

Experimental Evaluation of Alternative Water Softening Methods

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Abstract

Water hardness and deposition of incrustation is a problem in households and industry. In this regard, several technologies have been developed with purpose of water softening and preventing deposition of incrustation. The ion exchange method is the most commonly used method and is considered a conventional method. However, due to the shortcomings of this method, other methods have predispositions for greater and wider application. A promising alternative approach to water softening is application of sorbents such as synthetic zeolites and biosorbents such as moss *Leucobryum glaucum* for the purpose of removing water hardness and application of electrochemical methods. In this study, three alternative methods were tested: water softening method with application of biosorbent, electrochemical scale removal method and water softening method with application of natural and artificial adsorbent, and a comparison was made with the conventional method and previously conducted studies on alternative water softening methods.

1. Introduction

Water in Bosnia and Herzegovina, with respect to the concentration of dissolved minerals calcium and magnesium, is usually classified as hard water, which results in efforts to soften the water, and prevent the harmful effects of scale deposits. Hard water is a big problem both in industry and in the households. The most common problems in the households are the creation of scale depositions in washing machines and dishwashers and the visible deposition of scale on dishes after washing. Nevertheless, this property of water is a much bigger problem in the industry where the damage is estimated at dozens of billions of dollars a year globally (Kim et al. 2007). Scale deposition is a common problem that occurs in heat exchangers in industrial recirculating cooling water systems (Fathi et al. 2006; Seok-Jun et al. 2010). Scale are deposits on the heat exchanger surface mostly made up of concentrated hardness ions such as calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}), which reduce the flow rate and increase energy consumption (Zeng et al. 2007; Zarga et al. 2013; Lee and Lee, 2000).

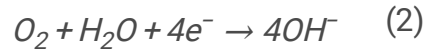
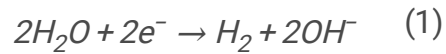
Taking into account all the mentioned harmful effects of hard water, various methods for its softening have been developed over time.

The method currently most widely used and considered the conventional method is the ion exchange method. However, due to the shortcomings of this method, under certain conditions, other methods have predispositions for greater and wider application (Ahn and Haan, 2017).

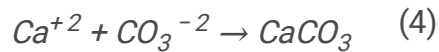
In recent years, considerable attention has been focused on the development and use of low-cost biosorbents based on renewable or waste materials (Tee and Khan, 1988; Nawar and Doma, 1989; Sharma and Forster, 1993). Aziz et al. (2019) used media made up from rice husks (RHAC), sands and zeolite. They concluded the media have great potential of use as a low-cost and environmentally friendly biosorbent for effective treatment of metal in groundwater and water softening.

Peat moss has been reported to comprise a rich array of polar functional groups such as alcohol (COH), aldehydes (CHO), (COOH), ketones (RCOR), and phenolic hydroxides, which are suitable for sorption or ion-exchange processes (Adler and Lundquist, 1963). Though without consensus, some researchers have suggested that the attachment mechanisms of metal ions binding to moss may include ion exchange and complexation (Gupta et al. 2009; Ringqvist and Öborn, 2002; Sharma and Forster, 1993).

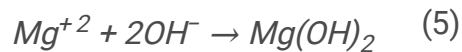
Although the possibility of electrochemical scale removal has long been recognized, industrial application of this technique is rather limited and technical information in the literature is scant. Electrolytic scale removal is based on the generation of a high pH environment around the cathode by the following cathodic reactions (David et al. 2010):



The high alkaline environment acts to convert the bicarbonate ions (HCO_3^-) ion into the carbonate ions (CO_3^{2-}). The ensuing high super saturation level of calcium carbonate ($CaCO_3$) promotes its precipitation:



The high pH conditions also promote precipitation of magnesium hydroxide ($Mg(OH)_2$):



In the conventional equipment currently used for hardness reduction in the water is in contact with both the cathode and the anode electrodes. The cathode performs two functions: it generates alkalinity and serves as a scale deposition surface (Khairi et al. 2015). A novel approach (Ceballos-Escalera et al. 2022) is conducted combining electrochemical water softening as a preliminary step for electro bioremediation of nitrate-contaminated groundwater. Consequently, the combined treatment produced an effluent that achieved high standards for drinking water in terms of both nitrates and nitrite at a competitive cost.

Zeolites and some natural adsorbents have a high adsorption potential for the purpose of removing certain metal ions present dissolved in water and therefore have a high potential for use as an adsorbent for water softening applications (Wang et al. 2003). In recent years, modification of zeolite for application in the field of water softening is the subject of intensive research. Mubarak et al. (2021) investigated the possibility of modification of zeolite Zeolite-4A as adsorbent via the introduction of titanium dioxide

(TiO₂). They observed improvement in the overall efficiency of the zeolitic sorbent towards removing total hardness, manganese ions (Mn²⁺) and iron ions (Fe³⁺) from water due to the new active functional group. Also, the modification significantly reduces the time needed for groundwater treatment and doesn't affect the main structure of zeolite. The principle of cation exchange using zeolite is based on the charge balance of zeolite and sodium ions (Na⁺). Oxygen binds molecules into large chains of sodium aluminium silicate (NaAlSiO₄ or NaZ) molecules. Negative ion charge is balanced with positive charge of Na⁺ located in the ionic crystal lattice (Aveen and Kafia, 2014). When softened water passes through the crystal lattice of zeolite, nothing happens because the electrostatic force keeps Na⁺ in the crystal lattice. However, when hard water passes through the crystal lattice of zeolite, Na⁺ leave the crystal lattice and been replaced by Ca²⁺ (Eq. 6.):



(Biskup and Subotić, 2000).

Evaluation of the ability to remove water hardness of *Leucobryum glaucum*, pyrophyllite shale, ZEOCHEM® Silicagel and electrochemical method as alternative methods under the conditions described in this paper has not been carried out before. The goal of the study is to make that assessment and thus contribute to science. The research was conducted in the laboratories of the Faculty of Technology (University of Tuzla) between dates: 7. 10. 2022 and 26. 10. 2022.

2. Materials and Methods

2.1. Materials

In all water softening experiments, water from the Tuzla water supply system was used as a raw water. In order to perform the experiment of water softening by ion exchange, ion exchange resin, which was originally regenerated, was used. For the needs of the experiment of softening water with moss biosorbent, the moss *Leucobryum glaucum* was harvested. In order to perform an experiment of water softening by electrochemical method, two versions of electrochemical cells were used. The first was formed of three aluminum (Al) plates measuring 10x6x0.3 cm and two graphite plates measuring 7.5x6x1 cm. The second is formed of three Al plates measuring 10x6x0.3 cm and two steel plates measuring 5x6x0.3 cm. For the needs of the water softening experiment using adsorbenses, synthetic zeolite ZEOCHEM® Silicagel registration number CAS # 7631-86-9 and raw pyrophyllite shale from the Parsovići deposit near the city of Konjic were used.

