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Facile and affordable synthetic route of nano powder zeolite and its application in fast softening of water hardness

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20 **Graphical Abstract**

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Abstract:

Herein, we proposed an affordable and facile way of treating the hardening of water from local groundwater and seawater sources. This was facilitated by synthesizing zeolitic materials via an effortless and affordable method from readily available disposed of waste materials. Firstly, by converting waste aluminium (scrap wire cables, takeaway foil, cans, and spray aerosol bottles) along with disposed of silica gel into active zeolitic materials with the aid of a conventional domestic microwave. Small amounts of the produced zeolites (NaX and NaA) were utilized in the removal of the hardness of water (10 g.L^{-1}), showing elimination of Ca^{2+} and Mg^{2+} ions within 30 minutes, removing 90% of the total hardness ($> 1000 \text{ ppm}$). The spent zeolite samples can be further used for more than two consequent cycles, then the regeneration can be promoted by using NaCl solution at ambient conditions. The total price for the synthesis of 1 kg of the zeolite produced herein is 14 \$/kg. This is 70% lower than the price of commercial zeolites available in the market. Our proposed facile route in zeolite preparation could potentially change the traditional costly softening treatment techniques. It also minimizes the use of extra chemical materials, templates and multi-step procedures. The excellent hardness removal capacity in groundwater and seawater using synthesized zeolite samples could open doors for various applications.

Keywords: Synthetic zeolite, Hardness elimination, Ion exchange, Seawater, Groundwater, Regeneration, Aluminium waste, Water hardness.

49 **1. Introduction**

50 Nowadays, great focus has been drawn towards water pollution globally as all living beings are in
51 continuous need of water. In almost all developing countries, groundwater is the most used water supply
52 for safe drinking water. High level of minerals in water resources adversely affects human health. In
53 addition to this, it can prevent water applications in many other disciplines. Two major cationic elements
54 in the form of calcium and magnesium are the primary reasons that lead to water hardness. These ions can
55 also cause clogging of a piping chassis due to scale formation which, consequently, reduces the flow of
56 water inside the pipe causing serious operational issues. It is well known that the foamy characteristic of
57 soap and detergent is extremely reduced by the hardness of the water. Furthermore, corrosion caused by
58 hard water lowers the lifespan of the internal surface network of equipment and heaters used in industry.
59 Hard water containing more than 500 mg.L⁻¹ is not suitable for consumption in most household applications.
60 Quicklime and washing soda are used profusely in water purification plants, especially for hardness
61 removal. One of the main disadvantages of this process is the generation of a large amount of discarded
62 materials, as well as the necessity for re-carbonation of the used water [1, 2].

63 The most traditional methods for groundwater or wastewater treatment include chemical
64 precipitation, ion-exchange, chemical reduction, filtration, evaporation, flocculation, solvent extraction,
65 adsorption by activated carbon and other sorbents, electrodialysis, and membrane separation methods. At
66 present, desalination can be employed as an accessible solution for managing the long-term needs for
67 drinking waters. Reverse osmosis (RO) and nanofiltration membranes (NF) are the commonly known and
68 preferred methods for desalination and softening of water [3]. Currently, over than 80% of countries
69 worldwide utilize membrane technologies in operation for desalination of seawater [4]. NF or RO
70 membranes have high selectivity for the removal of divalent ions and decreasing the high dissolved solids
71 content of saline water [5]. Also, electrochemical methods are utilized in water softening, and, the final
72 electro-precipitate structure highly depends on the initial water composition [6, 7].

73 Ion exchange treatment is considered one of the most frequently utilized methods for solving the
74 water hardening issue and is very active in the elimination of several elements. Also, some low-cost and
75 eco-friendly ion exchanging materials are used such as modified pinecone, sugarcane bagasse or coffee
76 husk. They usually are utilized at a low concentration level of total hardness as in the work of Werkneh et
77 al. with a calcium concentration of 120 mg.L^{-1} , while in Altundoğan et al. work it was 230 mg.L^{-1} [8, 9].
78 The main advantages of ion exchange materials are their selectivity, efficiency, less residual from sludge
79 production, and can also be regenerated and reused effortlessly. Cation exchange is an alternative process
80 to the use of lime in hard water softening. In most water treatment plants, cation exchange resin is commonly
81 used in a fixed bed reactor vessel at the end of a treatment process [10]. A well-known disadvantage of
82 saturated ion-exchange resins is their high power-consumption of supplies needed for periodical
83 regeneration [11].

84 Numerous categories of ion exchange materials are commercially available and renowned as resins
85 or zeolites [12]. Zeolites are considered as micro-porous minerals which have the capability to exchange
86 ions. Zeolite materials are unique when comparing to other inorganic oxides due to its properties like strong
87 ion exchangeability, high thermal stability with high temperature, the micro-porous characteristic with
88 uniform pore dimensions, ability to evolve interior acidity, and intensity of internal surface area. Owing to
89 their cage-like construction, zeolites are used as water softeners or ion exchangers.

90 Zeolitic materials are a group of substances with a rationally designed pore framework and active
91 sites distribution. Synthetic zeolites have some advantageous properties over the natural analogues. The
92 synthetic materials are manufactured in a regular pure phase. It is also possible to produce different zeolite
93 structures contrary to naturally occurring zeolites. The basic chemical structure of zeolite is hydrated
94 crystalline aluminosilicate with the formula $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.n\text{SiO}_2.x\text{H}_2\text{O}$ [13]. Zeolites are categorized based
95 on the ring size and their pore diameter. Among zeolitic materials, Zeolite-A contains 8 rings and possesses
96 pore diameters in the range of 3-5 Å [14]. Furthermore, faujasite X and Y have 12 rings with a larger pore

97 diameter of 7-8 Å. Zeolite-X, Zeolite-A, and Zeolite-Y are classified under the same family of zeolites due
98 to their crystallographic units required to construct their structures [15]. The Si/Al ratio is responsible for
99 the chemical composition of the zeolite type and strongly affects the selectivity for sorption species [16].

100 Zeolite A does not form naturally in nature but can be industrially produced. Synthetic zeolites have
101 received great attention globally for their wide application of molecular sieving in gas and liquid phases
102 systems [17]. Synthetic zeolites are distinguishable in that they contain a high surface area and possess great
103 ability for ion exchange compared with natural zeolites [18]. There are many methods for zeolite synthesis
104 using different chemical reagents such as bases, sodium aluminates and sodium silicate. These methods are
105 costly and sometimes not economically viable [19]. Whereas, there is great global demand on conversion
106 of waste and disposed of materials (e.g. aluminium waste) to resources. These can be used in innovative
107 applications and help locate more economically viable materials for desalination of water sources (i.e.
108 groundwater and seawater) [20]. Most developed countries have a throwaway culture of waste materials
109 and this has a negative impact in terms of environmental issues that are associated with increasing the
110 landfills of disposed of materials [21]. Recycling of Al waste to more beneficial products was reported by
111 Osman et al. for the successful conversion of Al foil to useful γ -Al₂O₃ which was used as an acidic catalyst
112 [22]. Furthermore, El-Nahas et al. showcased the recycling and valorization of Al building wire scraps
113 (AlBWS) and Al takeout food container waste (AlTFC) to active alumina for the removal of nitrate ions
114 from water supplies [23].

115

116 Herein we synthesized zeolitic materials using a facile and affordable process from readily available
117 and abundant aluminium waste. During the preparation procedure, a domestic microwave along with low
118 temperature has been used. Thus, no additional energy-intensive process in the form of temperature is
119 needed to valorize the raw waste materials. Consequently, the synthesized zeolites were utilized to remove
120 the hardness of water in groundwater well. This can affect human health and fulfil specific Sustainable

Development Goals (SDGs) such as the human health (goal no. 3), clean water (goal no. 6) and responsible consumption and production (goal no. 12). This helps industry and issues in general, as the water hardness can produce scaling and scale build-up in pipes which causes clogging. Furthermore, utilization of the synthesized zeolite in the pre-treatment step in seawater desalination can help prolong membrane lifespans. The synthesized zeolites can also be regenerated and help facilitate the circular economy of the materials contained within the zeolite as they can be directly reused again with high value and performance for 2-3 runs. Herein we maintain the synthesized zeolites, and this is ideal for the circular economy as no energy leakage or down-cycling occurs.

2. Materials and Methods

2.1. Chemicals and reagents:

Discarded aluminium waste materials (scrap wire cables, takeaway foil containers, cans and spray aerosol bottles) were obtained from our local recycling centre in Egypt. Firstly, the raw aluminium waste was cut into consistent size and homogenous pieces to increase the surface area-to-volume ratio of the particles, maximizing the reaction rate with NaOH. Furthermore, disposed of silica gel particles were used without any further purification or milling process.

