

Ion exchanges process for calcium, magnesium and total hardness from ground water with natural zeolite

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ABSTRACT

Presence of hardness ions in the municipal drinking water is the major health concern. So to minimize the hardness of drinking water up to the environmental protection authority (EPA) quality standard expensive treatments are available. This directly affects the rural and low community society. The aim of this research work is to remove the calcium, magnesium and total hardness from the municipal drinking water supply with natural zeolite. All the experiments on the research work were carried out in batch method. The experimental result illustrates that at 2M NaCl and 60 °C activation temperature is suitable to achieved maximum 80.2% calcium, 84.8% magnesium and 81.0% total hardness at optimum condition pH 6.9, dose 50 g/L, particle size 1 mm, treatment time 30 min and experimental temperature 25 °C. Regeneration of zeolite at 3M NaCl and 90 °C is appropriate to achieve 80.0% total hardness, 79.9% Ca ions, 85.6% Mg ion at pH 6.9, size 1 mm and regeneration time 15 min. The X-ray diffraction, scanning electron micrograph and Fourier infrared transfer analysis confirms that zeolite has participated on hardness removal. Overall zeolite is highly efficient for hardness removal and can be employed in the drinking water treatment plant.

1. Introduction

Water is a vital necessity of human, plant, and animals on the Earth (Manahan, 2017). Less than one percent of fresh water is accessible from ground level for human consumption. In some cases, the resource does not satisfy to the desirable levels regarding their chemical properties (composition), such as hardness, nitrate contamination, heavy metals, soluble iron, etc (Harper et al., 2017). From that undesirable chemical that most groundwater source has; water hardness is the dominant one and major challenge for most of the water supply system (Dunlap and Mertig, 2014). In general, water supplies with total hardness higher than 200 mg/L can be tolerated but considered to be poor resources; while values higher than 300 mg/L are not acceptable for most of the domestic consumptions (Hounslow, 2018). An existence of the calcium, magnesium and carbonate ions on the earth layer influences the hydrochemistry of groundwater (Tirkey et al., 2017). Hardness of water is due to moisture and carbon dioxide reacts with calcium and magnesium ion present on the earth surface (Boyd et al., 2016). The degree of hardness has been categories in temporary and permanent; temporary hardness can be reduced by boiling, but permanent hardness required specific treatment (MacAdam and Jarvis, 2015).

A number of technology like electro deionization process (Zhang and Chen, 2016), adsorption (Rolence et al., 2014; Ouar et al., 2017), lime soda (Bob and Walker, 2006), nanofiltration (Madarasz et al., 2014), microbial (Brastad and He, 2013) and ion exchange process (Apell and Boyer, 2010) has been reported in literature. Among all of them ion exchange process is found to be more convenient, economical, no sludge generation and easy to regenerate (Vaaramaa and Lehto, 2003). Commonly there are two types of ion-exchanger available i.e., synthetic and natural. Synthetic ion-exchanger is modified with a chemical and thermal process from natural ion-exchanger (Harland, 2007; Georgiev et al., 2009). Natural ion-exchanger is mineral compounds, such as clays (e.g., bentonite, kaolinite, and illite), vermiculite, and zeolites (e.g., analcite, chabazite, sodalite, and clinoptilolite) exhibit ion exchange properties (Rieman and Walton, 2013). Clay and vermiculite have been used as ion-exchanger but they have some negative aspect (Inglezakis, 2005). Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth metals, having infinite, three-dimensional atomic structures (Kulprathipanja, 2010). They are further characterized by the ability to lose and gain water reversibly and to exchange certain constituent atoms, also without major change of atomic structure. The structure of natural zeolite is very interesting and complex (Elizalde-Gonzalez et al., 2001). The primary building units

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(PBU) of zeolites are the SiO_4 and AlO_4 tetrahedral. They connect via oxygen ions into secondary building units (SBU), which are then linked into a three-dimensional crystalline structure of zeolite (Wells, 2012). Substitution of Si by Al defines the negative charge of the zeolite framework, which is compensated by alkaline and earth alkaline metal cations (Cai et al., 2015). Therefore, natural zeolites appear as cation exchangers due to they have a negative charge on the surface (Margita et al., 2013). Zeolites are extensively used in water (Ates and Akgul, 2016; Johari et al., 2016) and wastewater purification, as absorbent, adsorbent and catalyst in industries as well as odour control (Weitkamp, 2000; Wang and Peng, 2010).

The main objective of this research work is to remove the total hardness available in municipal drinking water supply by using locally available natural zeolite. Activation and regeneration of zeolite with the different operating condition have been studied. The ion-exchanger has been also characterized by X-ray diffraction, scanning electron micrograph and Fourier infrared transform analysis.

2. Material and methods

2.1. Material

Raw material: The drinking water was arranged from Aynalme borehole (groundwater), Mekelle town Ethiopia. The characteristic of drinking water is mention in Table 1. Natural zeolite collected from Maichewa area near to Mekelle City, shown in Fig. 1 Labotary grade chemicals hydrochloric acid (HCl) and sodium hydroxide (NaOH) has been used for an experiment.

Preparation of zeolite: The raw zeolite collected from the sedimentary deposit near maychew Tigrinya region Ethiopia, shown in Fig. 2. The chemical composition of zeolite is listed in Table 2. Collected sample was washed with distilled water to remove the impurities and dry in an oven at 25 °C for 12 h. The zeolite rock was ground with the hammer and divided into the fractions by mechanical sieves. The fraction 0.5 mm–1.5 mm was washed with distilled water to remove turbidity and was dried at room temperature (Tunç and Demirkiran, 2014). After that preliminary activation of the zeolite was carried out with 1M NaCl solution (Sepehr et al., 2013). Activated zeolite was again



Fig. 1. Natural zeolite used in experiment.

washing with distilled water to neutralize and dried at room temperature again. The prepared sample was collected and kept in the different poly-bags untilled experiment.

2.2. Method

Experiment: The ion-exchange process was carried out in 250 ml beaker with a magnetic stirrer. The experimental arrangement is shown in Fig. 3. To check the influence of different parameters experiment was conducted in batch mode at a constant speed of 60 revolving per minute (RPM). A calculated amount of zeolite 2 g, 5 g, 7.5 g, and 10 g was added at different pH 6.5, 6.9 and 7.4 in 100 ml of the hard water sample and run for the different time interval of 5, 15, 30 and 60 min.

Table 1
Drinking water characteristic of Municipal Supply.

S.No	Parameters	Analysis Result for S.Code- (PW-3)	Ethiopian Standards	WHO Guide Lines
1	Appearance	Non-objectionable	Non-objectionable	Un-objectionable
2	Color	Non-objectionable	Non-objectionable	Un-objectionable
3	Odour	Non-objectionable	Non-objectionable	Un-objectionable
4	Taste	Non-objectionable	Non-objectionable	Un-objectionable
5	Temperature	21.9 °C	25 °C	25 °C
6	pH	8.20	6.5–8.5	6.5–8.5
7	Turbidity	0.02 NTU	5 NTU	5 NTU
8	E C	1005 $\mu\text{S}/\text{cm}$	1500 $\mu\text{S}/\text{cm}$	2000 $\mu\text{S}/\text{cm}$
9	T D S	503 ppm	1000 ppm	1000 ppm
11	DO	3.1 mg/L	6 mg/L	6 mg/L
13	Iron, Total	0.1 mg/L	0.3 mg/L	0.3 mg/L
14	Copper	0.016 mg/L	2 mg/L	1.5 mg/L
15	Chromium	0.039 mg/L	0.05 mg/L	0.05 mg/L
16	Manganese	0.32 mg/L	0.5 mg/L	0.5 mg/L
17	Alkalinity, Total	156 mg/L	200 mg/L	500 mg/L
18	Magnesium, Mg^{2+}	165 mg/L	50 mg/L	200 mg/L
19	Calcium, Ca^{2+}	272 mg/L	75 mg/L	150 mg/L
20	Calcium Hardness, CaCO_3	560 mg/L	200 mg/L	200 mg/L
21	Total Hardness, CaCO_3	680 mg/L	300 mg/L	300 mg/L
22	Fluoride, F^-	0.89 mg/L	1.5 mg/L	1.5 mg/L
23	Nitrate, NO_3^-	2.47 mg/L	50 mg/L	45 mg/L
24	Nitrite, NO_2^-	0.12 mg/L	3 mg/L	3 mg/L
25	Phosphate, PO_4^{3-}	0.5 mg/L	2 mg/L	2 mg/L
26	Sulfate, SO_4^{2-}	15.6 mg/L	250 mg/L	400 mg/L
27	Total Coliform	Nill	Nill	Nill
28	Faecal Coliform	Nill	Nill	Nill

