

Removal of water hardness using zeolite synthesized from Ethiopian kaolin by hydrothermal method

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Abstract

The use of low cost materials in zeolite synthesis becomes an area of important interest in water softening. This research is aimed to utilize kaolin for zeolite synthesis with hydrothermal method. Mechanical, thermal chemical treatments of raw kaolin were used for zeolite synthesis. Fourier Transform Infrared Spectrometry (FTIR), AAS, XRD, surface area (BET), differential scanning calorimetry and TGA were used to characterize kaolin and zeolite and UV-VIS/spectrometer were used for adsorption capacity of ion exchange. Effect of contact time, pH solution and temperature of the solution were studied for batch experiments. XRD values indicated that the prepared material is showed as fully crystalline and primarily amorphous. Before and after hardness removal sample transmittance percentage intensity showed a wide range of difference. From this study, it can be deduced that Zeolite can be used as a low cost water softening agent. At room temperature, the residue is well with calcium and badly with magnesium, whereas affinity toward Mg ions increases to acceptable levels at 60 °C. The cation exchange capacity of zeolite was found to be dependent on contact time. The batch experiments of removing Ca²⁺ and Mg²⁺ show that the adsorption capacity of zeolite in calcium ion is higher affinity than magnesium ion.

Key words: cation exchange, hydrothermal, kaolin, Na -X zeolite, synthesized zeolite

INTRODUCTION

Zeolite is the universal type of synthetic zeolite in the area of industry application. This is due to its large ion exchange capacity, mechanical strength and particular crystal shape. Besides, it is environmentally safe with almost zero loading of harmful effect on the environment (Ajayi *et al.* 2010). Zeolites are, traditionally, known as advanced materials resulting from crystalline silicates and aluminosilicates linked through oxygen atoms, producing a three dimensional network within containing channels and cavities of molecular dimensions (Shams & Mirmohammadi 2007). With the application of the inherent characteristics of molecular pore size, superfluously extended surface area and corresponding pore volume per unit mass, constituent ions charge effects and chemical inertness of Zeolites (Chandrasekhar 1995). Natural Kaolin is the most common mineral of a group of hydrous aluminum silicate, which result from the breaking of aluminum-rich silicate rock, such as feldspar and nephalin syenite, either through weathering or hydrothermal activity (Mohammed & Ameen 2000). Kaolin when pure corresponds to the formula Al₂Si₂O₅ (OH)₄ and occurs in white clay-like masses. Kaolin has been identified as a very important group of clay mineral, which is copiously utilized as an industrial mineral commodity (Aveen & Kafia 2014). The various physical attributes of kaolin mineral have made it useful in various ways industrially and these include paints, ceramics, and rubber, paper, and petroleum and glass industries (Ríos *et al.* 2012).

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Zeolites are micro porous crystalline solids with well defined structure, consisting of a three-dimensional network of SiO_4 and AlO_4 tetrahedral linked together by common oxygen atoms (Apell & Boyer 2010).

Nowadays, the increasing interest in zeolite synthesis from low-cost materials has promoted the development of various studies on their conversion into zeolitic materials, giving rise to an extensive advantage particularly with regards to high quality drinking water and removal of pollutants from industrial, agricultural and municipal wastewater (Kesraoui-Ouki *et al.* 1994).

Kaolin possesses the Si-O or Al-O octahedral and tetrahedral sheets which are inactive to modification or activation. This means that it is difficult to directly synthesize Zeolites and the kaolin must be pre-activated to change this inert structure (Shukur 2015). The most effective way to activate such natural clay is to thermally transform the inert phase into the active phase at elevated temperatures in the presence of sodium hydroxide. Under the basic environment the inert skeletal structure of kaolin was converted into activated silicate and aluminates (Ukwuoma 2008).

The synthesis of zeolite from natural kaolin involves two basic steps: 1) metakaolinization, which is calcinations of the raw kaolin at high temperature to change chemically stable kaolin into very reactive and amorphous material, metakaolin; and 2) hydrothermal treatment of the calcined kaolin with sodium hydroxide (Atta *et al.* 2007).

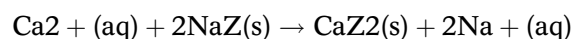
Zeolites have huge potential as a cost-effective, environmental-friendly solution that can improve the efficiency in various applications (Rahman *et al.* 2009). This is due to its large ion exchange capacity, and strength particular crystal shape (Lijalem 2015). Zeolites are hydrated aluminosilicates with a precise geometry of crystal structure and pores of uniform size, which form channels of molecular dimensions with high capacity exchange cations from their structure (João *et al.* 1991). Zeolites have a satisfactory capacity adsorption to remove certain metal ions presents in solutions, and therefore has potential to be used as an adsorbent in the treatment of water and other application (Wang *et al.* 2003).

At present, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes (Breck 1974; Szoztak 1998). However, the preparation of synthetic zeolites from chemical sources of silica and alumina is expensive. Such costs may be reduced by the use of clay minerals, volcanic glasses (perlite and pumice), rice husks, diatoms, fly ash or paper sludge ash as starting materials (Saija *et al.* 1983; Querol *et al.* 1997; Tanaka *et al.* 2004; Adamczyk & Bialecka 2005; Walek *et al.* 2008; Wang *et al.* 2008).

Water hardness problem is reported to exist in various places around the world. Among several known forms of pollution, water pollution is great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms (Degremont 1991). Worldwide, but its quality is constantly being change by various human activities which amount of money is spent yearly to ensure that water is softened (minerals are removed) to avoid its negative impacts such as degrading soaps and precipitate deposition on faucets changes physicochemical properties of water (Hossein *et al.* 2008). Water hardness is determined by measuring the total concentration of magnesium and calcium in a water source. Water hardness impacts ecological, fish cultures as well as many other species that rely on a steady calcium carbonate concentration (Wang & Lin 2009). Health request ions regarding drinking hard water has also begun to emerge. The World Health Organization states that hard water may lead to cardiovascular disease (WHO 1996). Different industries use water as a main source for processes, and for steam generation in the boiler. The textile industry, paper industry, sugar industry, dyeing industry, and beer industries are the main sectors that use water for steam generation. However, direct use of hard water (feed to the boiler) reduces the efficiency of the boiler to produce a high capacity of steam due to the presence of metals ions associated with water hardness in the water by forming scale and sludge, priming and foaming, and boiler corrosion (Hammer & Hammer 2005). Inadequate intakes of calcium have been associated with increased risks of osteoporosis, nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity (Ji-Suk *et al.* 2007).