2.2. Methods

Determination of pH value

Electrometric pH measurement was performed by direct measurement of the pH meter METTLER TOLEDO FE 20/EL 20 (BAS ISO 10523:2008).

Determination of electrical conductivity

Electrometric measurement of the conductivity of the sample was directly measured using a conductometer METTLER TOLEDO FE 20/EL 20.

Determination and calculation of total hardness

The analysis of total hardness was measured using EDTA titrimetric method (AOAC, 1980).

Determination of calcium hardness and calculation of Ca^{2+} content

Determination of calcium hardness was performed using volumetric titration method with standard solution ethylenediaminetetraacetic acid (EDTA). Solution was buffered with 0.1 M sodium hydroxide (NaOH) and 0.5 g of Murexid indicator was used. Ca^{2+} concentration was calculated using Eq. 7:

$$C_{\text{Ca}^{2+}} = \frac{560 \bullet V_{\text{EDTA}}}{V_S}$$

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where:

- V_{EDTA} - volume used for titration (ml)
- $V_S = 100$ ml
- $C_{\text{Ca}^{2+}}$ - mass concentration of Ca^{2+} (mg/l)

Calculation of Mg^{2+} content

The concentration of Mg^{2+} has been calculated using Eq. 8:

$$C_{\text{Mg}^{2+}} = \frac{TH - C_{\text{Ca}^{2+}}}{7.19}$$

8

Where:

$C_{\text{Ca}^{2+}}$ - Ca^{2+} concentration (°N)

TH – total hardness (°N)

$C_{\text{Mg}^{2+}}$ - Mg^{2+} concentration (mg/l)

Determination of alkalinity

The analyzed alkalinity parameter was determined by adding four drops of phenolphthalein (phph) to the sample. If the addition changed the color of the sample to pink, the sample was titrated with 0.1 M hydrochloric acid (HCl) solution until discoloration. If no discoloration occurs, two drops of methyl orange (mo) are added to the same sample. It would then be titrated with 0.1 M HCl solution until the color turned orange.

The results were expressed in ml of 0.1M HCl required for neutralization per liter of water, and the calculation was performed using Eq. 9 and Eq. 10:

$$P_{alkalinity} = A_{phph} \bullet 10$$

9

$$M_{alkalinity} = A_{mo} \bullet 10$$

10

Where:

- A_{phph} – 0.1 M HCl solution used for titration with phph (ml)
- A_{mo} – 0.1 M HCl solution used for titration with mo (ml)

2.3. Experimental design

Water softening using ion exchange method (0)

The setting of the ion exchange water softening experiment was performed in the form of an improvised ion exchange column consisting of a burette filled with cation ion exchange resin. The raw water was passed through the burette from top to bottom and hence softened water, as a sample to be further analyzed, was continuously collected at the bottom of the burette. 1500 ml of water was treated and used to form 15 samples with a volume of 100 ml. Samples were analyzed in order to obtain relevant parameters using the methodology described in the previous chapter.

Due to its high prevalence, this method is the reference method in this overall study.

Water softening experiment using *Leucobryum glaucum* as a biosorbent (1)

The moss was cleaned and traces of earth and other impurities were removed. The research was conducted in two series of samples. In the first setup (1–1), 15 g of cleaned moss was weighed, crushed and mixed with 1500 ml (0.01 g/ml) of water. The mixture was stirred for 5 minutes after which it was filtered. To prepare the second setup (1–2), 30 g of moss was weighed and put in 1500 ml (0.02 g/ml) of water. The rest of the procedure was the basically the same as in the previous setups. The obtained

filtrate, in both setups, was used to prepare 15 samples per 100 ml volume of sample, which were used to determine the above mentioned parameters according to the methodology described in the Methods section.

Experiment of water softening using electrochemical method (2)

The experiment was divided into two parts, in the first part (2 – 1) a Al/graphite electrode pair was used in which the graphite electrodes represented the cathodes, while the Al electrodes represented the anodes. The total surface of all three Al anodes was 342 cm², while the total surface of both graphite cathodes was 204 cm². The electrode pair is connected to a power supply. The setting of the electrochemical cell of the first part of the experiment is shown in Fig. 1.

The first part of the experiment was divided into two setups. The distance between the electrodes in the electrochemical cell, in both setups of the first part of the experiment, was 2.4 cm with a voltage of 20V and a current of 0.85 A. In the first setup (2–1–1) water was treated for 10 min, and in the second (2–1–2) 30 min. After the treatment, the water was transferred from the electrochemical cell to the bottles and used for the purpose of determining the mentioned relevant parameters.

In the second part of the experiment (2–2) a Al/steel electrode pair was used. Three Al electrodes represented anodes while two steel electrodes represented cathodes. The total surface of the three Al anodes was 360 cm², while the total surface of the two steel cathodes was 120 cm². The setting of the electrochemical cell of the second part of the experiment is shown in Fig. 2.

The second part of the experiment, too, was divided into two series. The distance between the electrodes, in both series, was 2.5 cm, the voltage value was 20 V with a current of 0.85 A. In the first setup (2–2–1) the water was treated for 10 minutes, and in the second (2–2–2) 30 min. As with the first part of the experiment, in the second, water, from both series of this part of the experiment, was transferred from the electrochemical cell to the bottles and used to determine the relevant parameters.

Water softening experiment using natural and syntetic adsorbents (3)

The experiment was also divided into two parts, in the first part of the experiment (3 – 1) synthetic zeolite was used as a sorbent, and in the second (3 – 2) raw pyrophyllite shale was used.

The first part of the experiment was done in two setups. In the first setup (3–1–1), synthetic zeolite was weighed and mixed with water at a mass concentration of 0.05 g/ml (75 g in 1500 ml of water). The mixture was stirred for 10 min and then filtered. The filtrate was used to form 15 samples with 100 ml volume. The second setup (3–1–2) was prepared in the same way, but with a contact time of 30 min.

The second part of the experiment involved the use of pyrophyllite shale and was done in two series as well as the first part (3–2–1 and 3–2–2). In general, the sample preparation procedure of the second part of the experiment, mixing times and other parameters are identical to the first part with the only difference being the use of pyrophyllite shale instead of synthetic zeolite.

It is important to note that despite the main drawback of the small parametric and sample size in this study, the findings were highly reproducible and consistent. This indicates that the study was conducted in a highly reliable manner, suggesting that the results are likely to be valid, albeit with a recognition of the limitations of the sample size.

3. Results and Discussion

Based on laboratory tests of water softening, the results shown in Table 1 were obtained and total hardness, Ca^{2+} and Mg^{2+} removal percentage for different setups was calculated and shown in Table 2.