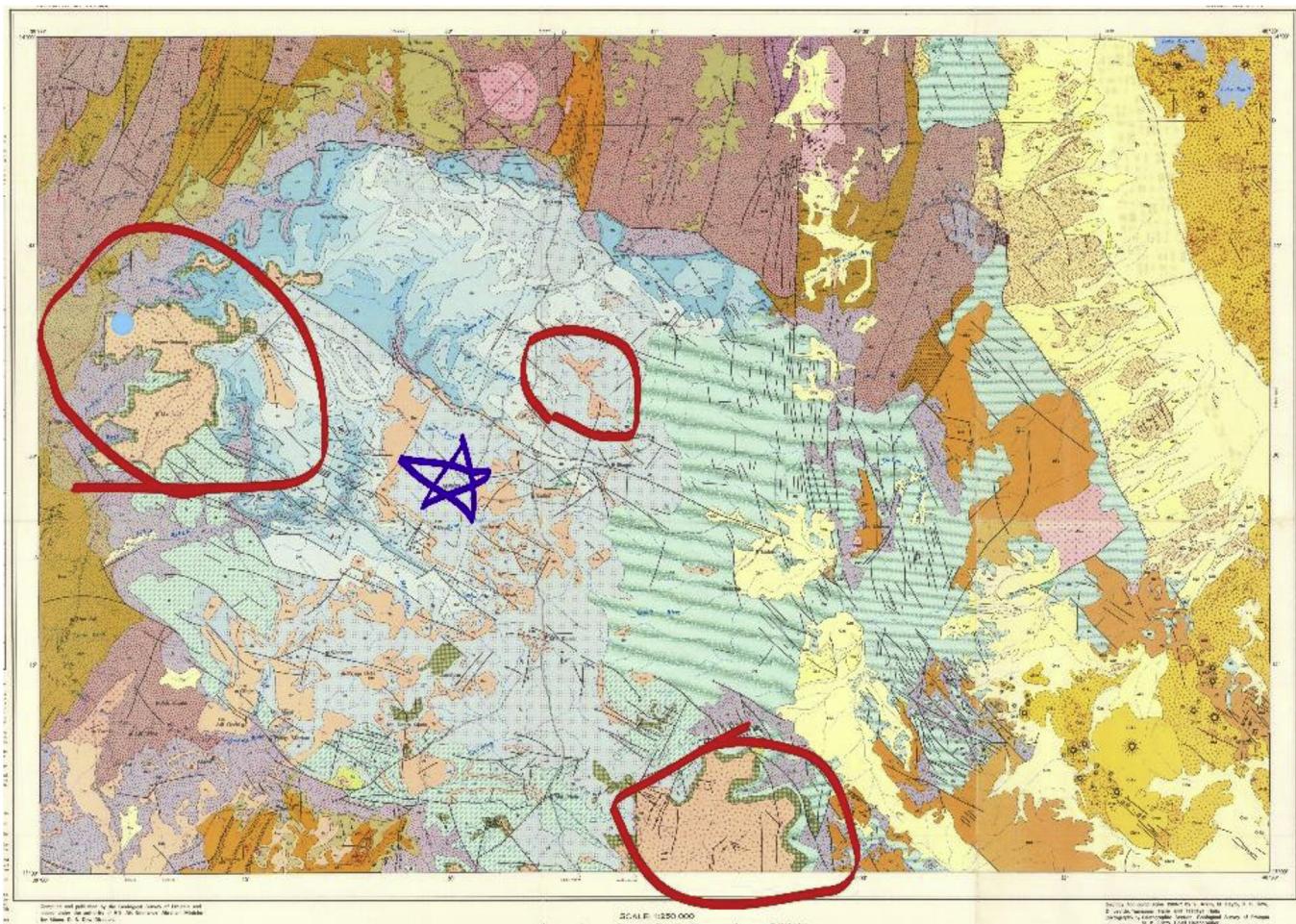


Fig. 2. Geographical map of Tigrinya region (Mekelle) Ethiopia were zeolite was collected (Printing with kind permission of geology department, Mekelle, Ethiopia).

Table 2
Chemical Composition of zeolite.

S.No	Chemical Composition	Chemical Symbol	Value (%)
1	Silicon oxide	SiO ₂	65.09
2	Ferric trioxide	Fe ₂ O ₃	2.45
3	Ferric oxide	FeO	0.20
4	Aluminium oxide	Al ₂ O ₃	12.45
5	Titanium dioxide	TiO ₂	0.51
6	Calcium oxide	CaO	2.94
7	Magnesium oxide	MgO	1.27
8	Manganese oxide	MnO	0.11
9	Potassium oxide	K ₂ O	3.52
10	Sodium oxide	Na ₂ O	1.25
11	Chloride	Cl	—
12	Fluoride	F	—
13	Moisture	H ₂ O	10.01

At the end of each experiment, the beaker was removed from the magnetic stirrer and the treated sample was separated from the zeolite with the help filter paper (Whatman filter paper; Whatman's No. 42). The hardness of filtrates obtained was measured using atomic absorption method (APHA, 1915).

Analytical method: Atomic absorption measurements were carried out using a Varian AA240 spectrometer with Mg/Ca hollow cathode lamp light source (7-mile ampere lamp current). Atomization was performed using an air/acetylene flame. The instrument was zeroed with 2% HNO₃ and rinsed between each collection with deionized water. Magnesium absorbance was measured at 285.2 nm, and calcium absorbance was measured at 422.7 nm. Calibration curves for

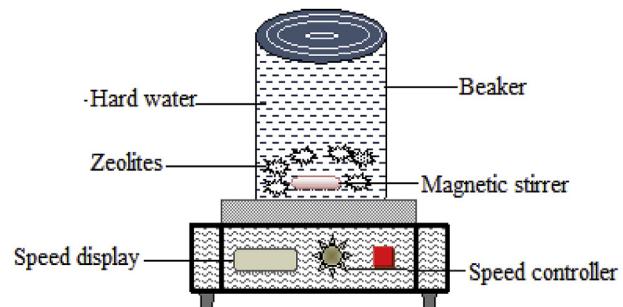


Fig. 3. Experimental setup of ion-exchange process with natural zeolite.

magnesium/calcium were generated using the previously described standard solutions. Sample data were collected directly after each respective calibration curve was obtained. The separation of zeolite from the treated sample was carried out in Buckner filter with Whatman filter paper (diameter 12.5 cm; pore size 2.5 µm; Cat. No.1001150). The total hardness of the samples was calculated according to Eq. (1) by using the value of Ca and Mg, which obtained from the atomic absorption spectrometer. The removal percentage of calcium, magnesium and total hardness were determined as per Eq (2). The pH was adjusted with 1M NaOH and 1M HCl solution and determine with digital pH PHH-26. To identify the structure of crystalline material, grounded zeolite was used in X-ray diffraction (XRD) instrument. XRD analysis of the sample was performed using CuKα-radiation of a DRON-3.0 X-ray diffractometer. The morphology and bond between the structures were

determined with scanning electron micrograph (SEM-JSM-7500FA). The infrared spectra of the zeolite rock were obtained using a Fourier transform infrared spectrometer NICOLET-5700. The FTIR spectra in the wavenumber range from 400 to 4000 cm⁻¹ were obtained by using KBr pellet technique.

$$\text{Total Hardness} = \left[\frac{2 \times \text{Ca content}}{\text{molecular weight of Ca}} + \frac{2 \times \text{Mg content}}{\text{molecular weight of Mg}} \right] \times 50 \quad (1)$$

Removal efficiency (%)

$$= \left[\frac{\text{Original sample hardness} - \text{Treated sample hardness}}{\text{Original sample hardness}} \right] \times 100. \quad (2)$$

3. Result and discussion

3.1. Characterization of zeolite

X-ray diffraction study of zeolite: The x-ray diffraction characterization was carried out for raw zeolite and after removal of hardness, which showed in Fig. 4(a) and (b). X-ray diffraction is a rapid analytical technique primarily used for phase identification of crystalline material and can provide information on unit cell dimensions. There are three major peaks were in the natural zeolite. The first peak clinoptilolite of the zeolite was found at the region 0–10 2θ, second peak mordenite at 10–23 2θ and third peak sepiolite were observed at 23–29 2θ. The leftover peaks in the patterns of the natural zeolite may be attributed to the presence of quartz, feldspar, and cristobalite, which shown in Fig. 4(a). This is expected that in sedimentary deposits the formation of zeolites is always associated with the presence of another alkali Al-silicates and SiO₂. It can be also easily identified that the intensity was decreased in Fig. 4(b) (after treatment). It reveals that the peak values decrease after the treatment confirms the sodium present in the zeolite is exchanged with the calcium (Ca) and magnesium (Mg) that are present in the hard water (Loiola et al., 2012).