Calcium and magnesium are the hard water minerals resulting in scaling problems and failures in pipelines of boilers and heat transfer equipment (Siger & Bergaut 1995). Hardness of water due to calcium and magnesium ions can be reduced by several methods, i.e., electro-dionization (Ji-Suk *et al.* 2007), electro membrane processes, capacitive deionization membrane and fluidized pellet reactors, ion exchange process and adsorption. The use of low cost sorbents for the adsorption process is a promising technique (Apell & Boyer 2010). Ion exchange and adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural sorbents such as clay materials, zeolite, biomass, perlite and diatomite (Baybars *et al.* 2012). In this regard synthesis Zeolites have a great interest used as packing material in subsurface reactive bed reactors designed to remove hard water minerals from surface and ground for purpose of industrial (Barros *et al.* 2003).

In the principle of cation exchange, oxygen is bonded together to form a huge macro anion similar in structure to a macro molecule such as zeolite, NaAlSiO_4 (Lijalem 2015). The negative charge of an ion is balanced by Na^+ ions trapped in holes in an ionic lattice (Aveen & Kafia 2014). Nothing will happen when pure water is passed through the zeolite because Na^+ cannot leave the crystalline lattice because in that case there would be an imbalance in charges. When hard water is passed through the zeolite some of the Na^+ ions migrate out of the lattice, being replaced by an equivalent number of Ca^+ ions (Biskup & Subotic 2000).



Since natural zeolites are environmentally and economically acceptable hydrated aluminosilicate materials with exceptional ion-exchange and sorption properties we are looking into synthesizing this adsorbent for hardness removal. Their effectiveness in different technological processes depends on their physical-chemical properties that are tightly connected to their geological deposits.

Therefore, the objective of this work is to synthesize zeolite from Ethiopian kaolin and characterize both the product and adsorption of Ca^{2+} and Mg^{2+} ion from aqueous solution using zeolite and raw kaolin. Other influences of adsorption parameter such as contact time, pH of solution and temperature effects were investigated.

METHODOLOGY

Raw material and chemicals

Kaolin was used for synthesised zeolite as source of silicon and aluminum for metal adsorption. 98% concentrated sulfuric acid was used to split it into its silica and alumina components. Anhydrous sodium hydroxide pellets (NaOH) were used as the activating agent. An electric furnace was used for calcinating natural kaolin at 750 °C for 3 hours. A digital balance (Sartorius with 0.01 mg sensitivity) was used for weighing of raw materials and chemicals. A sieve was used to determine the particle size of kaolinite clay powder. A jaw crusher (BB51) was used for crushing kaolinite clay to <0.075 mm and an oven dryer (PH-030A) was used to dry samples at a temperature of 105 °C for 24 hrs.

Instrumentation

An electric furnace was used for calcination of the raw kaolin at 750 °C for 3 hours. A Brunauer-Emmett-Teller (BET) machine was used to analyse surface area and pore size. X-ray diffraction (XRD) –700 SHIMADZU Technology was used to crystalize and purify the zeolite. A JASCO MODEL 4100 Fourier Transformed Infrared Radiation (FTIR) Spectrometer was used to measure the absorption of IR radiation by zeolite as the atoms vibrate about their bond. Atomic absorption spectrometry (AAS) was used for elemental composition analysis. A UV/Vis spectrometer was used

for determination of the adsorption/capacity of ion exchange with hardness causing metal. A differential scanning calorimeter (DSC) - 8000 and ATAT2012 Thermo gravimeter analyzer was used for thermal analysis of synthesized zeolite and kaolin.

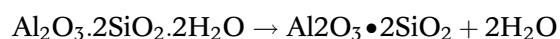
Zeolite synthesis

Beneficiation

The raw kaolin clay was wet beneficiated in order to purify it from physically and chemically combined impurities such as metallic oxide, soluble salts and impurities (quartz, pebbles, plant remains and grits) from the clay.

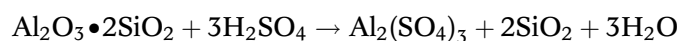
Calcination (metakaolinization)

The beneficiated and ground clay was calcined at 750 °C for 3 hr using a ceramic crucible container in a chamber furnace for processing into metakaolin. The essence is to dehydroxylate the beneficiated kaolin to form an activated amorphous material called metakaolin.



Splitting (delamination)

The metakaolin was completely split into its silica and alumina components by complete delamination of metakaolin in excess acid. The dealumination process was carried out using 98 wt. % concentrated sulfuric acid at room temperature.



Gel formation

Different concentrations of sodium hydroxide was dissolved in distilled water in the reaction vessel, and then metakaolin was added to the sodium hydroxide solution gradually. As can be seen from [Figure 2](#), the bright, pure gel-like solution has been formed.

- 1) 2, 2.5, 3 3.5 M NaOH
- 2) Mixing + Aging

Stirring at temp, 60, 70, 80, and 90 °C with in 30, 60, 90, and 120 min.

Crystallization/post treatment

The gel was crystallized at 100 °C for 24 hrs. After the crystallization, the resulting zeolite crystal was filtered and washed with demonized water until the pH was less than 10.

Characterization of kaolin and Zeolite

The FTIR spectra were used for qualitative characterization of surface functional groups of the kaolin. Functional groups present in the activated and raw kaolinite clay were confirmed before and after adsorption.