The study conducted showed a large variation of different methods and setups in the ability to soften water, as well as in the values of other parameters. The methods that showed the greatest ability to remove the total hardness of the entire study are the ion exchange method (0), the moss water softening method (1) with setup 1–2 and the water softening method using adsorbent (3) with setup 3-1-1. The concentration of Ca^{2+} , as one of the most important parameters for the assessment of water hardness, showed the highest percentage of reduction after treatment by the method of ion exchange (0) and the method 1 in setup 1–2. In addition to the above, the electrochemical method (2) in the 2-2-2 setup (35%), the moss water softening method (1) in the 1–1 setup (27%) and the adsorbent water softening method (3) had a significant percentage reduction in the Ca^{2+} content. Most setups of the water softening method using adsorbents (3) have shown great ability to remove Mg^{2+} , especially setups 3-1-1 (73%) and 3-2-2 (61%). In addition, the ion exchange method (0) and the moss water softening method (1) in setup 1–2 also showed a very high ability to remove Mg^{2+} .

The method of water softening with moss (1) with setup 1–2 and the method of water softening with adsorbent (3) with setup 3-1-1 in which synthetic zeolite was applied, showed a significant reduction in electrical conductivity with a reduction percentage of 43.1% setup 1–2 and 31.7% setup 3-1-1. A significant decrease in pH value was observed only in the ion exchange method (0) where the pH was reduced to 2.68 value compared to raw water where the pH has 7.2 value.

Table 1

Measured experimental results (EC – electroconductivity, TH – total hardness, $C_{Ca^{2+}}$ and $C_{Mg^{2+}}$ - Ca^{2+} and Mg^{2+} concentrations, P and M – P and M alkalinity)

Parameter		pH	EC	TH	$C_{Ca^{2+}}$	$C_{Mg^{2+}}$	P	M
Unit		-	($\mu S/cm$)	(°N)	(mg/l)	(mg/l)	-	-
Tap water		7.2	499.6	14	86.9	38.2	40.7	40.6
Ion exchange method (0)		2.7	507	3.6	18.6	12.9	0	0
Softening method using <i>Leucobryum glaucum</i> biosorbent (1)	Setup 1-1	6.8	443	10.8	63.8	32.2	33.6	33.6
	Setup 1-2	6.6	284.3	5.7	41.8	11.1	34.6	34.6
Electrochemical method (2)	Setup 2-1-1	7.2	502.6	12.6	75.6	36.9	44.6	44.6
	Setup 2-1-2	7	411	10.6	67.9	27.6	39.3	39.3
	Setup 2-2-1	7.2	417.3	11	69.8	29	47.6	47.6
	Setup 2-2-2	7.5	367.3	10.5	56.2	35.7	46.3	46.3
Softening method using natural and synthetic adsorbent (3)	Setup 3-1-1	6.7	341	7.8	64.7	10.2	35.6	35.6
	Setup 3-1-2	7	492	11.4	79.7	24.6	42	42
	Setup 3-2-1	7.4	628	16.8	142.9	18.3	37.3	37.3
	Setup 3-2-2	7.3	663.6	16.4	143.1	14.9	43.3	43.3

The method of water softening with moss (1) showed the ability to soften water with a moderate reduction in hardness in the setup with a moss content of 0.01 g/ml of water (1-1), when the total hardness was reduced by 23%. In the setup with a moss content of 0.02 g/ml (1-2), the water hardness was significantly reduced (59%). Setup 1-2 proved to be particularly effective in removing Mg^{2+} from water, and more efficient than the ion exchange method (0) with a percentage reduction in Mg^{2+} content of 71%. From the above results, it can be concluded that, with this method, the content of moss in the water has a significant impact on the efficiency of water hardness removal. The electrical conductivity of the analyzed sample was also significantly reduced (11.2%) in setup 1-1 and (43.1%) in setup 1-2, which indicates a decrease in the ion concentration in the sample. When softening the water using

Leucobryum glaucum, a by-product of moss is obtained which previously had the role of a biosorbent in the water and needs to be properly disposed.

In the first series of experiments of water softening using electrochemical method (2), where Al/graphite (2 – 1) was used as the electrode pair, prolonging treatment time significantly increased the water softening ability of the 2 – 1 method. The total hardness of water treated by the 2-1-1 setup was reduced by 9%, the Ca^{2+} content by 13% and the Mg^{2+} content by 4%. However, with the 2-1-2 version, the total hardness was reduced by 24%, the Ca^{2+} content by 22% and the Mg^{2+} content was most significantly reduced by 28%.

During the use of an electrochemical cell, the formation of a precipitate as a by-product was observed. The amount of sediment formed is not significant, but it is still necessary to dispose of it in an environmentally acceptable way.

Table 2

Total hardness, Ca^{2+} and Mg^{2+} removal percentage obtained in the study for different methods and setups

Parameter		TH	Ca^{2+}	Mg^{2+}
Unit		(Removal %)	(Removal %)	(Removal %)
Ion exchange method (0)		74%	79%	66%
Softening method using <i>Leucobryum glaucum</i> biosorbent (1)	Setup 1-1	23%	27%	16%
	Setup 1-2	59%	52%	71%
Electrochemical method (2)	Setup 2-1-1	9%	13%	4%
	Setup 2-1-2	24%	22%	28%
	Setup 2-2-1	21%	20%	24%
	Setup 2-2-2	25%	35%	7%
Softening method using natural and synthetic adsorbents (3)	Setup 3-1-1	44%	26%	73%
	Setup 3-1-2	19%	8%	36%
	Setup 3-2-1	-20%	-64%	52%
	Setup 3-2-2	-17%	-65%	61%

An experiment conducted using the electrochemical method using Al/steel electrode pair (2-2) showed that the method was not effective in either setup. The percentage of reduction in total hardness was reduced by 21% in the 2-2-1 setup and 25% in the 2-2-2 setup.

When performing the setup using synthetic zeolite with a mixing time of 5 minutes (3-1-1), 44% of the total hardness and 26% of Ca^{2+} were removed. Setup 3-1-1 showed the highest ability to remove Mg^{2+} of all methods applied in this study with a percentage reduction of 73%. The setup in which the zeolite was mixed for a time of 30 min (3-1-2), in fact, shows a smaller percentage reduction in total hardness, Ca^{2+} content and Mg^{2+} content compared to the previous series. The percentage of reduction in total hardness was 19%, the percentage of reduction of Ca^{2+} 8% and the percentage of reduction of Mg^{2+} 36%. These

results indicate the occurrence of desorption and release of Ca^{2+} and Mg^{2+} from the contact surface of the zeolite during a longer mixing time.

The results of the method using natural adsorbent (3 – 2) for both setups indicated that this method does not have the ability to soften water. The value of total hardness was increased 20% after treatment by performing a setup with a mixing period of 5 minutes (3–2–1) and 17% after treatment by performing a setup with a mixing period of 30 minutes (3–2–2). For both mixing times, the Ca^{2+} content was 64% higher than for a raw untreated water. On the other hand, the Mg^{2+} content was again significantly reduced by 52% for the 3-2-1 setup and 61% for the 3-2-2 setup. These results indicate the occurrence of the process of desorption and release of Ca^{2+} from the contact surface of the pyrophyllite shale into the water, which took place mainly in the first 5 min of mixing.