The stock solutions of Ca^{2+} were 4000 mg. L^{-1} . The desired pH values of solutions were fixed by either 0.1 M NaOH or 0.1 M HCl. Sodium hydroxide was analytical grade and used as received.

2.2. Method for synthesized zeolite samples:

The method for the 6 synthesized zeolite samples (101Z to 106Z) is outlined in Fig. 1 below and is described as follows:

Solution 1): the different raw aluminium sources (scrap wire cables, takeaway foil containers, cans, bottles and two types of spray aerosol bottles [105R&106R]) was dissolved in 10% NaOH solution whilst continuously stirring to obtain sodium aluminates (NaAlO_2) solution. Then after filtration, a clear solution

144 was produced. Solution 2): Disposed of silica gel was dissolved in 10% NaOH to produce sodium silicates
145 (Na_2SiO_4) solution. Solution 2 was added to solution 1 slowly with continuous stirring until a white
146 homogenous precipitate was formed. The gel was stirred under magnetic agitation for 1 h before transferring
147 the gel into a domestic home microwave for only 15 min at 170 W. All synthesis was achieved at a fixed
148 temperature (25 °C), except sample 104 Z, which was carried out at a very low temperature of ~ 5 °C (in an
149 ice bath). The resulting zeolite sample was aged for 20 h at 40 °C. Finally, the collected zeolites were
150 filtered, rinsed with de-ionized water, and then dried at 110 °C overnight.

151
152 **Figure 1:** Method for preparation of zeolite samples (101Z-106Z).
153
154
155
156

2.3. Characterization:

The synthesized zeolite samples were characterized by various analytical devices such as FTIR (Fourier Transform Infrared) of which, measurements were taken by a (Nicolet) Magna-FTIR – 560 (USA) with KBr technique. Powder X-ray Diffraction Analysis (XRD) of the zeolite, aluminium raw materials and Ca-zeolite samples were detected by a Brucker Axs-D8 Advance Diffractometer (Belgium) at ambient temperature in the 2θ range between 10° - 70° . TGA and DSC curves were used with an automatic recording model (50H Shimadzu thermal analyser, Japan). While the morphology and elemental analysis of the synthesized zeolite was characterized using SEM & EDX (Model FEI INSPECT S50) operating at 20 kV. BET was utilized for surface area measurements, total pore volume and pore radius. These were determined by Automatic ASAP 2010 Micromeritics sorptometer (USA) at liquid nitrogen temperature (77.350K) (Quanatachrome Instruments, version 11.04). XPS was performed in a Thermo-Fisher Scientific Instruments (East Grinstead, UK) with a quartz monochromator Al K α radiation of energy 1486.6 eV. For construction and fitting of synthetic peaks of high-resolution spectra, mixed Gaussian-Lorentzian functions with a Shirley-type background subtraction were used.

2.4. Adsorption Studies:

For purposes of studying sorption of Ca²⁺ ions onto tested zeolite samples, the sorption experiments occurred under the batch mode, separately because of its simplicity, reliability and ease to extrapolate at a larger scale for practical application. The adsorption experiments examined the individual effects of initial concentration (1000 - 4000 ppm), pH (2 - 10), contact time (1 - 180 min), adsorbent dosage (0.05 – 0.7 gm.50 ml⁻¹) and operating temperature (25 - 60 °C) have on the removal efficiency of Ca²⁺ by the synthesized zeolite. 0.5 g of zeolite samples were mixed with 50 ml of known Ca²⁺ solution in closed vials, continuously shaking at different time intervals to attain equilibrium at room temperature. The solutions were filtered, and the final Ca²⁺ concentrations were determined according to the standard method for 23rd

180 Edition no: 3500- Ca B [24]. The percentage of Ca^{2+} adsorbed by the zeolite materials was calculated by
 181 the following equation [1]:

182
$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \dots\dots\dots [1]$$

183 The value (q_e) (mg.g^{-1}) denotes the amount of the adsorbed Ca^{2+} onto the zeolite and was calculated
 184 according to the equation:

185
$$q_e = \frac{(C_o - C_e)}{m} \cdot \frac{V}{1000} \dots\dots\dots [2]$$

186 Where, the C_o and C_e are the initial metal ion concentration and the final metal ion concentration at
 187 equilibrium (mg.L^{-1}), respectively. m is the mass of adsorbent dose (g) and V is the volume of the solution
 188 (mL).

189 **2.5. Study of point of zero charge (PZC)**

190 0.1 g of dry zeolite sample was added to 50 mL of an aqueous solution of NaCl (0.01M), then the pH
 191 was adjusted in the range of 2-10 and stirred for 2 hr. The suspension was kept for 48 hours at room
 192 temperature to reach equilibrium, then the final pH was measured derived from the methodology described
 193 elsewhere [25]. Calculated ΔpH was according to equation ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) and then ΔpH was plotted
 194 versus pH_i .

195 **2.6. Regeneration of zeolite samples**

196 0.5 g of the spent materials after calcium adsorption was left in contact with 100 mL of 1 M of NaCl
 197 overnight. The spent adsorbent was filtered, washed, and dried at 40 °C.

198

199

200 **3. Result and Discussion**

201 **3.1. Characterization of the synthetic zeolite:**

202 **3.1. 1. XRD analysis**

203 The XRD results revealed the composition and the proper structure of the tested zeolite samples.

204 The raw materials of Al waste (scrap wire cables, takeaway foil containers, cans and two types of spray

205 aerosol bottles [105R & 106R]) were examined by XRD analysis. The results are presented in Fig. 2a, while

206 the composition of the synthetic zeolite in this work is shown in Fig. 2b. Based on the XRD pattern, the

207 result detected only pure synthetic aluminium sheet for all types of raw materials of aluminium waste

208 according to (JCPDS card no.: 04-0787). The XRD analysis obtained for zeolite (101Z, 102Z, 103Z, 104Z,

209 105Z and 106Z) in Fig. 2b confirmed and matched the standard card for the chemical structure of zeolite

210 type X, A and Y. The major constituent phase structure was recognized as a mixture of crystalline phase of

211 zeolite A and X according to (JCPDS no.: 38- 0241), (JCPDS no. :39- 0222) and (JCPDS no.:83- 2319),

212 respectively. Zeolite A had the highest intensity among all XRD peaks for all samples (101Z-106Z), and

213 the characteristic peaks of zeolite A at 2θ values were 7.2° , 10.3° , 12.6° , 16.2° , 21.8° , 24° , 26.2° , 27.2° ,

214 30° , 30.9° , 31.1° , 32.6° , 33.4° and 34.3° . Exceptions were considered for samples 103Z and 104Z, which

215 showed zeolite X phase as a major content at 2θ values of 5.7° , 11.41° , 19.59° and 23.02° [19]. Zeolite-X,

216 Zeolite-A, and Zeolite-Y are a member of the same zeolite family according to the crystallographic units

217 and their compositions [15]. Extending the reaction time & Si/Al molar ratio and increasing the degree of

218 temperature are the main reasons in the transformation of zeolite X, A and Y [26, 27]. The confirmed

219 chemical structure of zeolite samples from XRD technique are shown in Table 1. Sample 106Z was the

220 only sample which showed a small fraction of zeolite-Y. Similar results were reported in the literature [28-

221 31].

222 The crystallite size is conventionally determined by XRD analysis. All of the prepared zeolites were

223 crystalline materials in a cubic structure, as indicated by sharp XRD peaks, except for sample 104Z which

gave amorphous structure and had a different crystallite size. All samples were ranged in nano-scale and have cubic crystal shape (as shown in Table 1). Sample 104Z (prepared in an ice bath), had the smallest crystallite size in nano-scale (14.39 nm). This is likely due to the synthesis in low temperature, which has been reported to slow down the nucleation process and the growth of the crystal, leading to a small particle size [32, 33]. Conclusively, zeolite materials can be successfully synthesized from different aluminium waste resources, with no negative impact on the final products by using raw waste materials in terms of purity and morphology of the produced zeolites.

Table 1: Chemical structure, phases and the crystallite size for synthesized zeolite samples.