The range of infrared is 12,800–10 cm⁻¹ and can be divided into near-infrared (12,800–4,000 cm), mid infrared (4,000–200 cm⁻¹) and far-infrared (50–1,000 cm⁻¹). Before and after hardness removal,

zeolite samples were mixed with paraffin oil. The samples were then ground, desorbed and pressed to obtain IR transparent pellets. The absorbance FT-IR spectra of the samples were recorded using an FT-IR Spectrum JASCO model 4100 spectrophotometer. The spectra were collected within a scanning range of 450–4,000 cm^{-1} . The FT-IR was first calibrated for background signal scanning with a control sample of pure KBr and then the experimental samples were scanned. Powder X-ray diffraction patterns of the sample were measured using Cu Ka radiation by XRD – 700 SHIMADZU. Such prepared material was identified by measuring the 2θ values. Samples were scanned for 2θ ranging from 10 to 80°. Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature and is a very informative method in physical characterization of a compound. Differential scanning calorimetry has been used to study the thermal effects of a zeolite Na-X sample. A STAT2012 thermogravimetric analyzer was used for the thermal studies from the Bahir Dar Institute of Technology chemical analysis and characterization research grade laboratory. The TG/DTA measurements were carried out on BJHENVEN analysis system software from room temperature up to 1,000 °C in a nitrogen atmosphere, flow rate approximately 15 mL/min. Lithium metborate fusion, HF attack, gravimetric and AAS analytical methods, from the geological survey of Ethiopia, were used for quantitative analysis of basic oxide compositions. Digestion of samples with hydrofluoric and nitric acids (total decomposition) and fusion with lithium metaborate at 950 °C were employed. Elemental concentrations in milligram per liter in the solution have been converted in to weight percentage oxide composition as shown in the equation below.

$$\text{Elements (wt \%)} = \frac{\left(\frac{\text{mg}}{\text{l}}\right) * (\text{dilution factor}) * 0.01}{\text{grams of sample}}$$

The total surface area of synthesized powder zeolite Na-X was measured using the standard volumetric method by nitrogen adsorption and application of the BET equation by means of a Nova 4000 BET instrument. The resulting BET equation is expressed as:

$$\frac{1}{Q \times \left(\frac{P_0}{P} - 1\right)} = \frac{1}{Q_m \times C} + \frac{C-1}{Q_m \times C} \times \frac{P}{P_0}$$

P and P_0 are the equilibrium and the saturation pressure of adsorbate at the temperature of adsorption, Q is the adsorbed gas quantity at STP, and Q_m is the monolayer adsorbed gas quantity at STP. C is the BET constant.

A pH meter (ELE international) was used to control the pH of the solution during the experiments. A UV/Vis spectrometer was used to study the adsorption capacity of ion exchange.

Isotherm study

The adsorption measurements were investigated in batch experiments. The effect of contact time on adsorption efficiency by synthesized zeolite was investigated in the range of 30–240 minutes, having an initial concentration of 1,000 mg/l. The effect of adsorption temperature was also investigated at a temperature of 298, 303 and 313 K. Adsorption kinetics were studied using an initial concentration of 1,000 mg/l and an initial dosage of 2.5 g/50 ml. The adsorption isotherms were studied by taking different initial concentrations of Ca and Mg ions in solution. The amount of Ca and Mg ions adsorbed per unit mass of synthesis zeolite, which is the adsorbate phase, was determined by the following equation:

$$\text{Adsorption capacity} = Q_e = \frac{C_i - C_e}{m} V$$

where Q_e is the maximum adsorption capacity in mg/g, C_0 is initial concentration and C_e is the concentration of at equilibrium. Ca and Mg ion solution in mg/l, V is the volume of Ca and Mg solution in ml and m is the mass of adsorbate of synthesis zeolite in g.

The percentage of adsorption of metals ions was determined using the following equation:

$$\text{removal}(\%) = \frac{C_i - C_e}{C_i} * 10$$

The formation of a monolayer adsorbate on the adsorbent was represented by the Langmuir Sorption isotherm model. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases.

$$Q_e = \frac{Q_m k C_e}{1 + k C_e}$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{K Q_m}$$

where Q_e is the equilibrium amount of adsorbate (mg/g), C_e the equilibrium concentration of adsorbant (mg/L), Q_m and k are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption respectively. The values of Q_m (mg g⁻¹) and k (l mg⁻¹) can be determined from the linear plot of C_e/q_e against C_e .

RESULT AND DISCUSSION

Kaolin needs to be thermally activated in order to become reactive within the reaction mixture. This is promptly achieved by means of calcination, which provides enough energy to promote the required changes in the thermodynamic conditions. This process of activation results in drastic changes in the kaolin structure, drying it to lose its crystallinity. In the kaolin structure the Al atoms are octahedral coordinated with two vertex oxygen from the SiO₄ tetrahedral layer to an (OH) group from one side and three (OH) groups from the parallel hydroxyl layer from the other side. In the metakaolin, on the other hand, the Al atoms lose their initial configuration and are tetrahedrally coordinated. This scenario is closer to the zeolite structure than that observed in the kaolin structure; thus metakaolin is suitable as raw material for zeolite synthesis.

Characterization of kaolin and zeolite

Fourier transforms infrared spectroscopy (FTIR) analysis

The FTIR spectra of the natural kaolin and synthesis zeolite, in the lattice region of 400–4,000 cm⁻¹ was taken to identify the existence of some functional group which might be responsible for adsorption process. From Figure 1(a) as shown clearly, natural kaolin indicates a number of adsorption results which displays that the kaolin contains complex different groups. From the figure showed, the main bonds observed were stretching the OH⁻ group at 3,464 cm⁻¹ and 3,449 cm⁻¹. The broad band observed at 1,410 cm⁻¹ was assigned as the Si-O in the molecule of SiO₄. The other vibration band was seen at 1,060 cm⁻¹ attributed to the Al-OH group. The bands recorded at 662 cm⁻¹ and 604 cm⁻¹ were symmetrical stretching of Si-O. The band for absorption value at 572 cm⁻¹ was assigned for Si-O-Al, in which the Al is found in octahedral coordination.