Compared to the previous study (Lubbad and Mousa, 2020), where *Sphagnum peat moss* was used, in which the percentage of Ca^{2+} 32% removal was achieved with the content of the mentioned biosorbent 0.01 g/ml and mixing time 5 minutes, moss softening method (1) showed a relatively small difference in terms of Ca^{2+} removal with the same moss content in water and mixing time compared to the mentioned study. The percentage of Ca^{2+} removal of pretreated *Spahgnum* is 59%, which is a significant increase. The study (Shaik et al. 2017) also conducted study on assessing the possibility of using microscopic fungal culture as a biosorbent with the species used: *Aspergillus niger* with 30% Ca^{2+} removal, *Neurospora crassa* with 8% and *Rhizopus stolonife* with 32% (120 minutes sample preparation time). The results of Ca^{2+} removal using *Leucobryum glaucum* as a biosorbent (1) in relation to other studies, in which biosorbents were used in order to assess the efficiency of water softening, are shown in Fig. 3.

Khairi et al. (2015) conducted a study using a Al/graphite electrode pair which makes the study suitable for comparison with the method 2 – 1. The percentage of removal of the total hardness of the mentioned research was 39% for water treated for 10 minutes and 62% for water treated for 30 minutes. The obtained percentage of total hardness removal is significantly higher compared to method 2 – 1 as can be seen in the diagram of Fig. 4.

Previous research on water softening in an electrochemical cell using Al/steel electrode pair was conducted by Agostinho et al. The percentage of removal of the total hardness of the previous mentioned research was 49% for water treated for 10 minutes and 80% for water treated for 30 minutes. The obtained percentage of removal of total hardness is, in this case, significantly higher compared to the setup of the electrochemical method where Al/steel (2–2) was used as the electrode pair. The diagram in Fig. 5 shows a comparison of the percentage of removal of the total hardness of the two studies.

Possible causes of differences in the behavior of different electrochemical cells during treatment in terms of the ability to remove hardness are different parameters in which the treatment was carried out.

In a previously conducted study (El-Nahas et al. 2020) zeolites 101Z and 102Z were synthesized and the percentage of Ca^{2+} removal was measured. Samples whose parameters were analyzed after mixing for

30 minutes removed shows reduction of 85% Ca^{2+} using synthetic zeolite 101Z (percentage of removal significantly higher compared to the the method using synthetic zeolite (3 – 1)) and 83% Ca^{2+} using synthetic zeolite 102Z (significantly higher reduction compared to the method 3 – 1).

A study using zeolite synthesized from kaolin clay (Aragaw and Ayalew, 2019) for 30 minutes of mixing time resulted in a percentage reduction of Ca^{2+} 78% (significantly higher percentage of removal compared to the setup of the method using synthetic zeolite for 30 minutes of mixing 3-1-2).

The different behavior of different synthetic zeolites in terms of their ability to remove Ca^{2+} is common occurrence and usually requires no explanation. It is important to note that zeolites 101Z and 102Z as well as zeolite synthesized from kaolin clay were synthesized for the purpose of softening water as their primary role, which is not the case with the synthetic zeolite ZEOCHEM® Silicagel used in the study (3 – 1). A comparison of the results of water softening studies using different synthetic zeolites after all mixing times is shown in the diagram in Fig. 6.

A study conducted to determine the removal efficiency of Ca^{2+} and Mg^{2+} (Hailu et al. 2019) using natural zeolite was used for comparison with method 3 – 2. Natural zeolite was excavated from the sedimentary rocks of the Ethiopia and mixing time was 30 min. The percentage of Ca^{2+} reduction during this study was 80% and the percentage of reduction in total hardness was 81%. These two parameters had a negative value in both setups of method 3 – 2 and indicate an increase in the value of total hardness and Ca^{2+} content after treatment. Previous study by Hailu et al. achieved a reduction in the Mg^{2+} content of 84% (significantly greater reduction in Mg^{2+} than in both setups of method 3 – 2). A comparison of the parameters of the two studies is shown in the diagram of Fig. 7.

4. Conclusion

During the laboratory tests, the ion exchange method, used as a reference method, showed the highest efficiency of hardness removal, while the biosorption method is the most suitable of the alternative methods. The content of biosorbent (*Leucobryum glaucum*) in water in the biosorption method is a very important parameter and increasing the content of biosorbent significantly increases the efficiency of hardness removal. Electrochemical method conducted in this study with all four setups was relatively inefficient from the aspect of the water hardness removal compared to ion exchange method, method using biosorbent and previously conducted studies by electrochemical method using Al/graphite and Al/steel electrode pair. Increasing the effectiveness of water softening by the adsorption method by extending the mixing period is impaired by the desorption of Ca^{2+} and Mg^{2+} .

Currently, taking into account the significantly higher price of ion exchange resin compared to moss, the use of *Leucobryum glaucum* could be a favorable and environmentally friendly alternative for softening water in plants where a high degree of hardness removal is not required, where it is possible to solve the problem of adequate disposal of filtration byproducts and where biological moss material is easily available.

Declarations

Ethical Approval

The authors of the manuscript declare that ethical considerations for the research presented in this manuscript have been addressed in accordance with established guidelines.

Competing interests

The authors of the manuscript declare that they have no competing interests that could be perceived as influencing the objectivity, conduct, or interpretation of the research presented in this manuscript. A competing interest includes any financial, personal, or professional relationship that might be seen as potentially influencing the work reported.

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Data Availability Statement

The data generated experimentally during this study are available upon reasonable request. Please contact Armin Buljubašić at armin.buljubasic.91@gmail.com for inquiries regarding the availability of specific dataset. In addition, a portion of the data utilized in this research is sourced from open-source scientific manuscripts. The relevant references for these data are provided within the manuscript.

The materials utilized in this study are readily available on the open market.