Sample name	major phase	Produced phases	Chemical structure	JCPDS card	Crystal shape	Crystallite size nm
Z101	Zeolite A	Sod. Aluminum silicate hydrate Zeolite A	$\text{Na}_2\text{Al}_2\text{Si}_{1.85}\text{O}_{7.75}\text{H}_2\text{O}_{5.1}$	38-0241	cubic	32.62
		Sod. Aluminum silicate hydrate Zeolite X	$\text{Si}_7\text{Al}_5\text{O}_{24}\text{Na}_{7.4}\text{H}_2\text{O}_{5.2}$	83-2319		
Z102	Zeolite A	Sod. Aluminum silicate hydrate Zeolite A	$\text{Na}_2\text{Al}_2\text{Si}_{1.85}\text{O}_{7.75}\text{H}_2\text{O}_{5.1}$	38-0241	cubic	58.91
		Sod. Aluminum silicate hydrate Zeolite X	$\text{Si}_7\text{Al}_5\text{O}_{24}\text{Na}_{7.4}\text{H}_2\text{O}_{5.2}$	83-2319		
Z103	Zeolite X	Sod. Aluminum silicate hydrate Zeolite A	$\text{Na}_2\text{Al}_2\text{Si}_{1.85}\text{O}_{7.75}\text{H}_2\text{O}_{5.1}$	38-0241	cubic	21.0
		Sod. Aluminum silicate hydrate Zeolite X	$\text{Si}_7\text{Al}_5\text{O}_{24}\text{Na}_{7.4}\text{H}_2\text{O}_{5.2}$	83-2319		
Z104	Zeolite X	Sod. Aluminum silicate hydrate Zeolite A	$\text{Na}_2\text{Al}_2\text{Si}_{1.85}\text{O}_{7.75}\text{H}_2\text{O}_{5.1}$	38-0241	cubic	14.39
		Sod. Aluminum silicate hydrate Zeolite X	$\text{Si}_7\text{Al}_5\text{O}_{24}\text{Na}_{7.4}\text{H}_2\text{O}_{5.2}$	83-2319		
Z105	Zeolite A	Sod. Aluminum silicate hydrate Zeolite A	$\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384.216}\text{H}_2\text{O}$	39-0222	cubic	21.70
Z106	Zeolite A	Sod. Aluminum silicate hydrate Zeolite A	$\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384.216}\text{H}_2\text{O}$	39-0222	cubic	69.73
		Sod. hydrogen Aluminum silicate Zeolite Y	$\text{Na}_{0.275}\text{H}_{6.725}\text{Al}_7\text{Si}_{17}\text{O}_{48}$	76-0110

Figure 2: XRD pattern for a) raw aluminum waste b) synthesized zeolite samples.

3.1.2. SEM and EDX analysis

Scanning Electron Microscopy (SEM) was utilized to show the morphology of the synthesized zeolite materials using Everhart-Thornley Detector (ETD) at different magnification levels as shown in Fig.3. SEM images showed a marked change in the morphology of samples 101Z to 106Z. The SEM images for the synthetic zeolite samples showed fully granulated uniform fine particles. The well-defined regular cubic crystals were exhibited in samples 101Z, 102Z, 105Z and 106Z, respectively. The cubic shape is regular in zeolite type A, as illustrated by many published papers [26, 27, 34, 35]. Sample 103Z, on the other hand, gave cabbage-like structures which are constructed by many straight nanosheets. Sample 104Z, interestingly, showed a flower-like shape as reported by other authors [36, 37]. The flower-like shape morphology for sample 104Z is likely assigned to the formation of the amorphous phase which affected the growth of crystals at a low operating temperature (5 °C).

Increasing crystallinity and grain size of the zeolite strongly depends on the Si/Al molar ratio [26, 38]. As a result of utilizing different precursors from disposed of raw aluminum waste, distinguished changes in the morphology of the samples was due to change in Si/Al molar ratio for the zeolite samples. This ratio is ranged from 1.06 to 1.27 and is close to the corresponding ratio to synthetic NaA zeolite. Additionally, the cubic shape and high crystallinity were confirmed from XRD results (Table 1) which are

recognizable for NaA Zeolite [27, 35, 39, 40]. Obtained results pointed to factors which have a great influence on the structure and morphology of the synthetic zeolite as precursors of used raw material and the temperature used herein in the preparation process.

EDX analysis confirmed the elemental composition and constituents of the tested types of zeolite. It is noteworthy that EDX analysis Fig 3 showed only Na, Al, Si and O elements existing in all tested samples. This confirms the purity composite phase with no impurities in all zeolite samples. Table 2 indicates that the calculated (Si/Al) molar ratios from the experiments were approximately 1.1 which is close to the theoretical calculation (1), except for sample 103Z (Si/Al), which was 1.27. The major difference between Na-X, Na-A and Na-Y zeolites were due to the corresponding ratio of Si/Al and were similar to the theoretically calculated values of the synthesis [41].

Table 2: EDX analysis for synthesized zeolite samples (101Z-106Z).

Samples	Elemental Analysis %				Si/Al	pH z
	Si	Al	Na	O		
101 Z	13.01	11.03	12.20	63.76	1.16	8.20
102 Z	12.65	11.91	12.63	62.81	1.06	7.90
103 Z	14.83	11.68	11.58	61.91	1.27	8.90
104 Z	14.82	12.35	11.99	60.84	1.20	8.01
105 Z	15.41	13.51	13.34	57.74	1.14	8.28
106 Z	15.19	13.49	13.80	57.52	1.13	8.01

Figure 3: SEM morphology for synthetic zeolite samples (1-6).

3.1.3. FTIR analysis

Fig. 4 illustrates the IR spectra of all synthesized zeolite samples (101Z-106Z). IR spectrum given absorption bands at 3498.6, 1639.1, 1000.2, 660, 557.8 and 456.7 cm^{-1} , respectively. The 1000.5 cm^{-1} bands for zeolite samples may be attributed to antisymmetric stretching of T–O bonds (where T = Si or Al) for aluminosilicates in the zeolite composition. Furthermore, the band around 1000 cm^{-1} , is attributed to Si–O–Al bonds in the TO_4 tetrahedra, which indicates the $(\text{SiO}_4)^{2-}$ groups for the symmetric stretching vibration of Si–O–Si [11, 26]. A broad peak with low intensity is present around 547.7 cm^{-1} , this peak indicates the existence of zeolite A band, assigning the cubic shape as indicated before in its SEM image (Fig. 3). Also,

the absorption band located at 557.8 cm^{-1} is attributed to Al-OH vibrations [19]. The bands at 456.7 and 660 cm^{-1} , respectively, are characterized to the internal linkage vibrations of the tetrahedral TO_4 ($\text{T} = \text{Si}$ or Al) and to the asymmetric stretching bending vibrations of Si-O-Si bond of zeolite, respectively. Furthermore, the broadband at about 3498 cm^{-1} and a band at 1639 cm^{-1} are assigned to water bending vibration of the H-O-H bond [11, 40, 42].

Figure 4: FTIR spectra for synthesized zeolite samples (101Z-106Z).

3.1.4 Nitrogen adsorption isotherms and surface area measurements

SBET was used to determine the porous properties: such as specific surface area, pore volume and pore size. This helps in recognizing the structure, formation and possible applications of different materials as shown in Fig 5 (a, b) and Table 3. The results exhibit that sample 104Z has the greatest BET surface area ($294.6\text{ m}^2.\text{g}^{-1}$) and total pore volume ($0.13\text{ cm}^3.\text{g}^{-1}$) from all the prepared products. These results agree strongly with results obtained from the XRD analysis, and it seems reasonable that sample preparation in low-temperature conditions can lead to the formation of some amorphous particles besides the crystalline

structure, thus all the crystallite size of zeolite particles exists in nano-sized scale. This result is in agreement with the work done by Mori et al. who reported that zeolite preparation at low temperature is affected the growth and size of the crystal formation. Thus during the crystallization process, the growing of crystal size is governed by temperature and time leading to the formation of amorphous along with crystalline structure [43]. The surface area follows the order of 104Z > 105Z > 101Z > 103Z > 102Z > 106Z. The synthetic zeolites in this study have a higher surface area than others published in the literature [14, 20, 44].

Figure 5: Texture properties for zeolite samples a) N₂ adsorption isotherm b) surface areas by BET theory.

Fig.5a has exemplified shapes of N₂ adsorption curves isotherm which exhibits the characteristic of type (I) isotherm in accordance with the nomenclature of International Union of Pure and Applied

Chemistry (IUPAC), which is typically featured for mesoporous materials [45]. Primary adsorption increment of volume of N₂ occurs at relative pressures P/P₀ (<0.35), which pointed to a highly microporous structure with a probability distribution of narrow pore size. Also, a sharp uptake indicating the rapid adsorption of N₂ on the textural surface of zeolite [46]. The linear absorbance from 0.1 to 0.4 relative pressures P/P₀ is responsible predominantly due to the mesoporous region. Mesoporous substances are known to be wonderful host substructures, due to bulky, symmetrical pore diameters and large surface area [47, 48]. It is interesting to note that by application BET model onto the tested zeolite proved excellent adsorption ability of N₂, taking account of good surface area in the adsorbent sample [46].

Table 3: Surface properties for synthesized zeolite samples.