Fourier Transform Infra Red Analysis: The structural information has been obtained from the vibrational frequencies of the natural zeolite lattice observed in the range between 400 and 4000 cm⁻¹. Spectra were confirmed for the without ion exchanged raw zeolite and zeolite after ion exchange with water sample Fig. 5. The most intensive absorption band was observed at 1030 cm⁻¹ and corresponds to the asymmetric stretching vibrations of Si—O—Si (Breck, 1974). The absorption bands between 800 cm⁻¹ and 750 cm⁻¹ are associated with the stretching vibrations of Al—O—Al, and 475 cm⁻¹ and 450 are bending vibrations of O—Si—O. The small peak at 1650 cm⁻¹ is assigned to the bending vibration band of sorbed water. The strong wide bands in the range 3375–3750 cm⁻¹ are interrelated with the occurrence of absorbed water molecules that belongs to the asymmetric stretching vibration of H—O—H bond. The O—H stretching region, infrared spectra of zeolites gives important of information on hydroxyl groups attached to zeolite structures (Li, 2005). Other peaks can be assigned to zeolite water including the broadening peak at ~3580 cm⁻¹ that belongs to the asymmetric stretching vibration of H—O bond. The zeolite sample after hardness removal was filtered with Whatman filter paper and used for analysis. After hardness removal zeolite an addition vibration bands were found at 730, 845, 1350, 1735, and 2300 cm⁻¹. These vibration bands indicate the peaks of carbon-oxygen double bond in the carbonate ion. Overall the peaks agree with information available in the literature (Nazarenko and Zarubina, 2013).

Scanning Electron micrographs: Electron microscopy demonstrate various details of the structure of the zeolite and allows a through a study of crystalline forms of micro-crystals grown in voids. The micrograph analysis for zeolite before and after ion exchange process is shown in Fig. 6(a) and (b). The micrograph of before treated zeolite

Fig. 6(a), shows agglomerations of a crystal having thin fibers and plate-shaped. The particles size varies from 2.5 to 20 μm. This reveals that the zeolite (clinoptilolite) is a tuff and texture material (Diale et al., 2011). After ion-exchange zeolite, it can be seen from Fig. 6(b), on the surfaces particles, are irregular and having a bar shape. The particle size varies from 5 to 15 μm and having high porosity. Similarly, the pattern was observed with rice-husk based zeolite for 90% of fluoride removal at initial concentration 10 g/L from groundwater (Mukherjee et al., 2018).

3.2. Activation of zeolite

Effect of sodium chloride concentration: The activation of zeolite was carried for 1 mm particle size at 45 °C temperature for different NaCl concentration in a range of 1M–4M. The hardness removal efficiency experimental was done at pH 6, stirred time 5 min; dose 5 g/l; temperature 21 °C and total hardness 568 mg/L, which is shown in Fig. 7. It can be observed that with an increase in NaCl concentration from 1M to 2M the total hardness decreased from 610 mg/L to 580 mg/L. Further increase sodium chloride concentration from 3M to 4M, the total hardness increase from 597 mg/L to 612 mg/L. Therefore optimum sodium chloride solution concentration was considered to be 2M. This may be due to 2 M sodium chloride solution are effective to alter the chemical structure of zeolite. The ion-exchange and precipitation mechanism occurred simultaneously in zeolite reaction and depend on concentration of increasing or decreasing. Due to that 2M of sodium chloride solution is effective to remove maximum calcium and magnesium from hard water (Wiyantoko and Rahmah, 2017).

Effect of activation temperature: The activation of zeolite was carried out for 2M sodium chloride solution and 1 mm particles at different 45 °C, 60 °C, 90 °C and 110 °C of temperature range. The ion exchange experiment carried out at pH 6, stirred time 5 min; dose 5 g/l; temperature 21 °C and total hardness 568 mg/L, which represented in Fig. 8. It has been noted that minimum 555 mg/L total hardness was decreased at the 60 °C activation temperature. Increase in temperature 90 °C and 110 °C, increases 570 mg/L and 580 mg/L total hardness removal. At low-temperature 45 °C, it was 580 mg/L total hardness reduction. This is expected that porous structure, desiccation of the zeolite at 60 °C activation temperatures will increase its hydrophilic (water absorption) properties. Additional activation temperature increased the surface area of the zeolite but reduced crystallization time and particle size (Purbaningtias et al., 2017).

3.3. Optimization of operating parameters

Optimization of pH: pH plays an important character on hardness removal. To determine the optimum pH, water sample was maintained at three different pH, pH 6.5, pH 6.9 and pH 7.4 at constant dose 2 g zeolite; stirring time 5 min, size 1 mm and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L Mg). The result presented in Fig. 9. From the result it can be seen that maximum 165.3 mg/L of total hardness; 52.4 mg/L calcium and 8.2 mg/L magnesium were reduced at pH 6.9. Further increases or decrease in pH 6.5 or pH 7.4 the ion exchange performance was reduced. It was 210 mg/L total hardness (TH); 67.3 mg/L calcium (Ca) and 10 mg/L magnesium (Mg) hardness for pH 6.5 and 171.4 mg/L TH; 48.56 mg/L Ca and 12 mg/L Mg for pH 7.4. At low pH values, the exchange of hardness causing ions was low because a large amount of proton competes with the hardness ions at the active sites of the zeolite surface. Similarly the increase of exchange rate when pH of the solution increases is due to the decrease of proton quantity competing with hardness ions in the zeolite surface. The surface of zeolite materials becomes negatively charged and this increases the exchange rate of the positively charged hardness causing ions through electrostatic forces of attraction (Dimirkou and Doula, 2008). Sepehr et al. (2013) reported 96% calcium and 93% magnesium removal with modified pumice at pH 6.0 and