In the same way, Figure 1(b) shows the synthesis zeolite main adsorption results at 3,436 cm⁻¹ that is OH⁻ stretching. The band that at 1,384 cm⁻¹ confirms the Si-O bond. The bands at 637 cm⁻¹ and 616 cm⁻¹ were symmetrical stretching of Si-O. The synthesized zeolite (Figure 1(b)) shows a sharp peak with high intensity at 1,123.8 cm⁻¹. This strong vibration is assigned to asymmetric stretching vibration (1,250–950 cm⁻¹) which represents the presence of substituted Al atoms in the tetrahedral forms of silica frameworks.

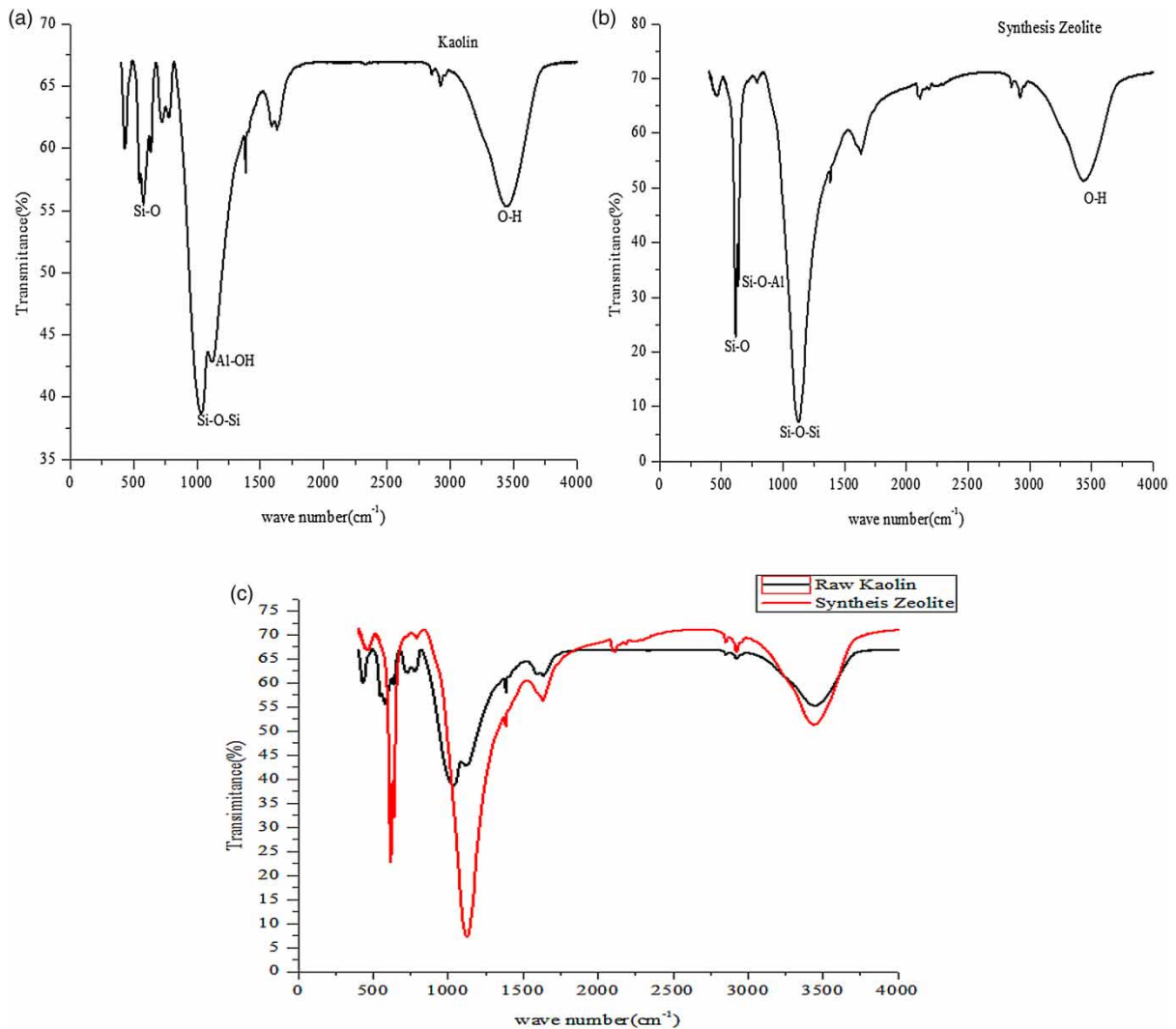


Figure 1 | FTIR spectra analysis (a) raw natural kaolin, (b) synthesis zeolite, (c) zeolite with kaolin.

The FTIR spectrum (Figure 1(c)) shows that the synthesis zeolite high sharp peak, which has a higher absorbance value than the raw kaolin. This indicated the synthesized zeolite is free from any contaminants or trace elements. However, in natural kaolin, some other minerals and oxides may be present before treatment and the absorbance value of natural kaolin is lower than the synthesized zeolite. Synthesized zeolite is therefore preferred over natural kaolin for adsorption.

Powder X-Ray diffraction (XRD) analysis

A XRD diffractogram revealed structural defects in kaolin because of variability in the peak positions and modulation of their intensities in kaolin XRD patterns. XRD identification of order/disorder is challenging because of overlapping peaks and interferences in kaolin (Peter *et al.* 2015).

The sodium-based (Na-x) synthesized zeolite has three major intense diffraction peaks at 2θ value of 19.04°, 32.12°, and 33.84°, and less intense results observed at 2θ of 67.48°, 61.24°, 18.74°, 49.95°, 78.78° and calcined kaolin observed amorphous metakaolin but a small diffraction peaks at 2θ value of 21.03, 24.11, 25.133, 27.95, 27.91 is observed as shown in Figure 2. The XRD pattern also indicates that the peak in the range of $2\theta = 20\text{--}35^\circ$ which is an indicative of degrees of crystalline which is fundamental properties of zeolite. This indicates that most of the zeolite amorphous material was being crystallized.