References

1. Adler, E.R.I.C.H., Lundquist, K.: Spectrochemical estimation of phenylcoumaran elements in lignin. *Acta Chem. Scand.* **17**, 13–26 (1963)
2. Agostinho, L.C.L., Nascimento, L., Cavalcanti, B.F.: Water Hardness Removal for Industrial Use: Application of the Electrolysis Process. *Op Acc. Sci. Rep.* **1**, 1–5 (2012). <https://doi.org/10.4172/SCIENTIFICREPORTS.460>
3. Ahn, M.K., Han, C.: Technologies for the Removal of Water Hardness and Scaling Prevention. *J. Ener Eng.* **26**, 73–79 (2017). <https://doi.org/10.5855/ENERGY.2017.26.2.109>

4. AOAC, Official Methods of Analysis, 13th Edition, Association of Official Analytical Chemists, Washington DC: (1980)
5. Aragaw, T.A., Ayalew, A.A.: Removal of water hardness using zeolite synthesized from Ethiopian kaolin by hydrothermal method. *Water Prac Tech.* **14**, 145–159 (2018).
<https://doi.org/10.2166/wpt.2018.116>
6. Aveen, H.M., Kafia, M.S.: Kinetics of cation exchange capacity of homoionic sodium form NaY zeolite. *Internat J. Innova Res. Sci. Enginer Tech.* **3**, 13137–13145 (2014)
7. Aziz, N., Othman, N., Ibrahim, N., Yunus, Muhammad, Z.M., Setiawan, I.: Optimization of pH and Contact Time of Media in Removing Calcium and Magnesium from Groundwater. *Internat J. Int. Enginer.* **11**, 63–72 (2019)
8. BAS EN: ISO 10523:2008 Kvalitet vode – Određivanje pH vrijednosti, Institute for Standardization of Bosnia and Herzegovina, 1st Edition (2012)
9. Biskup, B., Subotic, B.: Removal of heavy-metal ions from solutions by means of zeolites II: Thermodynamics of the exchange processes between zinc and lead ions from solutions and sodium ions from zeolite A. *Sep. Sci. Tech.* 35449–35466 (2000). <https://doi.org/10.1081/SS-100102104>
10. Ceballos-Escalera, A., Pous, N., Balaguer, M.D., Puig, S.: Electrochemical water softening as pretreatment for nitrate electro bioremediation. *Sci. Tot Envir.* **806** (2022).
<https://doi.org/10.1016/j.scitotenv.2021.150433>
11. David, H., Georgiy, S., Raphael, S.: Calcium carbonate hardness removal by a novel electrochemical seeds system. *Desal.* **263**, 285–289 (2010). <https://doi.org/10.1016/j.desal.2010.06.036>
12. El-Nahas, S., Osman, A.I., Arafat, A.S., Al-Muhtaseb, A., Salman, H.M.A.: Facile and affordable synthetic route of nano powder zeolite and its application in fast softening of water hardness. *J. of Wat. Proc. Engineer.* **33**, 101–104 (2019). <https://doi.org/10.1016/j.jwpe.2019.101104>
13. Fathi, A., Mohamed, T., Claude, G., Maurin, G., Mohamed, B.A.: Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate. *Water Res.* **40**, 1941–1950 (2006). <https://doi.org/10.1016/j.watres.2006.03.013>
14. Gupta, B.S., Curran, M., Hasan, S., Ghosh, T.K.: Adsorption characteristics of Cu and Ni on Irish peat moss, *Journal Environmental Management*, Vol: 90, Issue: 2, Page: 954–960, (2009).
<https://doi.org/10.1016/j.jenvman.2008.02.012>
15. Hailu, Y., Tilahun, E., Brhane, A., Resky, H., Sahu, O.: Ion exchanges process for calcium, magnesium and total hardness from ground water with natural zeolite. *Groundwat sustainable dev.* **8**, 457–467 (2019). <https://doi.org/10.1016/j.gsd.2019.01.009>
16. Khairi, R.K., Inmar, N.G., Mohammed, A.A.: Hardness Removal from Drinking Water Using Electrochemical Cell. *Eng. Tech. J.* **33**, 1–12 (2014). <https://doi.org/10.30684/etj.33.1A.7>
17. Kim, T.K., Park, S., Shin, E.B., Kim, S.: Dechlorination of disperse and reactive dyes by continuous electro coagulation process. *Desal.* **150**, 165–175 (2002). [https://doi.org/10.1016/S0011-9164\(02\)00941-4](https://doi.org/10.1016/S0011-9164(02)00941-4)

18. Lee, S., Lee, C.H.: Effect of operating conditions on CaSO₄ scale formation mechanism in nanofiltration for water softening. *Water Res.* **34**, 3854–3866 (2000). [https://doi.org/10.1016/S0043-1354\(00\)00142-1](https://doi.org/10.1016/S0043-1354(00)00142-1)
19. Lubbad, S.H., Mousa, E.A.: Softening of tap water via calcium removal using sphagnum peat moss sorbent by batch and flowthrough approaches. *Int. J. Environ. Stud.* **77**, 222–235 (2020). <https://doi.org/10.1080/00207233.2020.1719805>
20. Mubarak, M.F., Mohamed, A., Mohamed, G., Keshawy, M., el-Moghny, T.A., Shehata, N.: Adsorption of heavy metals and hardness ions from groundwater onto modified zeolite: Batch and column studies. *Alexandria Eng. J.* **61**, 4189–4207 (2022). <https://doi.org/10.1016/j.aej.2021.09.041>
21. Nawar, S.S., Doma, H.S.: Removal of Dyes from Effluents using low Costs Agricultural By-Products. *Tot Environ.* **79**, 271–279 (1989). [https://doi.org/10.1016/0048-9697\(89\)90342-2](https://doi.org/10.1016/0048-9697(89)90342-2)
22. Ringqvist, L., Öborn, I.: Copper and zinc adsorption onto poorly humified Sphagnum and Carex peat. *Water Res.* **36**, 2233–2242 (2002). [https://doi.org/10.1016/S0043-1354\(01\)00431-6](https://doi.org/10.1016/S0043-1354(01)00431-6)
23. Seok-Jun, S., Hongrae, J., Jae, K.L., Gha-Young, K., Daewook, P., Hideo, N., Jaeyoung, L., Seung-Hyeon, M.: Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications. *Water Res.* **44**, 2267–2275 (2010). <https://doi.org/10.1016/j.watres.2009.10.020>
24. Shaik, G., Naveena, L., Latha, J.: Converting of hard water to soft water using fungal bioremediation technology. *Dep Biotech.* **3**, 116–120 (2017)
25. Sharma, D.C., Forster, C.F.: Removal of Hexavalent Chromium Using Sphagnum Peat Moss. *Water Res.* **27**, 1201–1208 (1993). [https://doi.org/10.1016/0043-1354\(93\)90012-7](https://doi.org/10.1016/0043-1354(93)90012-7)
26. Tee, T.W., Khan, A.R.M.: Removal of Lead, Cadmium and Zins by Waste Tea Leaves. *Environ. Tech. Lett.* **9**, 1223–1232 (1988). <https://doi.org/10.1080/09593338809384685>
27. Wang, Y., Guo, Y., Yang, Z., Cai, H., Xavier, Q.: Synthesis of zeolites using fly ash and their application in removing heavy metals from waters. *Sci. China.* **46**, 967–976 (2003). <https://doi.org/10.1360/02yd0487>
28. Zarga, Y., Boubaker, B., Ghaffour, H., Elfil, N.: Study of calcium carbonate and sulfate co-precipitation. *Chem. Eng. Sci.* **96**, 33–41 (2013). <https://doi.org/10.1016/j.ces.2013.03.028>
29. Zeng, Y., Yang, C., Pu, W., Zhang, X.: Removal of silica from heavy oil wastewater to be reused in a boiler by combining magnesium and zinc compounds with coagulation. *Desal.* **216**, 147–159 (2007). <https://doi.org/10.1016/j.desal.2007.01.005>