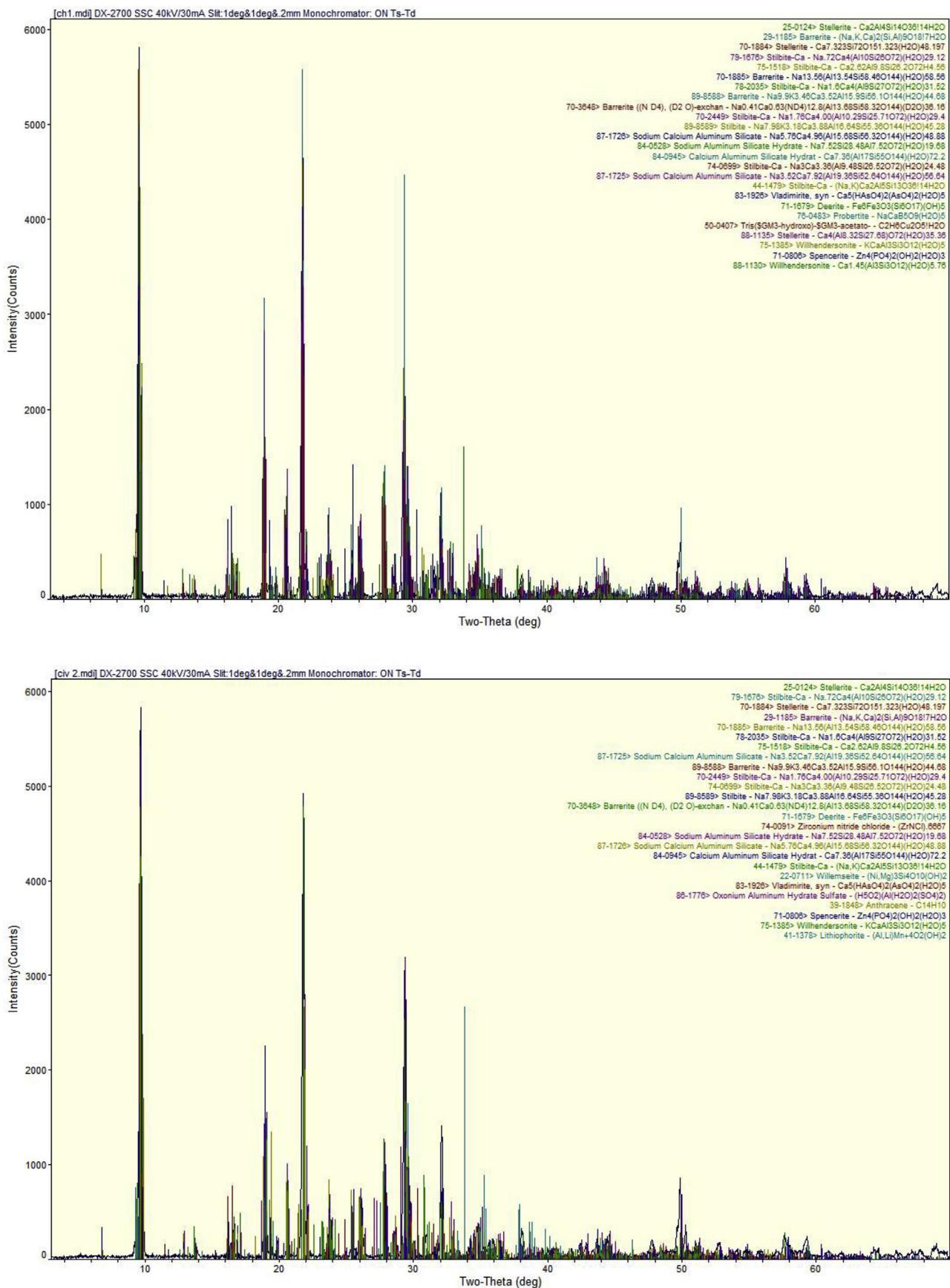


Fig. 4. X-ray diffraction of (a) raw zeolite before hardness removal and (b) after hardness removal.

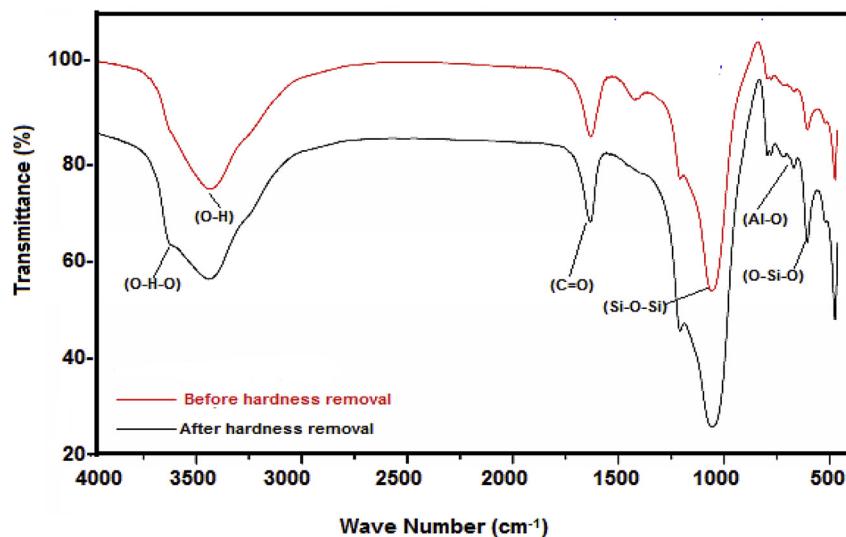


Fig. 5. Fourier Infra Red Transform study of natural zeolite.

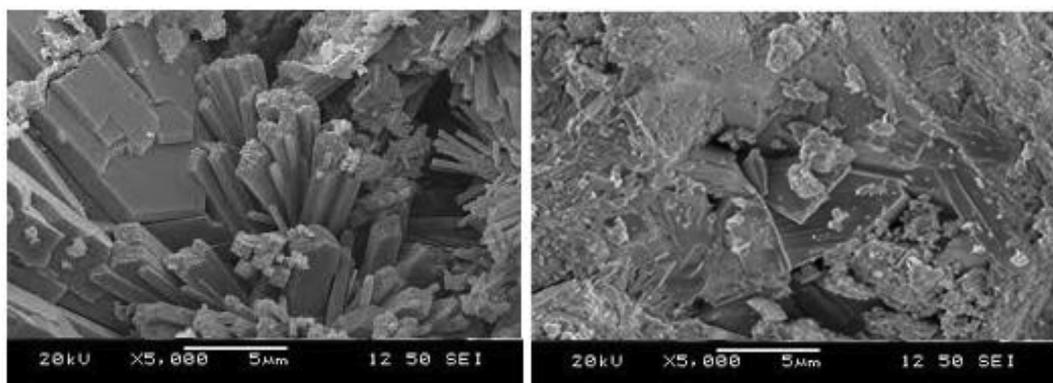


Fig. 6. Scanning Electron Micrograph analysis of natural zeolite (a) before ion exchange and (b) after ion exchange.

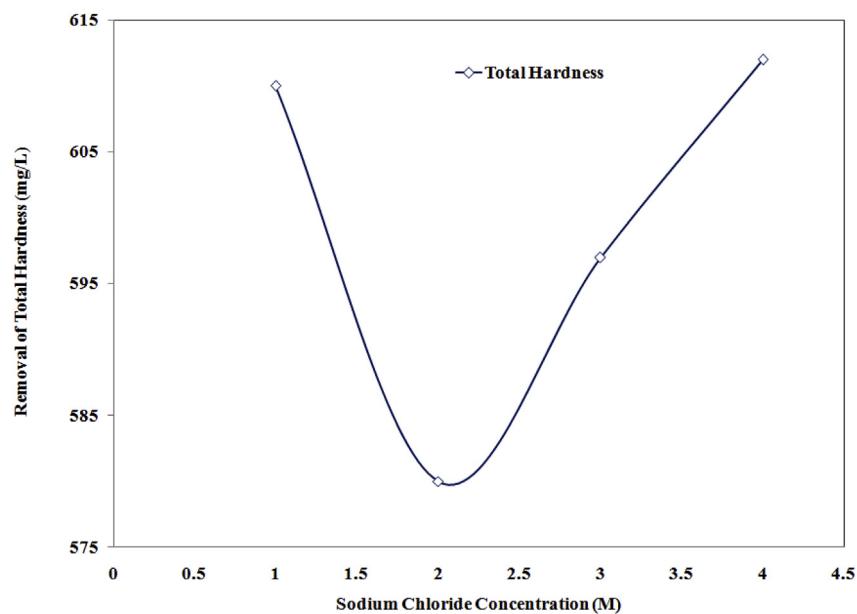


Fig. 7. Activation of natural zeolite with sodium chloride solution at different concentration at pH 6, stirred time 5 min; dose 5 g/l; temperature 21 °C and total hardness 568 mg/L