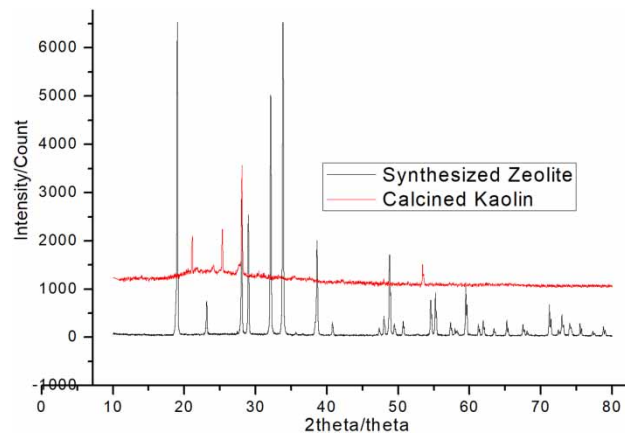


Figure 2 | XRD patterns of synthesized zeolite and calcined (750 °C) kaolin.

Surface area analysis

A considerable amount of empirical data supports the idea that complexation can also result in substantial increases in metal adsorption above that observed in the absence of metal binding ligands. A substantial enhancement of Ca (II) adsorption onto the surface of γ - Al_2O_3 in the presence of small amounts of organic solutes was reported by (Elliott & Huang 1979). The surface complexes have an effect for the adsorption of metal ions which corresponds to the surface area of the adsorbent. From N_2 adsorption/desorption isotherms, the surface area have been determined by using the BET (90.20 m^2/g) and Langmuir (99.32 m^2/g) which shows a promising result for zeolite.

Chemical composition analyses

The chemical composition of synthesized zeolite was determined by AAS as summarized in Table 1. The common chemical composition analysis detected is the basic components of the kaolin mineral: aluminum oxide, silicon oxide and loss on ignition (LoI). As can be seen from oxide composition analysis of the synthesis zeolite, the silicon oxide percent by weight is much higher than the others and the impurity responsible metal oxides (Fe_2O_3 , TiO_2 ) are low in percent by weight. This shows that the synthesized zeolite is pure and has a potential capacity for hardness adsorption. From the result, Na-X zeolite prepared by the modified hydrothermal crystallization method has a high molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

Table 1 | Quantitative oxide analysis of synthesized zeolite

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LoI
Weight%	57.36	24.72	2.32	1.68	1.34	3.46	5.28	<0.01	0.29	0.16	2.37	1.89
Si/Al	2.32											

Thermographic analysis of zeolite and kaolin

Differential scanning calorimetry (DSC) has been used to study the thermal effects during adsorption of Na-X samples. The dependence of the water uptake on temperature has been studied with a powdered sample. The zeolite synthesized was found to be structurally stable up to 480 °C (Figure 3(a)) and a new spinel-like phase was formed above this temperature. From this it can be deduced that synthesized zeolite from Ethiopian kaolin by the hydrothermal method can be used for water hardness removal. A large release of moisture and volatile matters was seen concurrent with the weight loss and