Sample	BET Surface Area (m ² .g ⁻¹)	Total Pore Volume (cm ³ .g ⁻¹)	Average pore Radius (Å)
101 Z	183.5	0.09	5.78
102 Z	110.7	0.05	9.88
103 Z	285.2	0.13	5.69
104 Z	294.6	0.13	6.19
105 Z	275.3	0.13	5.86
106 Z	102.4	0.04	10.36

317

3.1.5. Thermogravimetric analysis

Fig. 6 (A-F) evaluated TG, DTG and DSC thermograms for tested zeolite samples. All zeolite samples have total weight loss calculated from the TG curve to be approximately 18% at a temperature below 200 °C. A sharp main DTG peak occurs at range (149-156 °C) for all synthesized zeolite samples. This main peak around 140-200 °C is produced from loss of water hydration that is highly bound in the

zeolite structure [49]. While sample 105Z shows a shoulder in the DTG trace at approximately 74.63 °C and sample 102 Z has two significantly small shoulders in the DTG trace that occurs at approximately 52.9 and 82.9 °C, respectively. It is commonly known that peaks between 40-50 °C and 70-100 °C can be referred to the release of weakly bound water [26]. Fig. 6 for DSC curves shows two endothermic peaks, the strongest and sharpest one was between 160 and 185 °C and the other broad peak was around 350 °C. The highly sharp DSC peak described the exclusion of surface, physically adsorbed water when being below 200 °C. While the broad DSC peak around 350°C may be attributed to the removal of chemical adsorbed water in the pores [50, 51].

Figure 6: TG, DTG and DSC curves for zeolite samples a) 101Z, b) 102Z, c) 103Z, d) 104Z, e) 105Z and f) 106Z.

335 **3.1.6. XPS analysis**

336 The XPS analysis was performed on the synthesized zeolite materials (Z101-Z106) to detect the
337 composition and oxidation states of the oxygen surface species along with the binding energies as shown
338 in Figure 7. The *C1s* peak for both of them was mainly at the binding energy of 284.6 eV (C-C, C-H) as
339 shown in Figure S1 (supplementary information) along with small peaks at around 288.1, 285.9, 284.2,
340 282.3 eV which are attributed to the C=O, C-O, sp^2 hybridized carbon and Si-C bonding in the surface
341 structure of the synthesized zeolites [52]. On the other hand, the *O1s* spectra revealed that most of the
342 oxygen species are oxygen lattice in all the six samples (Z101-Z106) at a binding energy of 530.0 eV as
343 shown in Figure 7. The zeolite samples of 101Z and 104Z showed also OH group or CO₂ adsorbed in the
344 form of carbonate on the surface at a binding energy of 531.4 eV. While zeolite samples of 102Z and 103Z
345 showed Al-O-Al or Si-O-Al bonding at a binding energy of 531.6 eV. Finally, samples of 105Z and 106Z
346 showed similar surface oxygen species at binding energies of 527.9 and 532.6 eV which attributed to
347 nucleophilic oxide and oxygen in the SiO₂ structure, respectively.

Figure 7: XPS spectra of *O 1s* for the synthesized zeolites Z101-Z106.

3.2. Softening of water from Ca^{2+} ions:

Nowadays, a significant challenge in developing countries that has gained attention is to manage and solve water problems. Based on recent technologies, researchers and industries are concerned with finding and utilizing economically viable and inexpensive techniques for softening hard water supplies. Zeolitic material has a unique property to be used as ion exchanger in an aqueous solution [14]. Based on this specific property, our zeolite samples (101Z-106Z) shows an effective affinity for the elimination of Ca^{2+} from solution. The removal efficiency reached 85% at a very high level of Ca^{2+} content (1000 ppm). Based on the XRD analysis of loaded Ca-zeolite (Fig.S2), we proved undoubtedly that the tested zeolites were able to uptake Ca^{2+} ions from aqueous solution, according to the cards no.: 47-0003 (I), 76-1509(c), 88-0188(c) and 11-0589. All zeolite samples (101Z-106Z) changed their structure from Na-zeolite (mainly NaX, NaA) to Ca-zeolite and appear as sodium calcium aluminium silicate hydrate zeolite, calcium aluminium silicate hydrate zeolite A, calcium aluminium silicate hydrate zeolite X and calcium aluminium silicate hydrate Zeolite linde A, respectively. Two essential factors influence in the cation exchangeability of the zeolite. The first one is the Si/Al ratio. Zeolite samples with low Si/Al ratio below 2 have excellent ion exchange capability in water treatment. Another factor that affects cation exchange properties is the size and arrangement of cavities in channels and cages in the crystal structure of the zeolite. This allows the cations with a specific size to transport inside them. The common rule is that ion-exchange selectivity of zeolites is elevated for higher valance cations [13]. In this study, the zeolites have a Si/Al ratio around 1.1, making them a suitable adsorbent for the softening of water. Type A zeolite is considered the lowest Si/Al ratio with value equals 1 and display a good cation exchange capacity and high sorption attainment [53]. In addition, tested zeolite samples have high crystallinity that dominates a narrow range of pore sizes indicating the selective ability of the solid phase better than non-crystalline particles [54]. It is simple to understand the mechanism of ion exchange based on the negative charge in zeolite structures as AlO_4 and

SiO₄ are balanced by Na ions, which is exchangeable with an external medium such as Ca²⁺ present in the solution [13, 54]. Negatively charged zeolite molecules will easily withdraw positively charged calcium Ca²⁺ ions in their channels and monovalent sodium ions are substituted by divalent calcium ions. Only 10 g.L⁻¹ of zeolite samples are sufficient to remove 85% of Ca²⁺ present in aqueous solutions. Others feature of the tested zeolite samples is the ability for using 3 sequence cycles in the aqueous solution and it can be regenerated again effortlessly.

3.3. Effect of initial concentrations for calcium ions:

Considering the great effect of initial concentration values of water samples in the adsorption process, we investigated our zeolite samples at very high Ca level in water solution (1000 ppm-4000 ppm) at 20 °C. The effects of initial metal ions concentration had been explored and demonstrated in Fig. 8A. It is clear from obtained data, that all samples have high affinity to capture Ca²⁺ from aqueous solutions and is highly influenced by the concentration of loaded Ca ions in solution. With increasing the initial Ca²⁺ concentrations, the extent of Ca²⁺ ions removal is decreasing in most cases. This is maybe due to there are no more sites are available at fixed zeolite dose. It can be understood that the ion exchange sites are saturated with Ca²⁺ cation species and about to exhaust nearly all its exchange aptitude [7, 55, 56].

3.4. Effect of pH

pH values affected the adsorption capacity of zeolite samples in two distinguishable ways. One effect was on the metal solubility and evolution of distinct species onto the solution, the other is on the total charge of adsorbents [13]. The removal intensity of Ca²⁺ ions from the solution had been illustrated in Fig. 8B. First of all, zeolite samples showed a good removal ability in the entire range of pHs studied. Despite the fact that a slight decrease was observed at pH 2 (strong acidic medium) still, the removal of Ca²⁺ ions was high and removed 65% of the total. Taking into consideration, a pH value lower than 2, the zeolite may undergo

397 deformation due to the dissolution of Al atoms [57]. Final pH values after mixing synthesized zeolite
 398 samples with the CaCl₂ solution (1000 ppm) were illustrated in Table (4). The values of the pH increased
 399 significantly after the addition of adsorbents for the initial step of pH 2 to pH 4. This may be attributed to
 400 the competition between the large amount of H₃O⁺ with the Ca²⁺ onto the active sites [58]. At further
 401 increase in initial pHs of more than 4, no significant change was observed in final pH and remained constant
 402 around pH 7. It is notable, that zeolite samples have a buffer capacity over the studied pH range from 2 to
 403 10. The buffering behaviour of zeolite samples may be explained by the surface charge on zeolite materials,
 404 which can be measured by the point of zero charge for the tested zeolite surfaces. The point of zero charges
 405 (pH_{pzc}) values for the prepared zeolite are shown in Fig. 8F and Table (2). The pH_{pzc} values were 8.2, 7.9,
 406 8.9, 8.0, 8.3 and 8.0 for zeolite samples from 101Z to 106Z, respectively. At pH values below the pH_{pzc}, the
 407 surface of the zeolite will have a positive charge, while at a pH value higher than the pH_{pzc}, the exterior
 408 surface is dominated by negative charges [13, 59]. The zeolite surface charges, caused by ionization of
 409 external hydroxyl groups (Si-OH and Al-OH), is strongly dependant on acid/base reduction when the zeolite
 410 is exposed to water solution [14]. Firstly, increasing the initial pH up to 4.0 gave rise to raise the final pH.
 411 This may be explained as zeolite samples dominated alkalinity and ion exchange reaction between the Na
 412 ions in the zeolite and Ca²⁺ ions in the solution, which could increase the pH value readily at acidic pH [60].
 413 Further increase in the initial pH did not cause any changes of final pHs and the solution stayed constant at
 414 pH 7. The plateaus of the curve indicated that adding of the H⁺ ions or OH⁻ ions have no effect on the final
 415 pHs and they are close to point of zero charge of samples. This phenomenon shows buffer properties of the
 416 zeolite samples according to the total acidity of a zeolite (i.e. the total Lewis & Brønsted acidic site). Similar
 417 data were published by other authors [61]. The obvious observation from the above results is that the
 418 synthesized zeolite contained a high efficiency for the capture of Ca²⁺ in a broad range of pH values [62].
 419 **Table 4:** Final pH and final electrical conductivity (EC) measurement for aqueous solution.