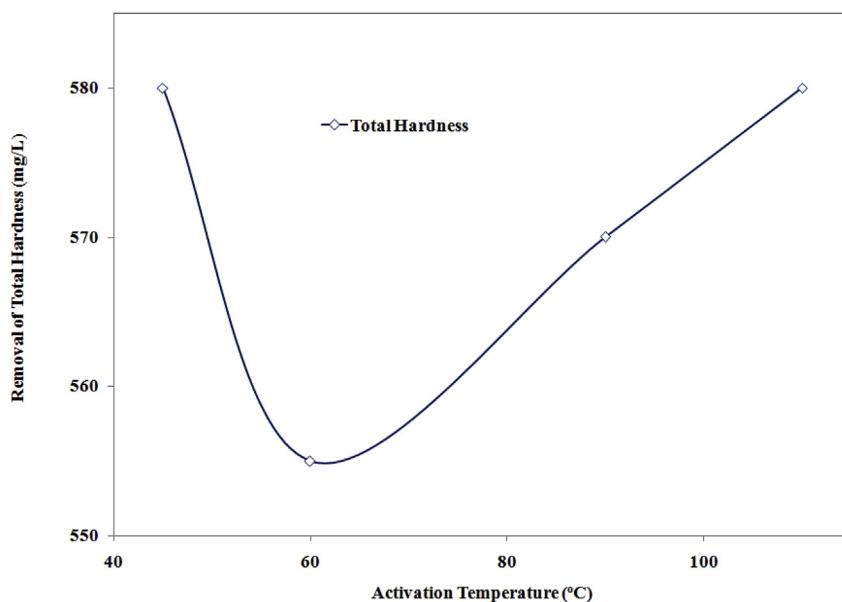


Fig. 8. Activation of natural zeolite with sodium chloride 2M solution at different temperature at pH 6, stirred time 5 min; dose 5 g/l; temperature 21 °C and total hardness 568 mg/L

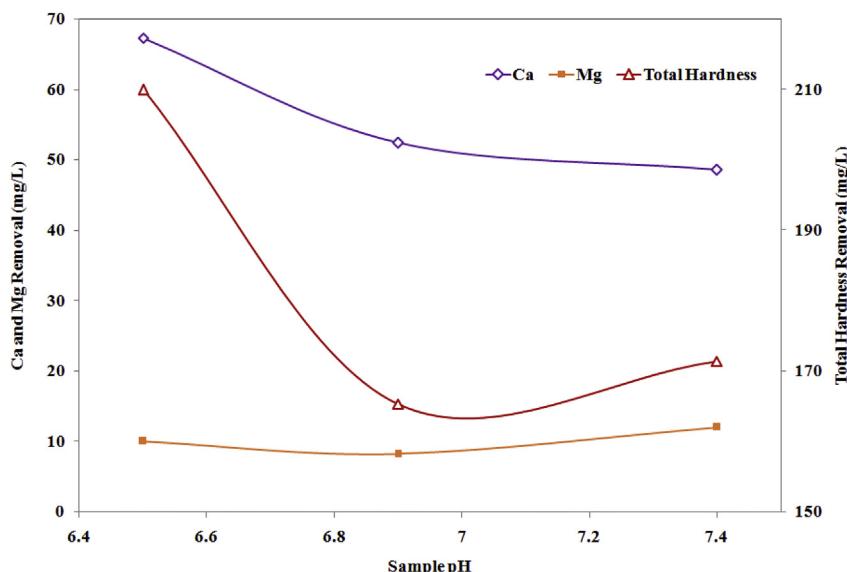


Fig. 9. Optimization of pH at constant dose 2 g zeolite; stirring time 5 min, size 1 mm; temperature 21 °C and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L).

10 g/L initial concentration.

Optimization of size: To determine the optimum size of natural zeolite, three different size range of 0.5 mm, 01 mm and 1.35 mm particle sizes were employed in the experiment. The total hardness concentration 658 mg/L; calcium 220 mg/L and magnesium 26 mg/L was consider an initial condition at pH 6.9 (optimum); dose 2 (gram); experimental temperature 21 °C and stirring time 5 min (50 RPM.). The result is shown in Fig. 10, that maximum 160 mg/L TH; 50 mg/L Ca and 8 mg/L Mg removal was occurred for 01 mm zeolite particles size. At lower size 0.5 mm the removal was 254.2 mg/L; 90 mg/L Ca and 07 mg/L and 265 mg/L TH; 72.6 mg/L Ca and 20 mg/L Mg at higher range 1.35 mm particle size. This may be due zeolite surface area is small and not actively participated for cation exchange properly at a lower size (Wang and Nguyen, 2018). At a large size, they did not dissolve with water and a proper exchange has not occurred. Hence the optimum size of zeolites have notable role on effectiveness of ion

exchange. These results agree with removal of heavy metal from petroleum industry wastewater at 0.5 mm size of natural zeolite (Salman et al., 2017).

Optimization of dose: The effect of dose on hardness removal was carried out at three different dose ranges of 10 g/L; 25 g/L and 75 g/L at optimum pH 6.9 and optimum particle size 1 mm and temperature 21 °C and treatment time 5 min. The calcium, magnesium and total hardness removal efficiency shown in Fig. 11. At 50 g/L dosing of zeolite was found to be appropriate to reduced maximum 154.7 mg/L TH; 53.5 mg/L Ca and 5 mg/L Mg. Further, decrease to 25 g/L and 10 g/L dosing the total hardness (TH) 160 mg/L; Calcium (Ca) 50.6 mg/L and magnesium 8 mg/L and 220.1 total hardness; calcium 69.7 mg/L and magnesium 11 mg/L were observed. At maximum dosing 75 g/L of zeolite the efficiency was not improved, in other words, TH 186 mg/L; Ca 62.06 mg/L and Mg 7.5 mg/L was found. Increase in ion exchange dose, the hardness exchange efficiency increased

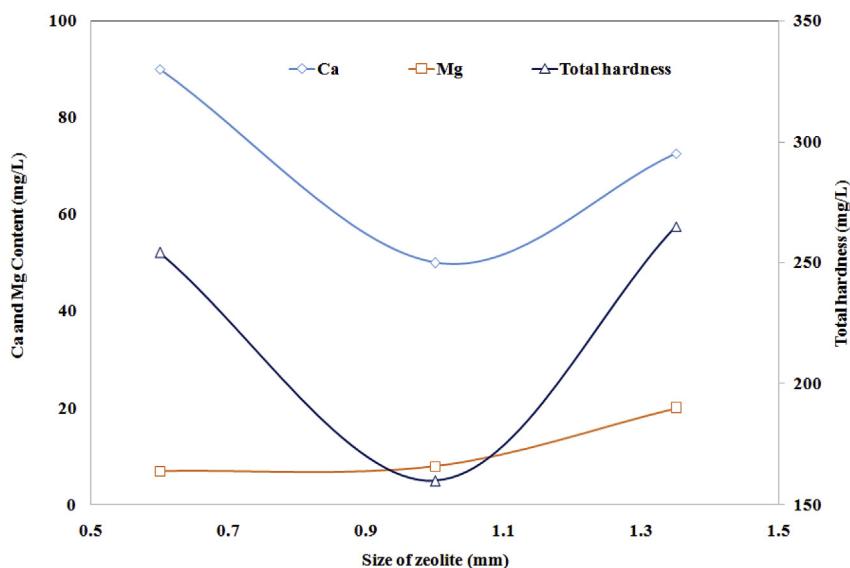


Fig. 10. Optimization of zeolite size at pH 6.9 constant dose 2 g zeolite; stirring time 5 min; temperature 21 °C and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L Mg).