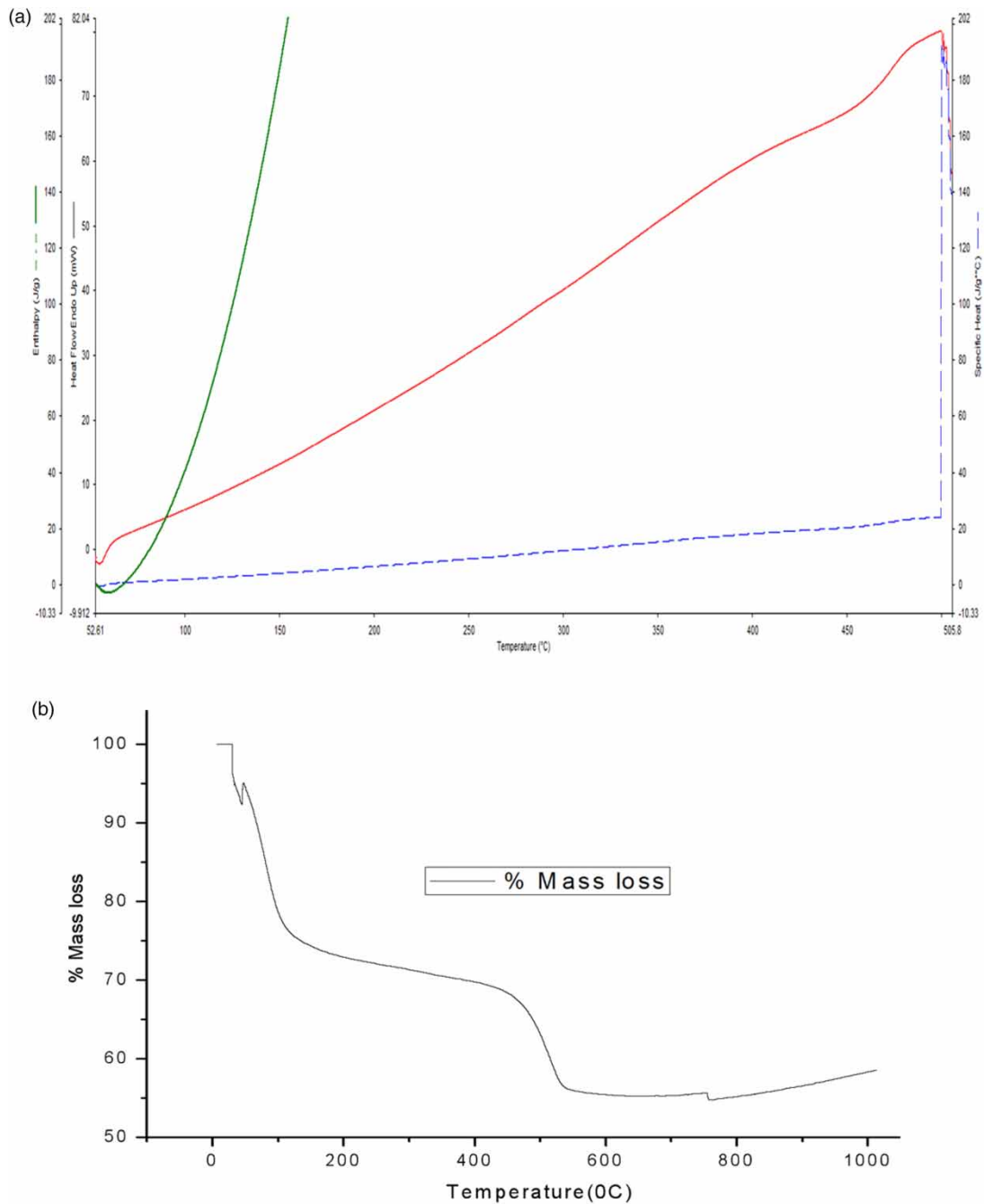


Figure 3 | Differential scanning calorimeter of synthesized zeolite.

endothermic reactions in the TG value as show in Figure 3(b). Intensive mass loss in Figure 3(b) is observed from 85 °C to 100 °C, which corresponds to surface moisture removal, and from 309 °C–400 °C slight mass loss is observed which represents volatile mater and interior moisture removal. A sharp mass loss is clearly observed from 500 °C to 550 °C, which is the dehydroxylation process.

Batch adsorption studies

Fourier transform infrared spectroscopy (FTIR) analysis

The major functional group present in the natural kaolin was revealed by the FTIR spectra. Raw kaolinite (before and after adsorption) and synthesized zeolite's (before and after) ion exchange capacity were

analyzed. Both samples showed same major peaks but their transmittance percentage intensity showed a wide range of differences. The major peaks of kaolin showed at 1,066, 593, 3,481, 2,964, 447, 1,659 and 791 wavelengths (Figure 4). The band position is compared with Gadsden (1975)'s results, the absorption bands observed at $3,481\text{ cm}^{-1}$ and $1,659\text{ cm}^{-1}$ could be corresponding to the OH^- vibration mode of the hydroxyl molecule, the bands between $3,450$ and $3,670\text{ cm}^{-1}$ are attributed to the OH^- stretching mode. In the $1,000\text{ cm}^{-1}$ and 500 cm^{-1} region, the main functional groups were Si-O and Al-OH. The region at $780\text{--}798\text{ cm}^{-1}$ is due to Si-O-Si inter tetrahedral bridging bonds in the SiO_2 and OH^- deformation band. Comparing the samples, the synthesized zeolite showed the smallest peaks due to the replacement of the calcium and magnesium ions on the active surface of the adsorbent.

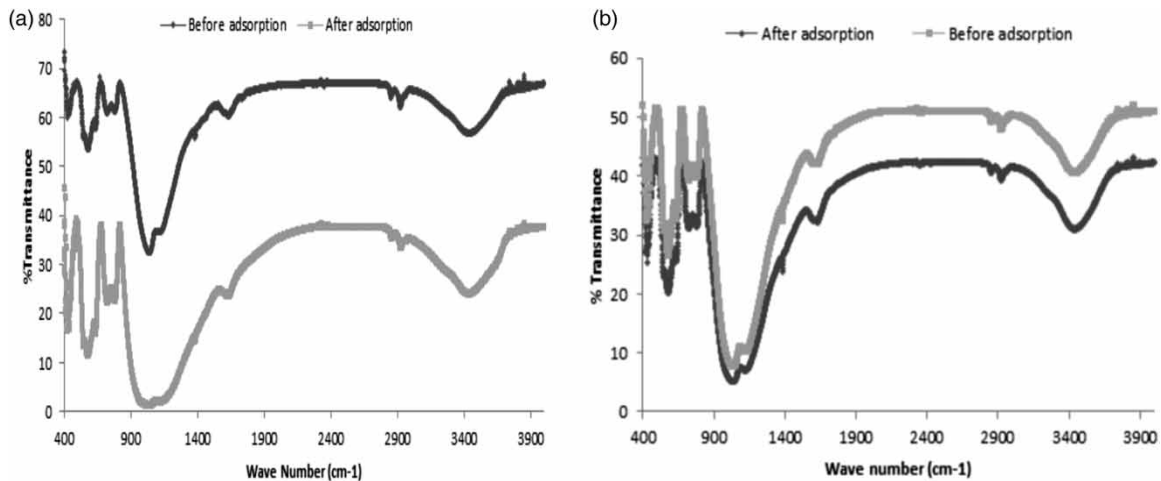


Figure 4 | FTIR spectra of synthesized zeolite: (a) raw kaolin; and (b) synthesized kaolin before and after adsorption of calcium and magnesium ions.

Effect of contact time

Examination of ion exchange of Ca^{2+} and Mg^{2+} was performed by batch method in Na-X zeolite/Ca or Mg aqueous solutions. Contact time is inevitably a fundamental parameter in all transfer phenomena such as cation exchange process. The experimental results of CEC showed Na^{1+} exchanged with Ca^{2+} in Na-X zeolite (Figure 5(a)). The data showed that a contact time of 150 minutes was required

