 6H_2SO_4 \rightarrow 2Al_2(SO_4)_{3(aq)} + (\text{amorphous silica and quartz})_{(s)}$$

A series of experiments were conducted to determine the effect of sulfuric acid concentration, the amount of sulfuric acid, the temperature, and the time of stirring (or shaking) on the yield of zeolite 4A. The optimum conditions were reported in the experimental section.

The aluminum sulfate produced in the dealumination process, in addition to the amount of aluminum hydroxide added externally, represents the sources of aluminum necessary for the synthesis of zeolite 4A. The iron ions in the solution were masked by the addition of triethanol amine.

The residue obtained after dealumination was treated with aqueous sodium hydroxide to break down the weakened silicate structure into sodium silicates. Upon mixing the solution containing the aluminum salt with the silicate solution an aluminosilicate gel was formed. This gel was aged in a warm water bath for crystallization.

Most of the previous synthetic methods are mainly based on the hydrothermal treatment of metakaolinite with NaOH, but with no assurance for the complete transformation of metakaolinite into zeolite. As though, they result in zeolite products with varying amounts of unzeolitic impurities. An important aspect of this work is the effective dissolution of natural raw kaolinite into two separate solutions containing the aluminum and silicate precursors necessary for the formation of zeolite 4A. With that, the synthetic procedure becomes almost similar to that of using pure chemicals, although we are using raw natural aluminosilicate clay.

3.1. Characterization of zeolite 4A

The XRD patterns of the starting raw kaolinite and metakaolinite are shown in Fig. 2. The pattern for raw kaolinite indicates the presence of kaolinitic phase with appreciable amounts of quartz. This suggests the need for an efficient method for the removal of quartz to obtain pure synthetic zeolite. Thermal treatment of kaolinite results in the collapse of the kaolinite crystalline structure as clearly shown by the disappearance of all kaolinite peaks (Fig. 2). A representative XRD pattern of the synthesized zeolite 4A and a calculated XRD pattern of zeolite 4A [17] are shown in Figs. 3 and 4, respectively. The position and intensity of the peaks in the diffraction pattern are unique features of the crystalline part of zeolite 4A (ICDD # 00-043-0142)

The crystal morphology and particle sizes of the raw kaolinite and the synthesized zeolite 4A are investigated from scanning electron micrographs (SEM) as shown in Figs. 5 and 6, respectively. The SEM of zeolite 4A reveals the presence of chamfered cubic particles with size ranging from 2 to 5 micron. The amount of amorphous material is negligible indicating a high degree of crystallization.

The calcium binding capacity (CBC) was determined by exchanging Na^+ by Ca^{2+} using 0.3 M calcium chloride solution. It has been observed that the CBC of the zeolite increases with increasing the concentration of calcium ion in solution and the time of contact. The calculated CBC at conditions specified in the experimental part is 1.7 mmol Ca/g zeolite.

3.2. Treatment of hard water

The synthesized zeolite 4A was tested for the removal of Ca^{2+} ions from solutions prepared with different Ca^{2+} concentrations. Three factors affecting

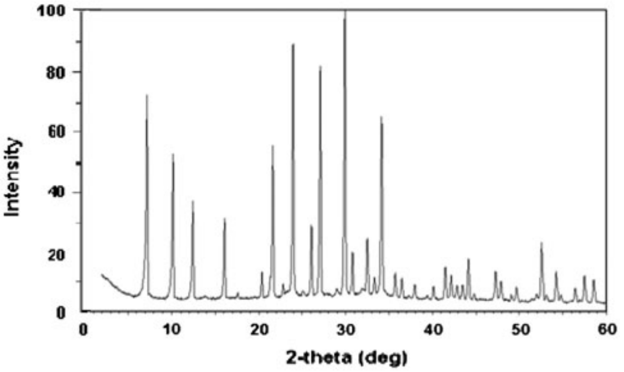

Fig. 3. XRD patterns of synthesized zeolite 4A.

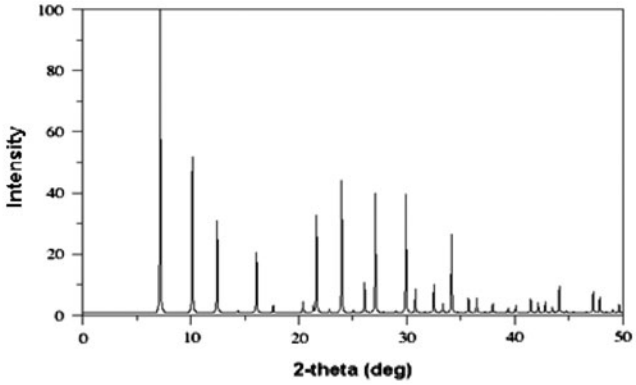

Fig. 4. Calculated XRD patterns of zeolite 4A.

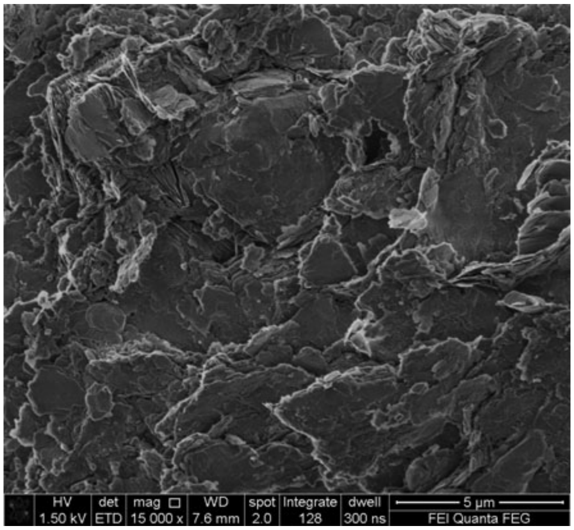

Fig. 5. SEM image of raw kaolinite.