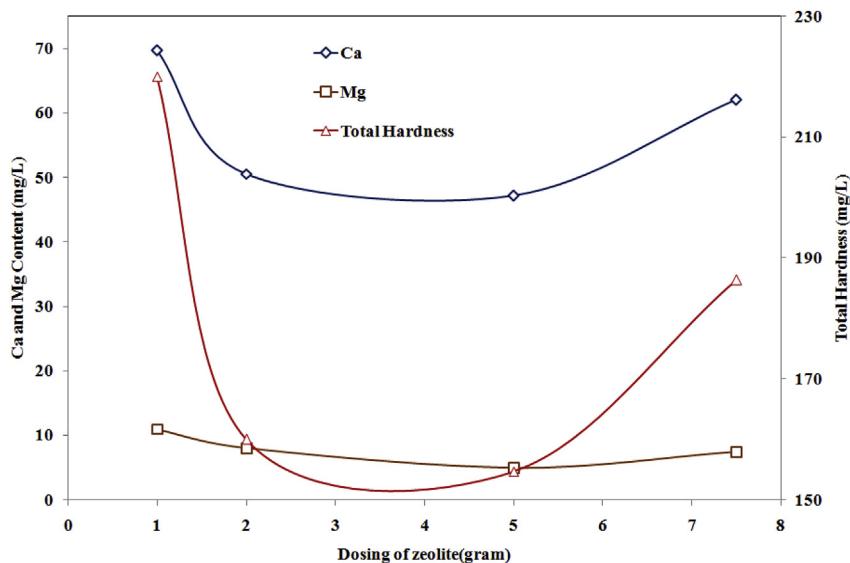


Fig. 11. Optimization of dose at pH 6.9; size 1 mm; stirring time 5 min; temperature 21 °C and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L Mg).

until at the optimized dose. The observed increment in removal with increasing exchanger dosage could be due to an increase in a number of possible exchanger sites and surface area of the zeolite (Abadzic and Ryan, 2001).

Optimization of treatment time: The effect of the treatment time was investigated for 3 min–60 min of contact time at optimum condition of pH 6.9, optimum size 1 mm; optimum dose 50 g/L; temperature 21 °C; TH 658 mg/L; Ca 220 mg/L and Mg 26 mg/L Mg. The data obtained was presented in Fig. 12. From the result it can be seen 130 mg/L TH; 45.1 Ca and 4.1 Mg ions were reduced at 30 min of treatment time. At this point, the amount of cation being exchanged by the zeolite was in a state of dynamic equilibrium with the amount of cation from the zeolite. Further, increase in contact time 45 min and 60 min the performance reduced to 155 mg/L; 54.8 mg/L and 4.3 mg/L and 162 mg/L TH; 56.55 Ca and 4.95 Mg respectively. This might be due to the occupancy of all sites of the zeolites. At lower treatment time 3 min and 5 min 168 mg/L TH; 58 mg/L Ca and 6.1 mg/L and 165 mg/L TH; 57.6 mg/L Ca and 5 mg/L Mg removal was observed. This might be due

to the lack of exchange site available in zeolite (Prasad et al., 2011). In literature, raw and synthesized zeolite was used for hardness removal and result has the same opinion as present hardness removal achieved (Dimova et al., 1999; Loiola et al., 2012). Loiola et al. observed 95% of calcium removal in 1 min of treatment time.

Optimization of temperature: The effect of temperature on ion exchange for cation was investigated as a function of temperature and result is presented in Fig. 13. The initial condition was optimum pH 6.9; dose 50 g/L; treatment time 30 min; particles size 1 mm; 658 mg/L TH, 220 mg/L Ca and 26 mg/L Mg at range of 18 °C; 25 °C and 30 °C temperature. It was noted from the result that 25 °C temperature is suitable to achieve 125 mg/L TH; 43.4 mg/L Ca and 3.95 mg/L Mg reduction. At lower experiment temperature 18 °C the removal was 144 mg/L; 50.43 mg/L and 4.3 mg/L Mg and higher temperature 30 °C it was 152 mg/L TH; 48.5 mg/L Ca and 4.7 mg/L Mg removal was observed. Increase in ion exchange efficiency with increases in temperature up to 25 °C then decreases, it may be due to the ion exchange rate decreases from the surface. Another possible description was that the cations were

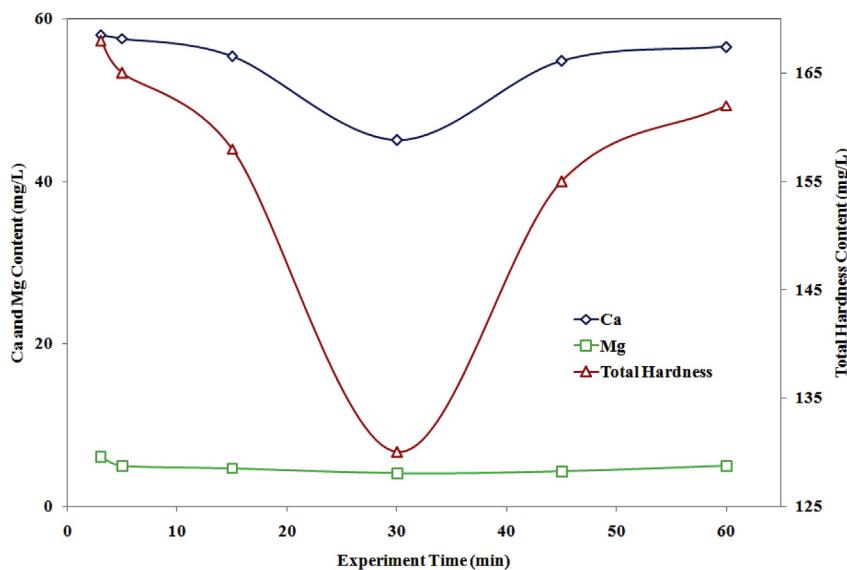


Fig. 12. Optimization of treatment time at pH 6.9; size 1 mm; dose 50 g/l; stirring time 5 min, size 1 mm; temperature 21 °C and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L).

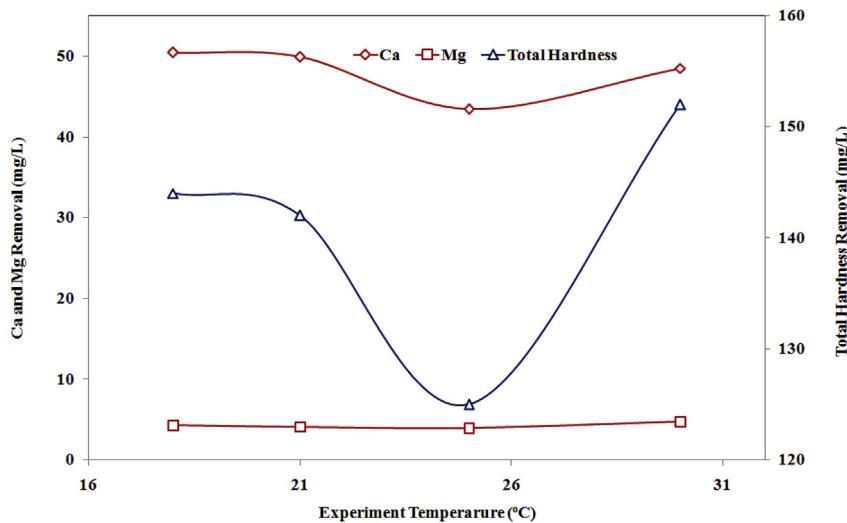


Fig. 13. Optimization of temperature at pH 6.9; size 1 mm; dose 50 g/l; stirring time 5 min, size 1 mm and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L).

well hydrated. They have to lose part of hydration sheath in order to be absorbed. This dehydration process of cation required energy. At higher temperatures, some accumulation occurs due to the shrinkage of the exchanger and releases some of the exchange ions resulting in increasing the ion concentration in the solution again (Woinarski et al., 2003; Ayele et al., 2015).

3.4. Regeneration of zeolite

Optimization of the molar solution: The regeneration of zeolite was carried out with four different (1M, 2M, 3M and 5M) molar sodium chloride solution at 60 °C regeneration temperature and 6 h s regeneration time. The ion exchange experiment was conducted at optimum condition pH 6.9; size 1 mm; dose 50 g/l and time 30 min for all 4 M NaCl solutions. The result represents in Fig. 14 it can be seen that maximum total hardness reduced from 658 to 139 mg/L at all optimum condition. Further increase in sodium chloride concentration 5M removal efficiency decreased to 145 mg/L. This may be due to excess occurrence of sodium ion in solution. At lower concentration of NaCl 1M and 2M solution, the reduction was also reduced to 213 mg/L and

186 mg/l respectively. These attributes to lack of sodium ion in a solution that may be not sufficient for calcium ion removal (Ahmad and Mirza, 2017). For this reason 3M sodium chloride solution provides suitable ion exchange capacity for maximum hardness removal (Farkas, 2005).