pH initial	pH final						Conductivity uS					
	101Z	102Z	103Z	104Z	105Z	106Z	101Z	102Z	103Z	104Z	105Z	106Z
2	6.2	5.86	6.2	4.81	5.74	5.94	5.05	5.07	5.14	5.54	5.07	5.07
4	7.18	7.25	7.62	7.76	7.46	7.34	5.15	5.12	5.14	5.18	5.15	5.19
6	7.33	7.03	7.70	7.88	7.56	7.31	5.12	5.16	5.16	5.18	5.29	5.36
10	7.18	7.65	7.94	8.32	7.57	7.30	5.12	5.12	5.10	5.2	5.07	5.21
Blank	7.5						5.01					

Otherwise, metal uptake capacity in the adsorption process is strongly influenced by partial dissolution of the zeolite material as an adsorbent in the solution used. Electrical conductivity (EC) measurements were illustrated in Table 4. The Electrical conductivity has a slender increase than the blank run of Ca^{2+} solution in the entire pH range tested. This increase is ranged from 5.05 to 5.21 $\mu\text{S}\cdot\text{cm}^{-1}$ in most cases and can be ascribed to the change of some soluble parts from the adsorbents achieved by the ion exchange performance of Na^+ by Ca^{2+} ions. Furthermore, structures containing zeolite units will be considered as promising future materials, due to their high resistance of pH and approximately constant EC values which allows them to be utilized in different acidic (achieved approximately 65% removal) and basic mediums (more than 80% removal). The buffer capacity of the zeolite samples is attributed to the presence of acidic and basic sites on the surface of zeolite (Brønsted & Lewis acidic and basic sites). The Si/Al ratio in the framework is the reason for the cation exchange capacity of zeolites. The high performance of the tested zeolites over the wide initial pH range is related to their buffering capacity.

3.5. Effect of contact time:

The equilibrium time is an indispensable parameter for economical water and wastewater treatment plant application of new adsorbent technologies [63]. It can be used in successful practical implementations, such as designing of the reactor and optimization the operation process [64]. The influence of contact time on Ca^{2+} ions removal was carried out over a period of time extended from 1 to 180 min. The results are shown in Fig. 8C. The removal of Ca^{2+} ions was very fast within the first-minute corresponding to >50% removal. With an increased contact time, the adsorption increased slowly to attain equilibrium at 30 min. The rapid initial stage is perhaps due to the accessibility of plentiful active sites on the zeolite surface, and with the progressive occupation of these sites, the sorption then became lower in the later stage. Rapid Ca^{2+} uptake by zeolite samples may be attributed to its highly porous and mesh structure of the binding sites [58, 65]. There was no need to elapse more time than 60 min, as there is no considerable variation in the reduction of Ca^{2+} after this period [62].

3.6. Effect of adsorbent dose:

Sorption capacity is strongly influenced by the adsorbent mass in solution or the Solid/Liquid ratio (S/L). The removal of Ca^{2+} is affected by (S/L) ratio as illustrated in Fig. 8D. The solid amount of the adsorbent is varying from 1 g.L⁻¹ to 14 g.L⁻¹ and the liquid volume was kept constant. It is clear from the obtained results that the removal of Ca^{2+} ion increased with increasing the S/L ratio. The increase in the Ca^{2+} uptake may be due to the greater availability of the exchangeable sites and different types pore on the surface of the zeolite [66].

3.7. Effect of temperature:

Figure 8: Factors affect the adsorption of Ca^{2+} ions: A) Effect of initial concentration, B) Effect of pH
C) Effect of time D) Effect of dose E) Effect of temperature F) pHpzc

The sensitivity of changing the temperature on the Ca^{2+} ions sorption process is demonstrated in Fig. 8E. The temperature range that was applied herein ranged from 25 to 60 °C. Increasing the temperature led to a slight augment in Ca^{2+} ions removal implying that the adsorption process will be endothermic in nature, thus enhances the adsorption of metal ions on the surface of the adsorbent substance [67]. It was evident from the obtained data that varying temperature values (25 – 60 °C), didn't strongly influence the adsorption capacity of the zeolite. This phenomenon may be a good and suitable feature for the utilization of these zeolites in contaminated groundwater and surface water with hardness ions in situ management. Interestingly, the synthesized zeolites could be used with a good performance in various water resources globally, where the water temperature varies with the climate and nature of location [68]. Furthermore, the endothermic nature was demonstrated from the results of thermodynamic calculations in section 3.8.

In Fig. 8, sample 104 Z behavior is almost different than other samples that may be due to the various reasons. It showed zeolite X phase as a major content, unlike other zeolite samples which showed zeolite A phase as a major content as shown in Figure 2 in the XRD section. It also had the smallest crystallite size of 14.39 nm as shown in Table 1 along with the largest surface area of 294.6 m²/g (Table 3) among the synthesized zeolite materials. It is well known that zeolite type X has more tendency and selectivity toward CO₂ capture from the air than other types of zeolite A and Y, which makes it less active in water solution application [69, 70].

3.8. Thermodynamic parameters:

Determination of thermodynamic constants is of significant use to investigate the spontaneity of the adsorption system and the probability of the process at a given temperature [67]. The thermodynamic adsorption parameters ΔG° , ΔH° and ΔS° are expressed with the help of the equation (3-5) and written in Table (5).

$$K_{CO} = \frac{C_{ad}}{C_e} \quad [3]$$

$$\Delta G^{\circ} = -RT \ln K_c^{\circ} \quad [4]$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad [5]$$

Where C_{ad} is the concentration of metal ion (mg.L^{-1}) on the adsorbent at equilibrium and C_e is the concentration of metal ion (mg.L^{-1}) in solution at equilibrium. The change in standard free energy, enthalpy, and entropy of the adsorption process is denoted as ΔG° , ΔH° and ΔS° , respectively.

Table 5 shows the thermodynamic parameter values of ΔG° , ΔH° and ΔS° , as these are used to recognize the characteristic of the sorption system. Sorption of Ca^{2+} ions has negative values for ΔG° for all studied zeolite samples. This illustrates the favorability and spontaneity of the adsorption process at all operating temperatures. Thus, increasing the negative sign of ΔG° by increasing the temperature, confirms preferable adsorption at elevated temperature. The sign of ΔH° values for all zeolite materials are positive and emphasize the endothermic nature for the adsorption process [19]. Another parameter, ΔS° has positive sign values for all the tested zeolites, and the increase of entropy is a result of adsorption. This arises from the energy redistribution among the adsorbate and the adsorbent. Displaying a positive value of ΔS° , the rotational and translational energy distributed amongst a small number of molecules will have augmentation in adsorption, leading to a rise of the randomness at the solid-solution interface during the adsorption process [71]. In general, the value of ΔH° is observed in the range of 7.9 to 10.83 kJ.mol^{-1} and was <40 kJ.mol^{-1} , which refers to physical adsorption. An ion exchange process would have an exothermic or endothermic nature. In the exchange process, the limits of the adsorption energy have ranged between 0.6 kJ.mol^{-1} and 25 kJ.mol^{-1} [72]. The obtained results belong to the same range; indicating ion-exchange taken place herein.

513 **Table 5:** Thermodynamic constants for sorption system of Ca²⁺ ions onto zeolite.