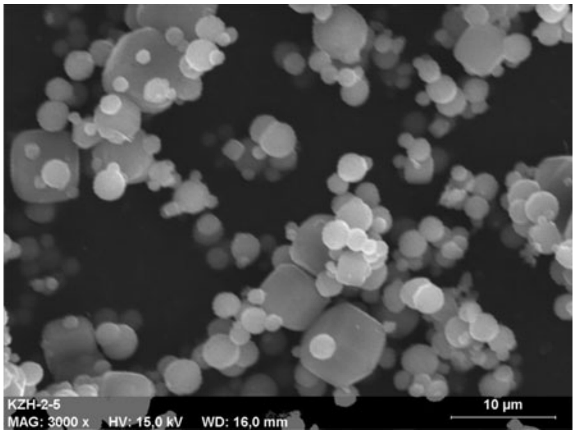

Fig. 6. SEM image of synthesized zeolite 4A.

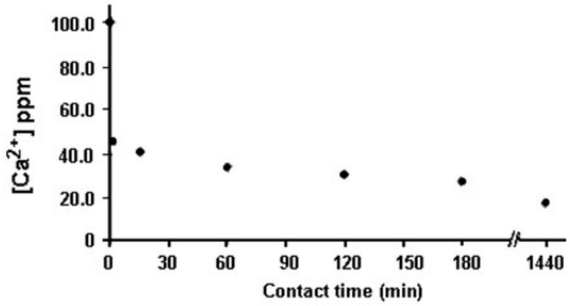

Fig. 7. Effect of time on the uptake of Ca^{2+} ions by zeolite 4A; initial $[Ca^{2+}] = 100$ ppm, mass of zelite = 0.050 g.

this process were studied: contact time, Ca^{2+} concentration, and mass of zeolite 4A.

3.2.1. *Contact time effect*

In view of the difficult exchange of Na^{+} with Ca^{2+} [18], the uptake of Ca^{2+} ions was studied at short intervals and then left for a long period of time. The results (Fig. 7) show a sharp drop in the concentration of Ca^{2+} ions to less than half its initial concentration within the first minute, followed by slow decrease till a concentration of 15.7 ppm after 24 h.

3.2.2. *Effect of Ca^{2+} concentrations*

Solutions of Ca^{2+} ions with initial concentrations in the range 80–120 ppm containing the zeolite were shaken at room temperature for 2 h. The results (Fig. 8) show a constant decrease in the concentration of Ca^{2+} ions by about 70 ppm, irrespective of its initial concentration.

3.2.3. *Effect of mass of zeolite*

Results for the effect of mass of zeolite on the uptake of Ca^{2+} ions (Fig. 9) show a decrease in the

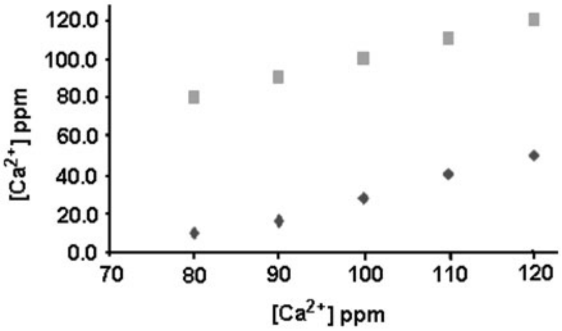

Fig. 8. Effect of Ca^{2+} concentration on the uptake of zeolite 4A; mass of zelite = 0.050 g.

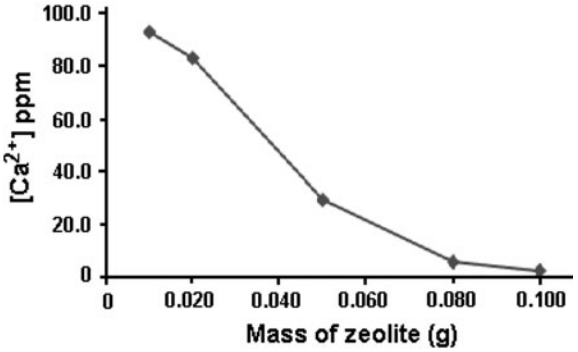

Fig. 9. Effect of zeolite mass on the uptake of Ca^{2+} ions by zeolite 4A; initial $[Ca^{2+}] = 100$ ppm.

concentration of calcium ions with increasing the mass of zeolite used, and at a mass of 0.10 g the concentration of calcium ions drops to less than 2 ppm. Analysis of these data gives an idea about the optimum amount of zeolite that should be used for water softening. It also shows that the capacity of the zeolite for uptake of calcium ions is about 24 mg calcium/g zeolite.

4. Conclusion

In the present work a new method for the synthesis of zeolite 4A from high-silica raw kaolinite has been introduced. The method involves transformation of raw kaolinite into metakaolinite, which was then treated with acid followed by a base. The synthesized zeolite 4A is characterized with its crystallinity and water softening ability.

Acknowledgments

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