Optimization of temperature: The optimum regeneration temperature was done for four temperature range 45 °C, 60 °C, 90 °C, and 110 °C at 3M of sodium chloride solution, which shown in Fig. 15. All optimized parameters pH 6.9, size 1 mm, dose 5 g and time 30 min was maintained for hardness removal. From the result, it can found that maximum 127 mg/l total hardness; 44.05 mg/l calcium ion and 4.05 mg/L magnesium ion removed at 90 °C regenerated zeolite. At lower temperature 45 °C 165 mg/l total hardness; 57.8 mg/l calcium ion and 4.9 mg/l magnesium ion and at 110 °C 135 mg/l total hardness; 47.5 mg/l calcium ion and 3.9 mg/l magnesium hardness was observed. This attributes to at 60 °C regeneration temperature provides better nutrition, redevelop the active site and binding conditions (Murphy et al., 1978; Rao and Khatoon, 2016).

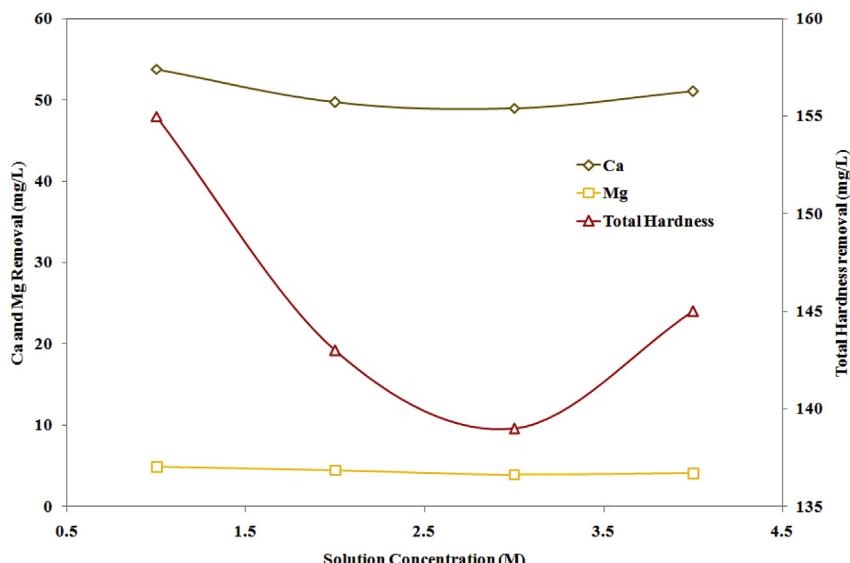


Fig. 14. Regeneration of zeolite at different sodium chloride solution; regeneration temperature 60 °C and regeneration time 6 h at optimum experimental condition (pH 6.9; size 1 mm; dose 50 g/l; stirring time 5 min, temperature 25 °C and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L).

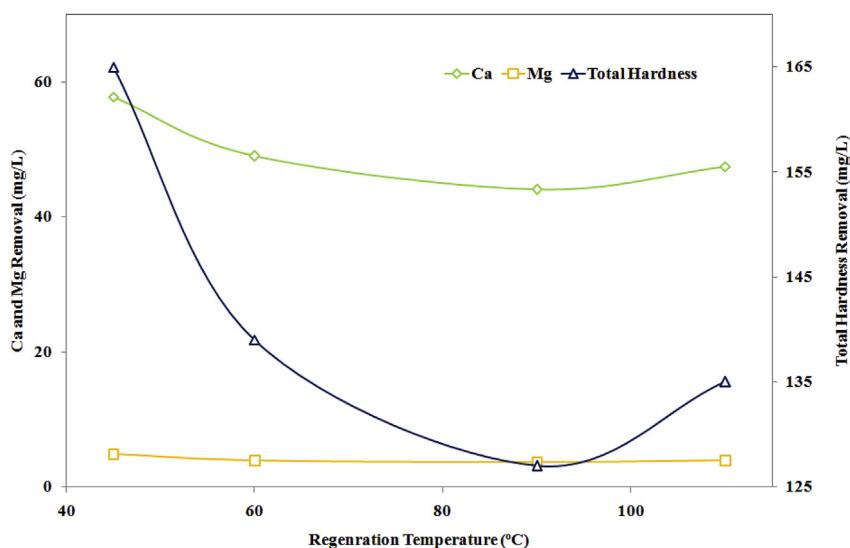


Fig. 15. Regeneration of zeolite at different regeneration; 3M sodium chloride solution and regeneration time 6 h at optimum experimental condition (pH 6.9; size 1 mm; dose 50 g/l; stirring time 5 min, temperature 25 °C and initial hardness concentration (658.3 mg/L total hardness; 220 mg/L Ca and 26 mg/L).

4. Conclusion

It concludes that zeolite is found to be suitable for the reduction of hardness (calcium and magnesium ions) up to pollution control authority quality standard. Activation of zeolite was found to good at the 2M solution of sodium chloride and temperature 60 °C, the total hardness removal was 555 mg/l from 658 mg/L. At optimum conditions, sample pH 6.9, zeolite size 1 mm, dose 50 g/l, stirring time 30min and temperature 25 °C, maximum 43.4 mg/L from 220 mg/L (80.2%) calcium ion, 3.95 mg/L from 26 mg/L (84.8%) magnesium ion and 125 mg/L from 658 mg/L (81.0%) total hardness was reduce. After treatment zeolite regeneration was carried out at optimum temperature 90 °C, 3M sodium chloride solution, pH 6.9, size 1 mm, dose 50 g/l and treatment time 30 min total hardness was reduced from 658 mg/l to 127 mg/l (80.6%), calcium ion from 220 mg/l to 44.05 mg/L (79.9%), and magnesium ion 26 mg/L to 3.74 mg/L (85.6%) respectively. X-ray diffraction peaks indicated stellerite, barriete, and stellrite at different wave number and reduced after removal. The Fourier transform infrared analysis confirms the presence of aluminum silicate and

hydrogen bond that participated in hardness removal. The micrograph study show particles are plate-shaped and regularly distributed after treatment, it was an irregular structure. In the end, a zeolite is found to be very relevant for calcium and magnesium ion removal from municipal drinking water supply by an ion-exchange technique. It can be employ for the large volume of drinking water supply.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gsd.2019.01.009>.

References

- Abadzic, S.D., Ryan, J.N., 2001. Particle release and permeability reduction in a natural zeolite (clinoptilolite) and sand porous medium. *Environ. Sci. Technol.* 35 (22), 4502–4508.
- Ahmad, R., Mirza, A., 2017. Heavy metal remediation by Dextrin-oxalic acid/Cetyltrimethyl ammonium bromide (CTAB)-Montmorillonite (MMT) nanocomposite. *Groundwater for Sustainable Development* 4, 57–65.