Figures

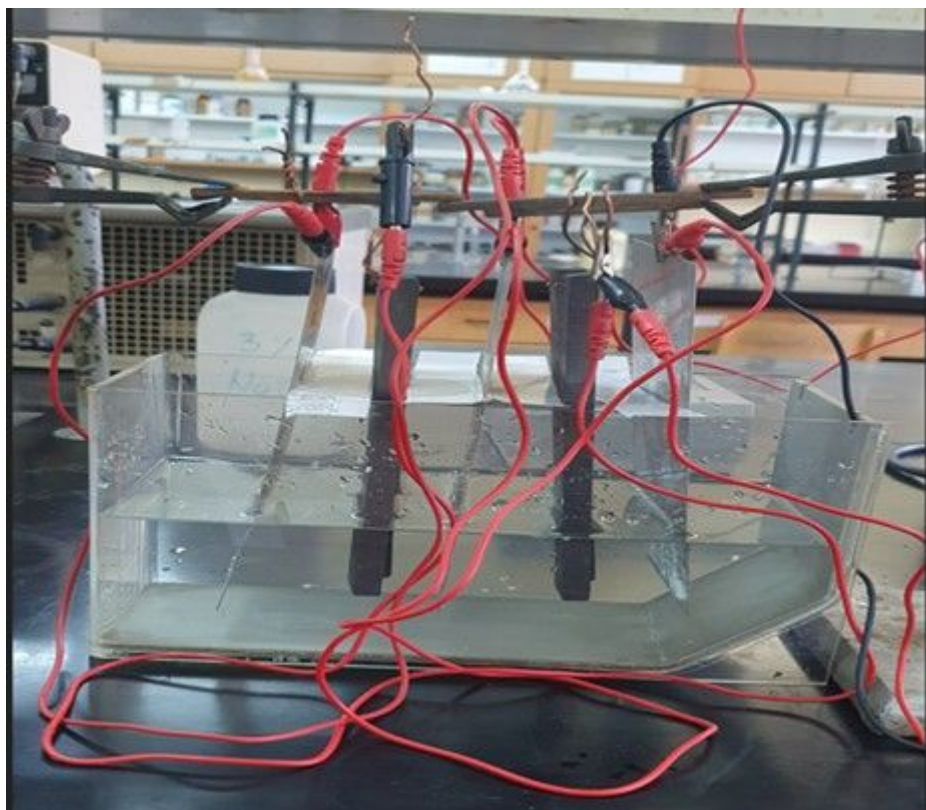


Figure 1

The setting of the electrochemical cell of the first part of the experiment

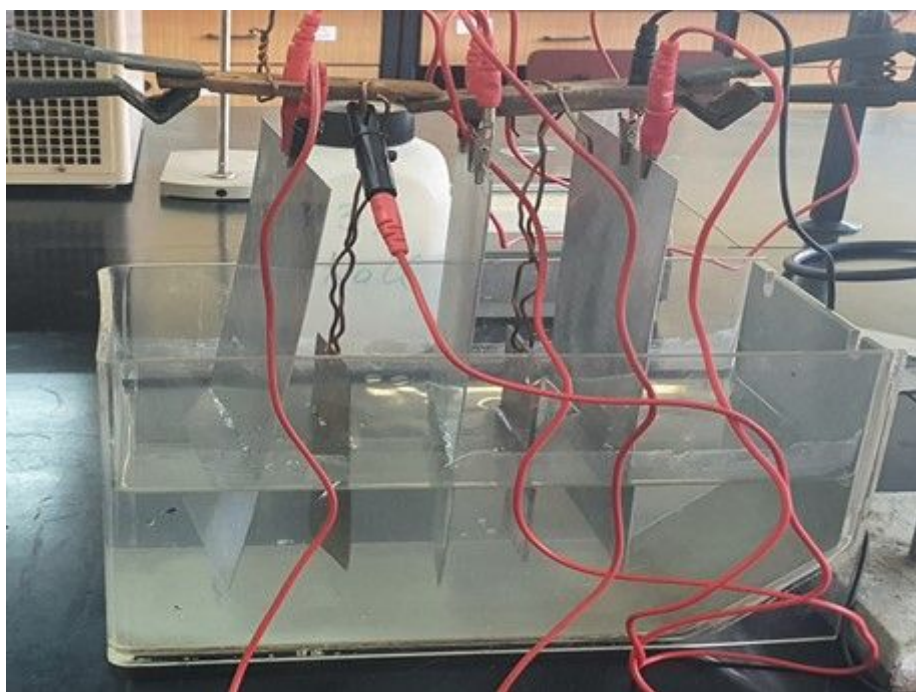


Figure 2

The setting of the electrochemical cell of the second part of the experiment