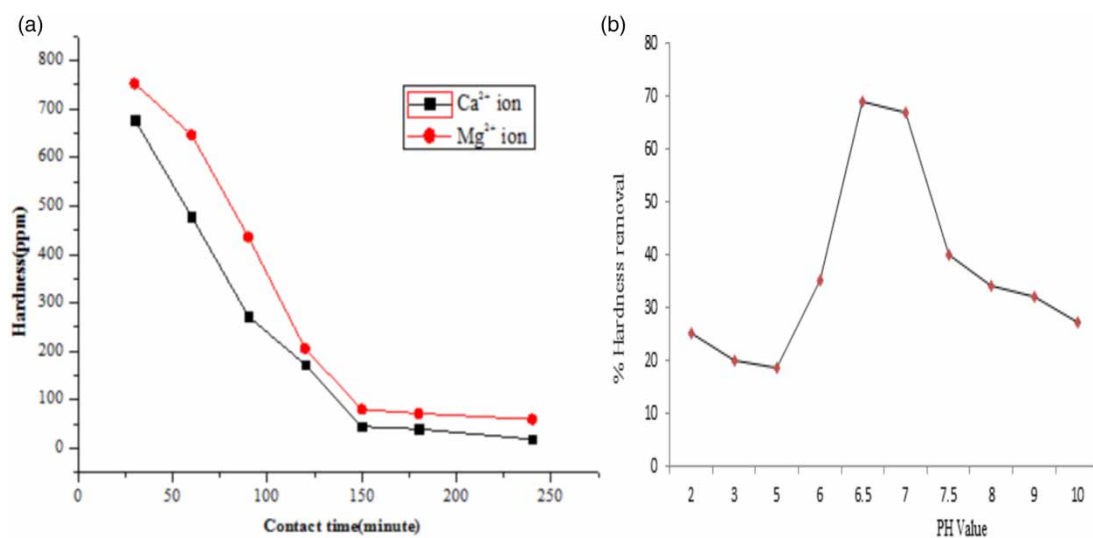


Figure 5 | Effects of contact time on calcium and magnesium removal with zeolite (a) and (b) effect of pH value on hardness removal.

to achieve the equilibrium. Ion exchange capacity of Ca^{2+} is rapid at initial times with prolonged slower exchange until equilibrium. During the first few minutes of Na-X. zeolite/Ca aqueous solutions contact time (from 30–150 minutes) the rate of cation exchange is found to be very rapid, and thereafter, the rate of metal ions exchange decreased. During the initial stage of the process, a large number of Na^{1+} is available for exchange. After lapse, the ingoing metal ions (Ca^{2+}) are binded into the mesoporous material, which is almost saturated with binding metal ions during the initial stage of exchange. It is found that the removal of hardness-producing ions increase with increase in contact time to some extent.

Effect of pH

The pH of the solution is considered as an important factor affecting metal adsorption processes due to its impact on the degree of ionization of metal species and the surface charge of the adsorbent. pH has the effect of neutralization and re-acidification on metal concentrations in solution in the absence and presence of zeolite. When pH was increased by NaOH addition, the precipitation phase was observed in the experiment. With further pH increase these precipitates gradually changed color at pH 7. pH is one of the important parameters to be considered in the adsorption/ion exchange process, because in many cases it changes the surface charge on the sorbents. As shown in Figure 5(b) the percentage of the hardness removal increases from 25% to 69% with increasing pH from 2.5 to 6.5 and then decreases from 7.5 to 9.5. This is due to the high degree of deprotonation of the functional group on the surface of hydrogen bond, which occurs at high pH. The highest adsorption capacity towards Ca^{+2} and Mg^{+2} was achieved at pH 6.5. The lower removal efficiencies observed in acidic medium (from 2–5) can be attributed to the protonation of ion exchange in functional groups or competition of H^+ with metal ions to bind and occupy the active sites of the adsorbents. On the other hand, in neutral and alkaline media (from pH 8–10), the formation of metal hydroxide can be considered as the main reason for decreasing metal uptake.

Effect of temperature

Temperature is another important factor that greatly influences the ion exchange process. The effect of solution temperature was investigated at 298 K, 303 K, and 313 K. The results summarized in Figure 6 shows that the ion exchange rate decreased with increase in temperature. The result

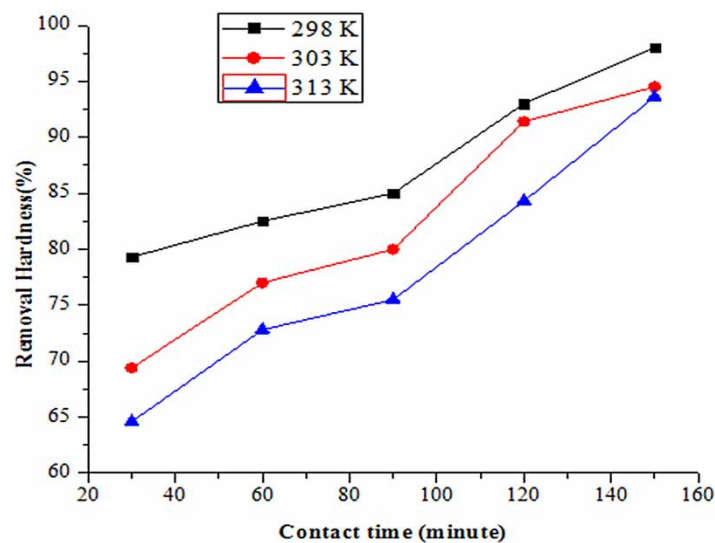


Figure 6 | Affect of temperature on hardness removal.

indicated that the low temperature favors the removal of hardness producing molecules by facilitating adsorption/ion exchange of an exothermic nature. The decrease of removal efficiency is due to a high temperature, as the thickness of the boundary layer decreases due to the increased tendency of the molecules to escape from the adsorbent surface to the solution, which results in a decrease in the adsorption/ion exchange capacity as temperature is increased.

Adsorption isotherm modes

Isotherms give an equilibrium relationship between the amounts of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. The two most important isotherm models are Langmuir and Freundlich.

Langmuir isotherm model

The Langmuir isotherm model was applied to determine the mechanics of achieving equilibrium in the solution when Ca and Mg are adsorbed on the surface of synthetic zeolite. This adsorption model was applied assuming that adsorption is on a monolayer on the surface, with finite sites available. The linear form of the Langmuir expression is:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{kQ_m}$$

where C_e is the equilibrium concentration of metals (mg/L), q_e is the equilibrium capacity of metals on the adsorbent (mg/g), Q_m is the monolayer adsorption capacity of the adsorbent (mg/g), and k is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption. These constants are determined from the graph slope and the interception of the linear plotting of C_e/q_e against C_e . The Langmuir constants Q_m and k can be determined from the slope and intercept of the line (Figure 7).