- American Public Health Association, American Water Works Association, Water Pollution Control Federation and Water Environment Federation, 1915. Standard Methods for the Examination of Water and Wastewater, vol. 2 American Public Health Association.
- Apell, J.N., Boyer, T.H., 2010. Combined ion exchange treatment for removal of dissolved organic matter and hardness. *Wat. Res.* 44 (8), 2419–2430.
- Ates, A., Akgül, G., 2016. Modification of natural zeolite with NaOH for removal of manganese in drinking water. *Powder Technol.* 287, 285–291.
- Ayale, L., Pérez-Pariente, J., Chebude, Y., Díaz, I., 2015. Synthesis of zeolite A from Ethiopian kaolin. *Microporous Mesoporous Mater.* 215, 29–36.
- Bob, M., Walker, H.W., 2006. Lime-soda softening process modifications for enhanced NOM removal. *J. Environ. Eng.* 132 (2), 158–165.
- Boyd, C.E., Tucker, C.S., Somridhivej, B., 2016. Alkalinity and hardness: critical but elusive concepts in aquaculture. *J. World Aquacult. Soc.* 47 (1) 0.6–41.
- Brastad, K.S., He, Z., 2013. Water softening using microbial desalination cell technology. *Desalination* 309, 32–37.
- Breck, D.W., 1974. Zeolite Molecular Sieves: Structure, Chemistry and Use. Jonh Wiley and Sons. Inc., New Ypirk, Malabar, Flórida.
- Cai, Q., Turner, B.D., Sheng, D., Sloan, S., 2015. The kinetics of fluoride sorption by zeolite: effects of cadmium, barium and manganese. *J. of Con. Hy.* 177, 136–147.
- Diale, P., Muzenda, E., Zimba, J., 2011. A study of South African natural zeolites properties and applications. In: Proceedings of the World Congress on Engineering and Computer Science October 19–21, San Francisco, USA.
- Dimirkou, A., Doula, M.K., 2008. Use of clinoptilolite and an Fe-overexchanged clinoptilolite in Zn²⁺ and Mn²⁺ removal from drinking water. *Desalination* 224 (1–3), 280–292.
- Dimova, G., Mihailov, G., Tzankov, T., 1999. Combined filter for ammonia removal—part I: minimal zeolite contact time and requirements for desorption. *Water Sci. Technol.* 39 (8), 123–129.
- Dunlap, R.E., Mertig, A.G., 2014. Trends in public opinion toward environmental issues: 1965–1990. In: American Environmentalism. Taylor & Francis, pp. 101–128.
- Elizalde-Gonzalez, M.P., Mattusch, J., Wennrich, R., 2001. Application of natural zeolites for preconcentration of arsenic species in water samples. In: Presented at the Whistler 2000 speciation symposium, Whistler resort, BC, Canada, June 25–July 1, 2000, pp. 22–26. *J. Environ. Monit.* 3(1).
- Farkas, A.R.M.-M., 2005. Ammonium Exchange in Leakage Waters of Waste Dumps Using Natural Zeolite from the Krapina Region. pp. 131–136.
- Georgiev, D., Bogdanov, B., Angelova, K., Markovska, I., Hristov, Y., 2009. June. Synthetic zeolites—Structure, classification, current trends in zeolite synthesis. In: Economics and Society Development on the Base of Knowledge: In. Sci. Conf., vol. 7. pp. 5–14.
- Harland, C.E., 2007. Ion Exchange: Theory and Practice. Royal Society of Chemistry.
- Harper, C., Harper, C.L., Snowden, M., 2017. Environment and Society: Human Perspectives on Environmental Issues. Routledge.
- Hounslow, A., 2018. Water Quality Data: Analysis and Interpretation. CRC press.
- Inglezakis, V.J., 2005. The concept of “capacity” in zeolite ion-exchange systems. *J. of Coll. and Inter. Sci.* 281 (1), 68–79.
- Johari, S.A., Kalbassi, M.R., Soltani, M., Yu, I.J., 2016. Application of nanosilver-coated zeolite as water filter media for fungal disinfection of rainbow trout (*Oncorhynchus mykiss*) eggs. *Aq. Cul. international* 24 (1), 23–38.
- Kulprathipanja, S. (Ed.), 2010. Zeolites in Industrial Separation and Catalysis. John Wiley & Sons.
- Li, G., 2005. FT-IR Studies of Zeolite Materials: Characterization and Environmental Applications.
- Loiola, A.R., Andrade, J.C.R.A., Sasaki, J.M., Da Silva, L.R.D., 2012. Structural analysis of zeolite NaA synthesized by a cost-effective hydrothermal method using kaolin and its use as water softener. *J. Colloid Interface Sci.* 367 (1), 34–39.
- MacAdam, J., Jarvis, P., 2015. Water-formed scales and deposits: types, characteristics, and relevant industries. *Min. Scal. and Dep.* 6, 3–23.
- Madarasz, D., Szentí, I., Sápi, A., Halász, J., Kukovecz, Á., Kónya, Z., 2014. Exploiting the ion-exchange ability of titanate nanotubes in a model water softening process. *Chem. Phys. Lett.* 591, 161–165.
- Manahan, S., 2017. Environmental Chemistry. CRC press.
- Margeta, K., Logar, N.Z., Šiljeg, M., Farkas, A., 2013. Natural Zeolites in Water Treatment—How Effective Is Their Use. In: Water Treatment. InTech.
- Mukherjee, S., Barman, S., Halder, G., 2018. Fluoride uptake by zeolite NaA synthesized from rice husk: Isotherm, kinetics, thermodynamics and cost estimation. *Groundwater for Sustainable Development* 7, 39–47.
- Murphy, C.B., Hrycik, O., Gleason, W.T., 1978. Natural Zeolites: Novel Uses and Regeneration in Wastewater Treatment. Natural Zeolites: Occurrence, Properties, Use. Pergamon, Oxford, UK, pp. 471–478.
- Nazarenko, O., Zarubina, R., 2013. Application of sakhaptinsk zeolite for improving the quality of ground water. *En. and Env. Eng.* 1 (2), 68–73.
- Ouar, M.A., Sellami, M.H., Meddour, S.E., Touahir, R., Guemari, S., Loudiyi, K., 2017. Experimental yield analysis of groundwater solar desalination system using absorbent materials. *Groundwater for Sustainable Development* 5, 261–267.
- Prasad, B., Sangita, K., Tewary, B.K., 2011. Reducing the hardness of mine water using transformed fly ash. *Mine Water Environ.* 30 (1), 61–66.
- Purbaningtias, T.E., Wiyantoko, B., Kurniawati, P., Prasetyoko, D., Suprapto, 2017. December. The effect of aging temperature on natural zeolite modification. AIP Conference Proceedings AIP Publishing Vol. 1911, No. 1, p. 020013.
- Rao, R.A.K., Khatoon, A., 2016. Adsorption characteristics of chemically modified Caryota urens seeds for the removal of Cu (II) from aqueous solution: Isotherms and kinetic studies. *Groundwater for Sustainable Development* 2, 42–52.
- Rieman, W., Walton, H.F., 2013. Ion Exchange in Analytical Chemistry: International Series of Monographs in Analytical Chemistry. Elsevier.
- Rolence, C., Machunda, R.L., Njau, K.N., 2014. Water hardness removal by coconut shell activated carbon. *J. of Sci. Tech. and So.* 2 (5), 97–102.
- Salman, H., Shaheen, H., Abbas, G., Khalouf, N., 2017. Use of Syrian Natural Zeolite for Heavy Metals Removal from Industrial Waste Water: Factors and Mechanism.
- Sepehr, M.N., Zarrabi, M., Kazemian, H., Amrane, A., Yaghmaian, K., Ghaffari, H.R., 2013. Removal of hardness agents, calcium and magnesium, by natural and alkaline modified pumice stones in single and binary systems. *App. Sur. Sci.* 274, 295–305.
- Tirkey, P., Bhattacharya, T., Chakraborty, S., Barai, S., 2017. Assessment of groundwater quality and associated health risks: a case study of Ranchi city, Jharkhand, India. *Groundwater for Sustainable Development* 5, 85–100.
- Tunç, T., Demirkiran, A.Ş., 2014. The effects of mechanical activation on the sintering and microstructural properties of cordierite produced from natural zeolite. *Powder Technol.* 260, 7–14.
- Vaaramaa, K., Lehto, J., 2003. Removal of metals and anions from drinking water by ion exchange. *Desalination* 155 (2), 157–170.
- Wang, S., Peng, Y., 2010. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem. Eng. J.* 156 (1), 11–24.
- Wang, X., Nguyen, A.V., 2018. Potential Desalination of Coal Seam Gas Coproduced Water Using Zeolite.
- Weitkamp, J., 2000. Zeolites and catalysis. *Solid State Ionics* 131 (1–2), 175–188.
- Wells, A.F., 2012. Structural Inorganic Chemistry. Oxford university press.
- Wiyantoko, B., Rahmah, N., 2017. December. Measurement of cation exchange capacity (CEC) on natural zeolite by percolation method. AIP Conference Proceedings AIP Publishing Vol. 1911, No. 1, p. 020021.
- Woinarski, A.Z., Snape, I., Stevens, G.W., Stark, S.C., 2003. The effects of cold temperature on copper ion exchange by natural zeolite for use in a permeable reactive barrier in Antarctica. *Cold Reg. Sci. Technol.* 37 (2), 159–168.
- Zhang, Z., Chen, A., 2016. Simultaneous removal of nitrate and hardness ions from groundwater using electro-deionization. *Separ. Purif. Technol.* 164, 107–113.