Sample	ΔH (kJ.mol ⁻¹)	ΔS J.mol ⁻¹ .K	ΔG (kJ.mol ⁻¹)				
			26 °C	37 °C	40 °C	50 °C	60 °C
101 Z	10.83	44.06	-2.33	-2.82	-2.95	-3.39	-3.83
102 Z	9.27	38.18	-2.14	-2.56	-2.68	-3.06	3.44
103 Z	13.95	52.74	-1.81	-2.39	-2.54	-3.07	-3.60
104 Z	16.33	59.59	-1.48	-2.13	-2.31	-2.91	-3.50
105 Z	11.81	48.07	-2.55	-3.08	-3.22	-3.70	-4.18
106 Z	7.96	36.33	-2.89	-3.29	-3.40	-3.77	-4.13

514
515 **3.9. Competitive adsorption in binary solution competing between Mg²⁺ & Ca²⁺ ions**

516 Ions of calcium and magnesium usually exist concurrently in most water supplies and can be
517 expressed as total water hardness. With a view to studying the competing effect of Ca²⁺ and Mg²⁺ ions on
518 adsorption capacity of zeolite samples, tests were undertaken for a mixture of Ca²⁺ and Mg²⁺ cations (1:1)
519 with total concentration 1000 mg. L⁻¹ and mixture (2:1) with high total hardness 3800 ppm. Results were
520 demonstrated in Fig.9 (a,b). The removal of cations were 92% and 89% for calcium and magnesium,
521 respectively. As a result, the total water hardness was eliminated by 90%. Without doubt, increasing the
522 total hardness to 3800 ppm in a mixture of Ca²⁺ and Mg²⁺ (2:1), showed selective removal of Ca²⁺, rather
523 than Mg²⁺ ions. Therefore, the total hardness decreased by 55%, while the average removal of Ca²⁺ was
524 about 80% and only 18% for Mg²⁺ ions. The decrease in ion exchange of Mg²⁺ ions by zeolite type A may
525 be due to size and charge of Mg²⁺ ions. Mg²⁺ ions surrounded by large hydration zone makes it hard to enter
526 and pass through the sodalite cages of zeolite- A [73]. Notably, adsorption efficiency decreased when
527 compared with the observed values in single ion adsorption measurement. This can be explained by fast

occupation and saturation of the active sites of the adsorbent by the competitiveness between Ca^{2+} and Mg^{2+} ions on the surface of the zeolite. Regarding the tests observed for single ion adsorption, zeolite materials have great adsorption capacity and showed higher selectivity toward Ca^{2+} rather than Mg^{2+} ions [11]. Other publications showed that zeolite of NaA type exhibited higher Ca^{2+} removal more than Mg^{2+} from solution at ambient temperature [41].

Figure 9: Competitive adsorption in mixture Mg^{2+} & Ca^{2+} ions a) mixture (1:1) b) mixture (2:1).

3.10. Cycles and regeneration of exhausted zeolite

An additional and unique characteristic for zeolite samples is having a tendency for regeneration and utilization for more than a few cycles after sorption of metal. Adsorption and desorption experiments were applied to reprocess the tested zeolite samples for a more economically viable utilization in consecutive sorption cycles. The synthesized zeolite samples can be used competently for consecutive cycles at high Ca content (1000 ppm) without washing or regeneration of the samples. The 1st cycle of zeolite removed more than 83% of Ca^{2+} , while, in the 2nd cycle removed about 24% and in the 3rd cycle

552 removed about 6% as displayed in Fig. 10. The decrease in the adsorption capacities for recycled zeolites
553 may be attributed to saturation of the zeolite pores with the overflow of Ca^{2+} . It is better to reactivate the
554 zeolite after the 2nd cycle, especially at very hard water content to be reused once more with high capability
555 for Ca^{2+} adsorption.

556 Cost-saving regeneration and performance capacity in the sorption process preferred simple and
557 low-price reagent. Saturated Ca-zeolite samples (Ca-adsorbed zeolites) were impregnated in 1 M of NaCl
558 solution, shaken for 6 hours at room temperature and then filtered and dried. Regeneration did not require
559 a high temperature or costly solvent, only NaCl solution is used as a facile way. The regenerated zeolites
560 after 4 hours, showed an increase in the adsorption efficiency by up to 40 %. This may be due to the
561 magnitude of the ion-exchange ability of sodium ions to replace calcium ions inside the zeolite samples
562 when using the NaCl solution [60]. According to the rules of cation exchange capacity (CEC) on zeolite
563 previously published [13], all aluminous zeolite prefer trading NH_4^+ and/or Na^+ ions from solution. In this
564 research, we chose to use NaCl to regenerate synthesized zeolite samples for lowering the cost of the
565 regeneration process. Our result assured us that the zeolites samples are distinctly reusable. The
566 regeneration of the spent zeolite materials was performed using a sodium chloride solution, this means that
567 the brine solution left after the softening of the seawater could be used to regenerate the zeolite materials.

Figure 10: Removal of Ca²⁺ ions in consequence cycles.

3.11. Equilibrium studies

Adsorption isotherm means a correlation between the quantity of a substance adsorbed (mg.g⁻¹) from the liquid phase and its equilibrium concentration at a fixed temperature. Information from adsorption equilibrium constants and the fundamental thermodynamic hypotheses of the used equilibrium models often help in understanding the adsorption mechanism and explaining the characteristic of sorbent surface. They are useful to determine the characteristics of an adsorbent if they suitable for application related to design purposes [13].

The adsorption behaviour of prepared zeolites for the removal of Ca²⁺ was analyzed in terms of isotherm models. There are three commonly used isotherm models namely; Langmuir, Freundlich and Temkin isotherms which were applied to fit the experimental data. The linear and non-linear forms of these equations are given by:

Freundlich isotherm eq (6): $q_e = K_f C_e^{\frac{1}{n}}$ and linear form $\log q_e = \frac{1}{n} \log C_e + \log K_f$

Langmuir isotherm eq (7): $q_e = \frac{q_{\max} K_a C_e}{1 + K_a C_e}$ and linear form $\frac{1}{q_e} = \frac{1}{K_a q_{\max}} \cdot \frac{1}{C_e} + \frac{1}{q_{\max}}$

Temkin isotherm eq (8): $q_e = B \ln A + B \ln C_e$ $B = RT/b$

Where:

C_e (mg.L⁻¹) and q_e (mg.g⁻¹): are the equilibrium concentrations in liquid and solid phase, respectively.

$q_{\max}$: is the maximum metal uptake (mg.g⁻¹), K_a : is Langmuir constant, K_f (L.g⁻¹) and n : are Freundlich constants, b : is Temkin constant related to the heat of sorption (J.mol⁻¹.) and A is the Temkin equilibrium binding constant (L.mg⁻¹).

In addition, the non-linear regression modality was used to set the alternative isotherm parameter. Comparisons between Langmuir, Freundlich and Temkin, isotherm linear regressions for equilibrium data of the present work were shown in Fig. S3, while the nonlinear fitted curves were demonstrated in Fig. 11 (A-F) and their correlating parameters were presented in Table (6). The experimental data fitted well to Langmuir, Freundlich and Temkin isotherm models for all zeolite samples in linear and nonlinear forms. Nevertheless, Freundlich and Temkin's isotherm gave the highest regression coefficients, with R² closest to unity compared to Langmuir isotherms. This result confirmed the ion exchange effect in the adsorption process [74]. Moreover, the three tested models were close in the regression values, and this suggested the surface of the adsorbent contained a heterogeneous structure [11]. Based on data derived from the Langmuir isotherm model, the maximum monolayer adsorption capacity of synthetic zeolite to Ca²⁺ ions have high values are 90.9, 90.9, 85.47, 85.0, 105.2 and 111.1 mg. g⁻¹ in zeolite samples (101Z-106Z), respectively. High discerned $q_{\max}$ values were observed, compared with different adsorbents materials published for hard water softening [1, 2, 19, 49, 68]. Therefore, all synthesized zeolites can be regarded as a promising material that can be successfully used in desalination processes.

According to R_L (equilibrium constant or dimensionless separation factor), values derived from the Langmuir isotherm model is referred to the nature of adsorption (Table 6). R_L values were ranged from 0.03

613 to 0.067 and fall between $0 < RL < 1$. This indicated adsorption of Ca^{2+} ion on the zeolite surface is a
614 favourable operation [2, 49]. Based on the results Freundlich model, the affinity coefficient (K_f) values
615 were high and ranged from 38.8-51.64 for samples 101Z to 106Z, this indicated the high affinity for cation
616 in the present medium. Also, the Freundlich constant (n) were > 1.0 and this indicated the favorable
617 adsorption process. A similar trend was reported by [55].

618 At a fixed temperature (298K), the obtained Temkin constants b (J.mol^{-1}) ($b = RT/B$) for all zeolite
619 samples were less than 80 KJ.mol^{-1} , which revealed that the heat of adsorption of Ca^{2+} onto zeolite is
620 considered a physical adsorption behavior [2]. Furthermore, the constant A (L.g^{-1}) has high values (Table
621 6) and refers to its strong bonding of Ca^{2+} ions onto the zeolite samples [55]. In addition, high b values
622 indicated rapid sorption of adsorbate at the initial stage that fast sorption equilibrium was achieved in 30
623 min and has been previously discussed (Fig.8C). The fitting of the three isotherm models to the Ca^{2+} ion
624 zeolite samples system suggested that both monolayer sorption and heterogeneous surface co-exist under
625 these experimental circumstances. This indicated that the adsorption of Ca^{2+} ions on these adsorbents is
626 quite complex and more than one mechanism is involved [75]. It is widely known that the Langmuir
627 isotherm model illustrates the ion-exchange mechanism, while the Freundlich isotherm confirmed complex
628 reactions going on in the adsorption process [76]. These models cannot totally demonstrate all interactions
629 occurring in an adsorption system or explain the fundamental mechanism. That may be understood, because
630 the interaction between the active functional groups on the adsorbents surface and the metal ions in solution
631 may be associated by involving electrostatic attraction, adsorption/precipitation, hydrogen bonding, ion-
632 exchange or chemical interaction [4].