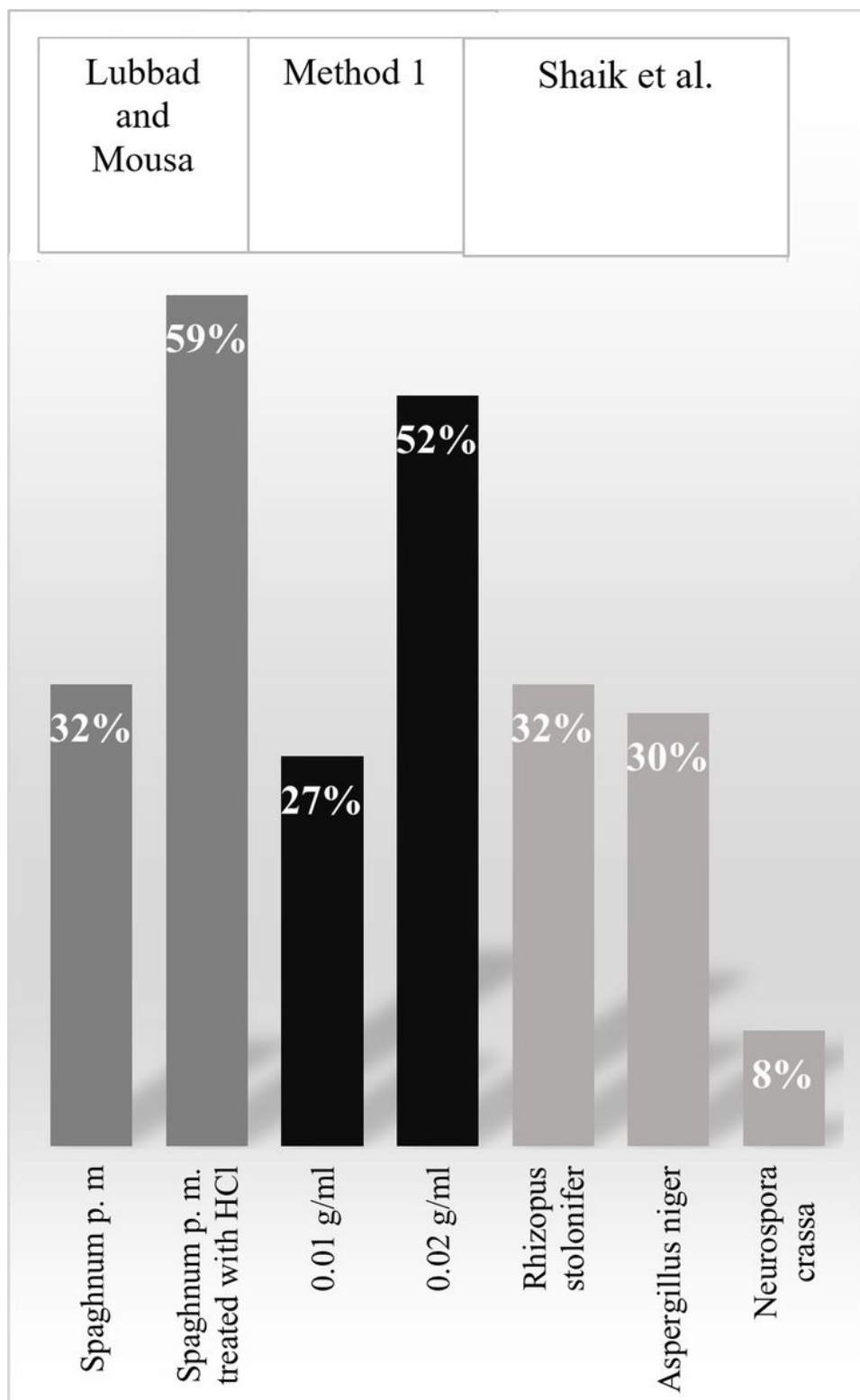


Figure 3

Percentage reduction in Ca^{2+} content of method 1 compared to biosorbents used in previous studies

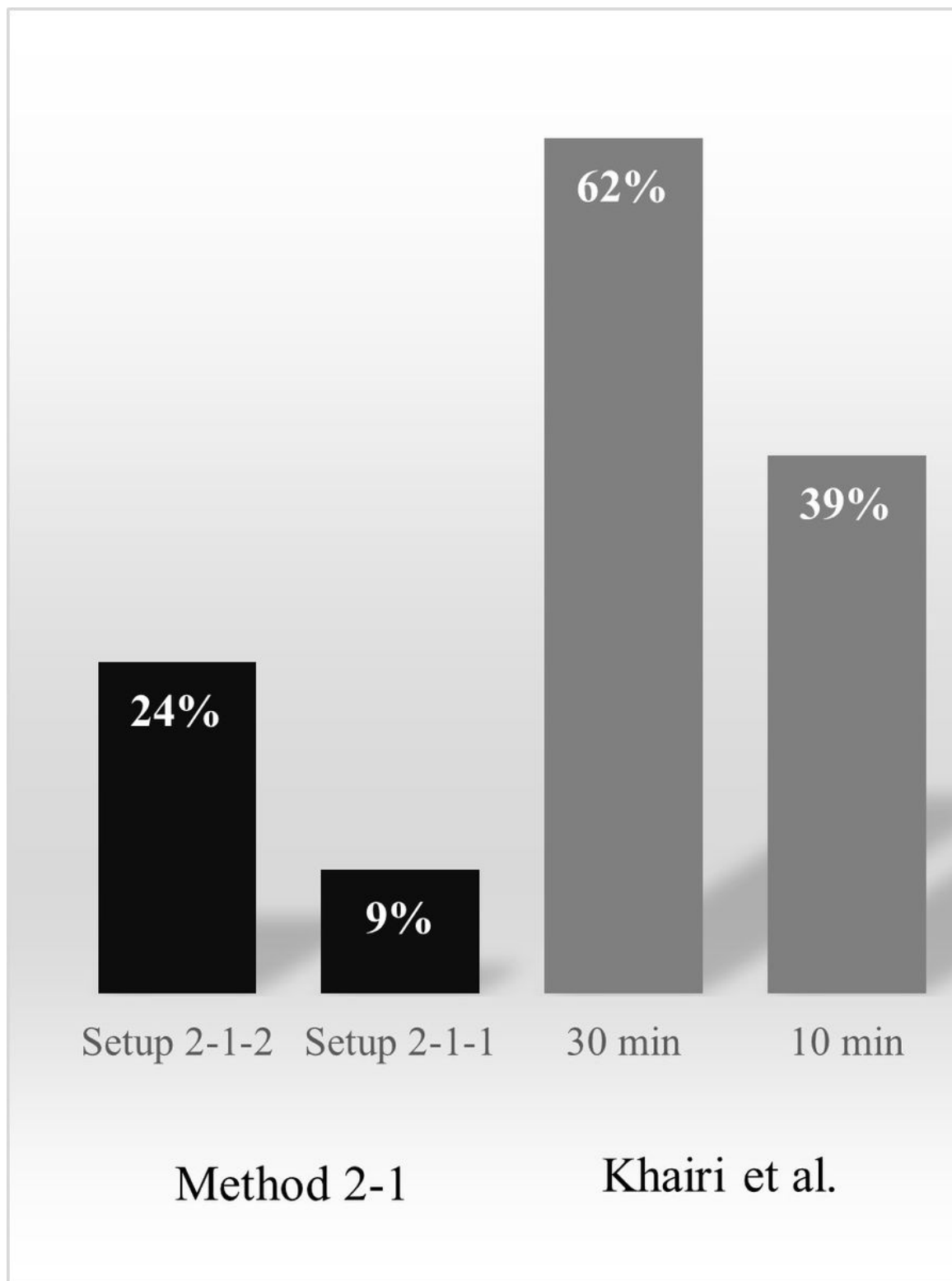


Figure 4

Percentage reduction in total hardness of Khairi et al. in relation to method 2-1