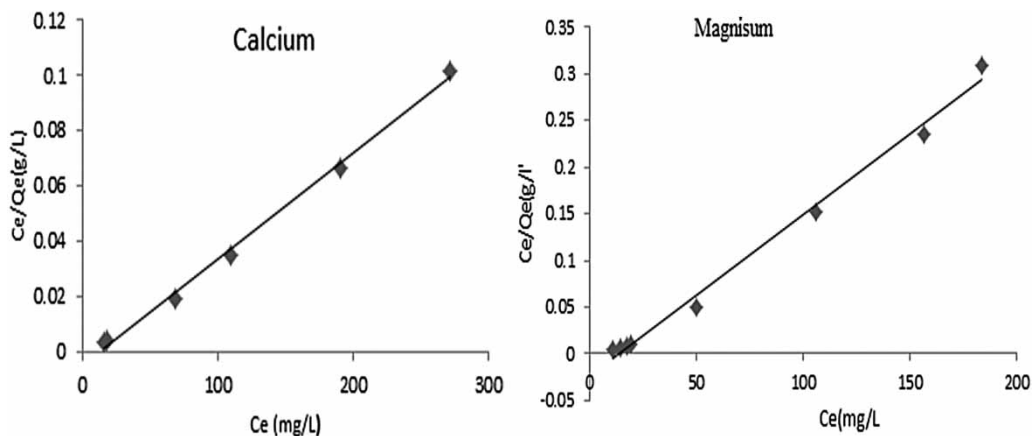


Figure 7 | Langmuir isotherm plot for adsorption of Ca and Mg ions on the synthetic zeolite.

Freundlich isotherm mode

The Freundlich model is based on the assumption that metal ions are adsorbed on a heterogeneous surface and is not restricted to formation of monomolecular layer.

The linear form can be written as:

$$\ln q_e = \ln k f + \left(\frac{1}{n}\right) * \ln C_e$$

where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constant, which indicates the capacity and intensity of the adsorption, respectively. When $\ln q_e$ is plotted versus C_e , a straight line with slope n and intercept KF is obtained, as can be seen in Figure 8.

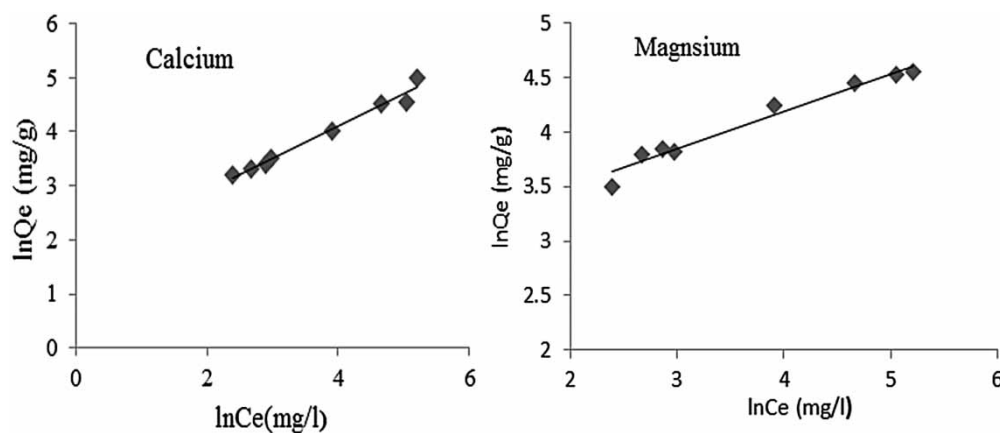


Figure 8 | Freundlich isotherm plot for adsorption of Ca and Mg ions on synthetic zeolite.

From this study, (Table 2) the value of the Freundlich constant n ($n = 1.68$ for Ca ions and $n = 2.86$ for Mg ions is greater than 1, which indicate that the adsorption process is good). From the Freundlich equation the value of K_f showed that the synthetic zeolite has a high adsorption capacity for calcium and magnesium ions. Since the R^2 are fairly close to 1, thus both the models describe the system well. However, the Langmuir isotherm model is more preferred than Freundlich isotherm.

Table 2 | Langmuir, Freundlich parameters for the adsorption of Ca^{2+} and Mg^{2+} onto synthetic zeolite

	Langmuir isotherm Constant			Freundlich isotherm Constant			
	Qm	k	R ²	Kf	n	R ²	
Ca ²⁺	12.5	0.53	0.995	5.6	1.68	0.976	
Mg ²⁺	15.7	0.75	0.992	16.61	2.894	0.965	

CONCLUSION

The results of the present investigation show that natural kaolin is an abundant and low cost material that can be synthesized for the removal of metals such as calcium and magnesium from water. Synthetic zeolite contains a high percentage SiO_2 , which makes it a useful material for hardness removal. The removal efficiency is influenced by the pH of the adsorbent. The best adsorption capacity for Ca^{+2} and Mg^{+2} ions is achieved at pH 6.5. Equilibrium time after stirring is reached in 150 minutes for synthetic zeolite. The effect of solution temperature influences the adsorption/ion exchange process. Low temperatures favor the removal of hardness.

The removal rate of calcium increased from 37.2% to 94.1% and magnesium from 22.5% to 81.4% at the same adsorption temperature. The order of adsorption/ion exchange capacity in removal of hardness by synthetic zeolite is $Ca^{2+} > Mg^{2+}$. Experimental results were also evaluated with Langmuir and Freundlich isotherm models. The corresponding higher value of correlation coefficient monolayer capacity (Qm) and adsorption intensity (n) is determined from Langmuir isotherm and Freundlich isotherm respectively. The result indicated that it was appropriate for calcium and magnesium metal adsorption. Generally, it can be concluded from this research that the adsorption

capacity for calcium and magnesium ion removal is more significant for synthesized zeolite than raw kaolin for water hardness treatment.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ETHICAL APPROVAL

This article does not contain any studies with human participants or animals performed by any of the authors.

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