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Table 6: Langmuir, Freundlich and Temkin Isotherm constant.

Sample	Langmuir constants				Freundlich constant			Temkin constant			
	$q_{\max}$ (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R^2	R_L	n	K_f (mg.g ⁻¹)	R^2	b J.mol ⁻¹	B	A	R^2
101 Z	90.90	0.037	0.873	0.030	13.51	51.64	0.971	403.18	6.145	1306	0.958
102 Z	90.90	0.028	0.842	0.039	11.76	46.99	0.948	356.99	6.94	204.9	0.927
103 Z	80.645	0.0124	.079	0.037	9.71	38.82	0.842	306.28	8.089	19.34	0.811
104 Z	83.33	0.014	0.99	0.067	10.58	38.79	0.968	364.2	6.803	58.66	0.973
105 Z	105.26	0.016	0.842	0.06	8.85	43.35	0.956	234.84	10.55	8.52	0.936
106 Z	111.1	0.015	0.833	0.062	9.09	44.06	0.947	241.95	10.24	10.68	0.922

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Figure 11: Non-linear form of Freundlich, Langmuir and Temkin Isotherm on adsorption of Ca^{2+} on:

A) sample 101Z, B) sample 102Z, C) sample 103Z, D) sample 104Z, E) sample 105Z, F) sample 106Z.

Curves in Fig. 11 (A-F) show concave downward (type I), which can be referred to as favorable behavior for the uptake process. This shows the advantage of the expected regenerative operations. Favorable isotherm may be also suitable for effective regeneration [77]. The experimental data showed good fitness on Freundlich and Temkin on non-linear curves rather than Langmuir curve.

3.12. Kinetic studies:

Various kinetic models illustrate and classify the order of adsorbent–adsorbate interactions, where traditionally, the pseudo-first and pseudo-second-order model are used as shown in equations (10-11) and (12), respectively. To identify the intraparticle diffusion, Weber-Morris equation [12] was applied.

$$\text{Log}(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad \text{Equation [10]}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \quad \text{Equation [11]}$$

$$q_t = K_d t^{0.5} + C \quad \text{Equation [12]}$$

Where q_e and q_t (mg. g⁻¹) are the amounts of sorbate that are adsorbed at equilibrium and at any time (t). K_1 (min⁻¹) and K_2 (g.mg⁻¹.min⁻¹) are the equilibrium rate parameters of pseudo-first and pseudo-second-order sorption, respectively. The calculated values of correlation coefficients (R^2) based on the obtained data demonstrate very good linearization to the pseudo-second-order model more than the pseudo-first-order model as illustrated in Table (7). Furthermore, the computed q_e values derived from the pseudo-second-order model are more sensible than those of the pseudo-first-order, by comparing to those of q_e calculated from the experimental data. Thus, pseudo-first-order kinetics might not be adequate to describe the mechanism of the interactions of Ca²⁺ ions–adsorbent.

Many publications relating to salt ions on zeolite samples fitted well with the pseudo-second-order among the kinetic models and always referred to chemisorptions as the rate-controlling step. Therefore, a

more detailed future work is needed to shed light on the nature of chemisorption sites. Furthermore, the pseudo-second-order kinetics are not exclusively emphasis of chemical sorption [2, 13]. It is explicit from the antecedent results of thermodynamics (Table 5) and from Timken constant isotherm (Table 6), that adsorption of Ca^{2+} ions tested with zeolite was well-thought-out as physical adsorption. Thus, we suggested that the mechanism for adsorption of Ca^{2+} ions onto the zeolite surface can be explained by the electrical double layer (EDL) theory. This hypothesis is based on an existing electrical double layer around each zeolite particle when dispersed in the salty solution. The first layer is engaged by strongly bound ions (Stern layer), while the next layer is surrounded by less strongly bound ions (diffuse layer). When zeolite particles have a higher electrical charge, then the diffusion layer will be greater and more cations will be easily adsorbed [2, 13, 78].

Based on the previous results that confirmed rapid removal of Ca^{2+} ions by zeolite surface, the intra-particle diffusion model (Weber and Morris equation) were illustrated to identify the diffusion mechanism of the adsorption processes. The adsorption mechanism may be governed by single or multiple steps. These processes are predominantly external or film diffusion, pore diffusion at macropore (or micropore), surface diffusion, adsorption on the pore surface, or all together [49]. According to results from the intra-particle diffusion model (Fig.12 IV), the adsorption of adsorbate on zeolites is dominated by more than one mechanism, thus this yields a multi-phase step for sorption mechanism. This indicated that both intra-particle diffusion and film diffusion participate in the ion exchange processes [49, 79]. Furthermore, the C value derived from the intercept of the equation [12] described the thickness of boundary layer [80]. The thickness of the boundary layer is the region of the surface adsorbent that is responsible for adsorption ability to attract the sorbent. The higher intercept C value gave a better impact on the boundary layer, which is responsible for fast adsorption [49]. All zeolite samples have fast adsorption within 30 min and reduced the hardness significantly. The interpreted C values had greater values, which indicated a quick adsorption process for all synthesized zeolites. The ion exchange mechanism may involve more than one step and is

comprised of both film diffusion and intra-particle diffusion processes [12]. Fig. 12 IV of intraparticle diffusion, the graph dominated more than one step that was involved in the sorption mechanism [49, 80]. The uptake of salt ions may be ascribed to ion-exchange as well as adsorption mechanisms. Calcium ions moved through the pores and channels of the zeolite lattice to be exchangeable by sodium ions during the ion exchange process. Furthermore, diffusion through the smaller diameter channels is achieved rapidly when the ions moved [79].

Figure 12: Kinetic Studies: I) pseudo-first, II) pseudo-second and intra diffusion (III, IV).

710 **Table 7:** Kinetic Studies, pseudo-first, pseudo second and intraparticle diffusion constant.

Sample	Pseudo-first order			Pseudo-second order			Intraparticle diffusion			q _e (Exp)
	K ₁	q _e	R ²	K ₂	q _e	R ²	K _{ad}	R ²	C	
101 Z	0.014	4.68	0.613	0.033	71.43	0.999	0.914	0.715	62.34	72.8
102 Z	0.014	3.09	0.647	0.039	71.43	0.999	0.481	0.792	64.88	70.6
103 Z	0.015	4.14	0.626	0.034	66.67	0.999	0.777	0.732	57.78	66.7
104 Z	0.025	19.95	0.918	0.006	68.39	0.999	1.517	0.853	49.98	68.2
105 Z	0.023	16.59	0.808	0.0076	81.04	0.999	0.518	0.894	73.83	80.7
106 Z	0.019	17.49	0.769	0.0072	83.33	0.999	0.433	0.859	76.13	82.8

711

712 **3.13. Applications in field study and real samples**

713 Expediency of the recently synthesized zeolite materials was used in hard water experimental
714 samples obtained from two different real water sources: 1) A groundwater well in the surrounding area
715 where the total hardness was measured to be 1326 ppm 2) Seawater samples obtained in Hurghada City,
716 Egypt and has a measured total hardness of 7506 ppm. The preliminary data displayed an elimination
717 efficiency for hardness ions of approximately 96% for Ca²⁺, around 50% for Mg²⁺ ions in groundwater well
718 samples and removing 75% of the total hardness. While efficiency for hardness removal in seawater was
719 around 45% for removing Ca²⁺ ions and only about 10% for Mg²⁺ resulting in a decrease of 15% in the total
720 hardness. The results are demonstrated in Fig. 13. The reduction in percentage removal of hard ions by
721 some tested adsorbents in the field samples compared to the pure solutions may be due to the competing

effect of some interference anion such as Cl, SO₄ or NO₃ and existence of suspended organic substances. This data may be used for wide application in the reduction of a large amount of seawater hardness in the pretreatment process, helping to prolong the lifespan of membranes used in wastewater companies. A similar trend was published in works by Hatas et al. and Song et al. [58, 80].

Figure 13: Removal efficiency for Ca²⁺ and Mg²⁺ ions removal from a) groundwater well b) seawater

3.14. Removal comparison with literature

Table 8 shows the comparison between capacity of the tested zeolite materials herein and other published adsorbent materials for the elimination of hardness ions in literature. The efficiency of the zeolitic materials derived from waste showed excellent removal affinities even more than other available low-cost materials. Most of the previously reported hardness removal in the literature were performed at low initial hardness concentration such as 80 ppm [40, 61], 100 ppm [58], 120 ppm [1], 150 ppm [3, 11], 220 ppm [57] for Ca²⁺ ions and 250 ppm for Mg ions [81]. Furthermore, other low- cost materials for reduction of Ca²⁺ were attained as modified sugarcane bagasse & coffee husk [8], Raw pine cone & modified pine cone [9], MIEX-

Na resins [10] and grafting copolymerization of acrylic acid [65]. The aforementioned materials, again have been tested in solutions containing small Ca^{2+} content (120, 230, 103 and 20 ppm, respectively) which is not considered hard water. While the zeolite materials herein exhibit great benefits for application in water remediation at extremely high salt concentrations (1000- 4000 ppm) and are the as promising substances for removal of hardness from water supplies. Furthermore, it is worth noting that the Ca^{2+} removal herein was achieved in such a short time about 30 minutes along with the synthesized zeolite materials were effective in acidic, basic and neutral solutions. It can also be used at different temperature range from 25- 60 °C, alongside the ease of activation using cheap materials is another advantage. Finally, considering the circular economy, time savings and inexpensive chemicals are factors that need to be taken into considerations. Herein we aimed to achieve three of the SDGs such as the human health (goal no. 3), clean water (goal no. 6) and responsible consumption and production (goal no. 12).

Table 8: Comparison between tested zeolite materials with other published materials for removal of Ca^{2+} and Mg^{2+} ions.

Materials	Max adsorption	Initial conditions	%Removal efficiency	Ref
Modified bentonite	14.63 mg/g for Ca 14.63 mg/g for Mg	Ca 120 ppm Mg 120 ppm Time 90 min	66.6% for Ca and Mg	[1]
natural zeolite	27. 1 mg/g for salt	Saline 9.0 g/L, dose 35 g/L Time 24 h	2.2 %	[2]
MFI-type zeolite	0.0006 mmol for Ca 0.0001 mmol for Mg	Ca 150 ppm Mg 9500 ppm	0.2 % for Ca 0 % for Mg	[3]
modified sugarcane bagasse coffee husk	46.8 – 52.9 mg/g for Ca 37.35- 41.23 mg/g for Mg	Ca 120 ppm Mg 120 ppm Dose 2 g/L Time 2h	88- 90% for both Ca and Mg	[8]

Raw pine cone modified pine cone	Not included	Ca 230 ppm Mg 155 ppm; dosage: 5 g/L; time: 12 h	total hardness 11.6% Raw 85% modified	[9]
MIEX-Na resins	Not included	Total hardness 275 ppm Ca 103 ppm Dose 4 ml/L Time 20 min	12.3 % single dose 55% total hardness with Combined ion exchange treatment	[10]
Natural pumice modified pumice stones	57.2 - 62.3 mg/g for Ca 44.5 - 56.1 mg/g for Mg	150 ppm for Ca 150 ppm for Mg Dose 6 g/L Time 5 h	83% - 94% for Ca 48% - 73% for Mg	[11]
zeolite Na-X(Mod) Na-Y (Mod)	Not included	Ca 80.2 ppm Mg 24.2 ppm.	85.7 - 80.4 % for Ca 43.1 - 34.1 % for Mg	[40]
natural zeolite	Not included	Ca 220 ppm Mg 26 ppm. dose 50 g/L 60 min	80.2% Ca 84.8% Mg	[57]
modified zeolite A	129.3 mg/g for Ca	Ca 100 ppm Dose 1 g/L Time 1 h	95.0% for Ca	[58]
commercial zeolite synthesized zeolite NaA	17 mg/g 31 mg/g	Ca 80 ppm Dose 1- 4 g/L Time	95% for Ca	[61]
Grafting copolymerization of acrylic acid	90.7 mg/g for Ca 34.6 mg/g for Mg	20 ppm from each metal Ca &Mg 0.5 g/L of the polymeric ligand	86.6% for Ca 81.1% for Mg	[65]
Natural and modified zeolite and bentonite	26.2 mg/g for Mg 35.6 mg/g for Mg	Mg 250 ppm Dose 20 g/L	85.21% for Mg 81.73% for Mg	[81]

synthetic Zeolite	101 Z	90.9mg/g for Ca	Ca 1000 ppm Dose 10 g/L Time 1	85.7% for Ca	This study
	102 Z	90.9mg/g for Ca		83.4%	
	103 Z	80.6mg/g for Ca		78.6 %	
	104 Z	83.3mg/g for Ca		70.8%	
	105 Z	105.2mg/g for Ca		80.0%	
	106 Z	111.1mg/g for Ca		82.0%	

3.15. Cost assessment of synthesized zeolite:

Demand for synthetic zeolites is strong globally. One such area of application is the wastewater sector in which zeolites can be used to remove water hardness allowing water to be consumed again by humans and improving its overall quality. Couple with this, the fact that synthetic zeolites can be regenerated easily using reagents at room temperature without the need for additional energy. Decreasing the production price is required for its utilization in industrial purposes. The inexpensive technique and reasonable price of chemical reagent (NaCl solution) were the emphases of this study in which successfully prepared zeolites was made from abundant aluminium waste in a low cost and facile way. For each 1 kg of synthesized zeolite, only 1 kg of NaOH is needed (price about 6.5 \$/kg). The charged ensued with the disposal of waste Al sources is very low, approximately 10 EGP/Kg (0.56 \$/kg) compared with other sources for Al salts. One of the fundamental costs of production within the industry is electricity. A domestic home-microwave running at 170 W for just 15 min without auxiliary calcinations was utilized for this preparation method. Electricity cost for the synthesis and ageing of zeolite samples is about 6.5 \$/kg. The total price for production of 1 kg of zeolite is no more than 14 \$/kg. Manufacturing zeolite from waste and disposal materials decreases the production price by at least 70% compared to commercial zeolites available in the market. The published production price of zeolite NaA from rice husk was 26.092 \$.100g⁻¹ [82]. While in this work, the fabrication cost for NaX, NaA or NaY type is only 1.4 \$.100g⁻¹. An extra feature for these synthesized zeolites in this study is the affordable regeneration using a low price and readily

available reagent such as NaCl. Just 2 \$/kg is enough to make zeolite samples reusable for more than one cycle by NaCl solution. In addition, a miniscule amount of zeolite achieved high performance for capturing and reducing 90 % of the high hard water concentration. The cost associated with such an effective amount (10 g.L⁻¹) is approximately 0.14 \$. 10 kg of tested zeolite could be utilized in the treatment of 1 ton of groundwater or even of wastewater by this economically viable and regenerative zeolite for a cost of 140 \$/ton. This will aid and facilitate the circular economy of synthesizing highly active adsorbents and value-added products for various industrial applications, however, keeping the cost and related emissions into consideration [83-89].

4. Conclusion

Synthesized zeolites are required for wider applications in the marketplace globally. The mass-production price until now has been a barring factor for large-scale implementation. An eco-friendly methodology was utilized for the synthesis of nanopowder (14 nm) zeolite using an inexpensive, non-toxic reagent and readily available abundant waste raw materials with the assistance of a domestic-microwave to produce zeolite materials that can be used to reduce the hardness of the water in groundwater and in seawater desalination applications. Herein a successful conversion of disposed Al raw material (scrap wire cable, foil takeaway, cans, and spray aerosol bottles) along with disposed silica gel were used to produce active zeolitic materials (type X and A zeolite phases). The synthesized zeolites were used to eliminate the hardness of water (> 1000 ppm), which showed 90% rapid removal of Ca²⁺ and Mg²⁺ within 30 min using small amount of materials (10 g.L⁻¹). Zeolite samples can be used for 3 consequent cycles, indicating a high capacity with successful elimination of Ca²⁺ was achieved in a broad range of pH values, then spent zeolites can be easily regenerated by 1M NaCl at room temperature. Freundlich and Temkin's isotherm were more suitable than the Langmuir isotherm model herein. The physical adsorption process was verified by Temkin approach for all used zeolite samples along with the positive value of ΔH° which was below 40 kJ.mol⁻¹.

The obtained data fitted pseudo-second-order model and intraparticle diffusion model. Zeolite sample can be used either in a single or binary metals system simultaneously and achieve >85% decrease in salt ions. The synthesized zeolite materials showed excellent capacity in reducing hardness of water in a real sample of seawater and groundwater. According to our approach, the total price for the synthesis of 1kg of zeolite is only 14 \$/kg which is 70% lower the commercial price of zeolite materials. Herein we aimed to achieve three of the Sustainable Development Goals (SDGs) including human health, clean water and responsible consumption and production.

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