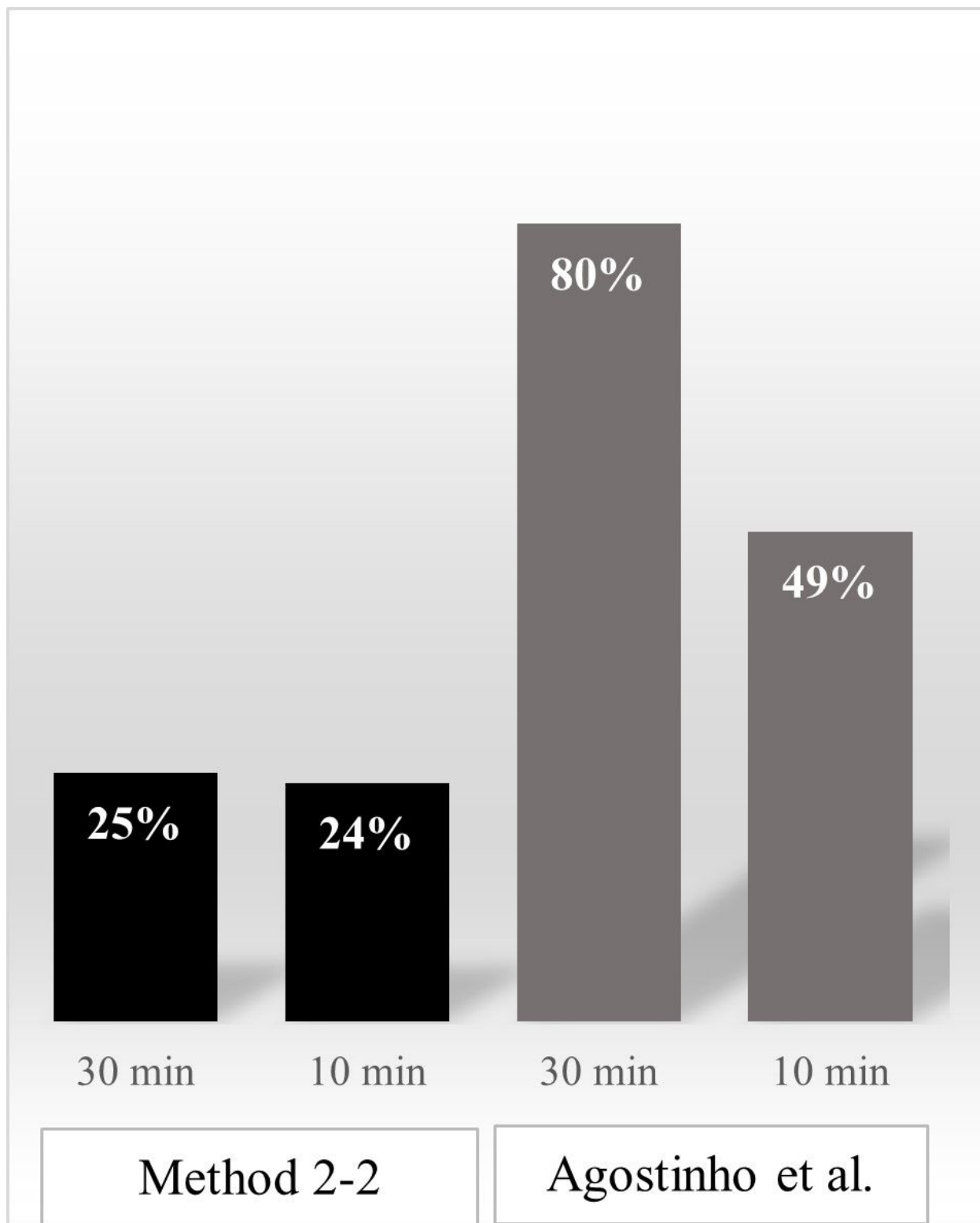


Figure 5

Percentage reduction in total hardness studies of Agostinho et al. compared to method 2-2

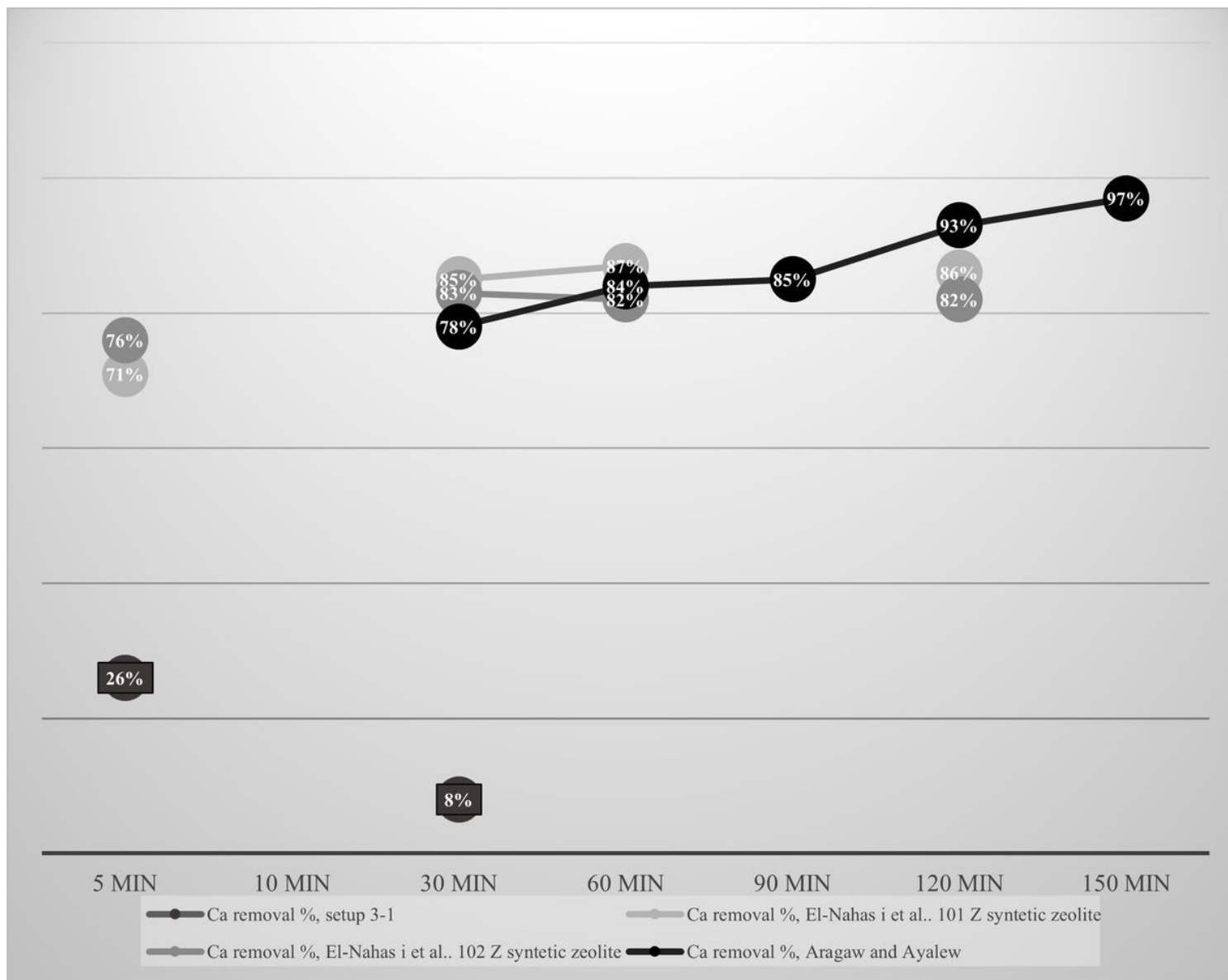


Figure 6

Comparison of Ca^{2+} removal percentage using different synthetic zeolites of setup 3-1, study El-Nahas et al. and the Aragaw and Ayalew study

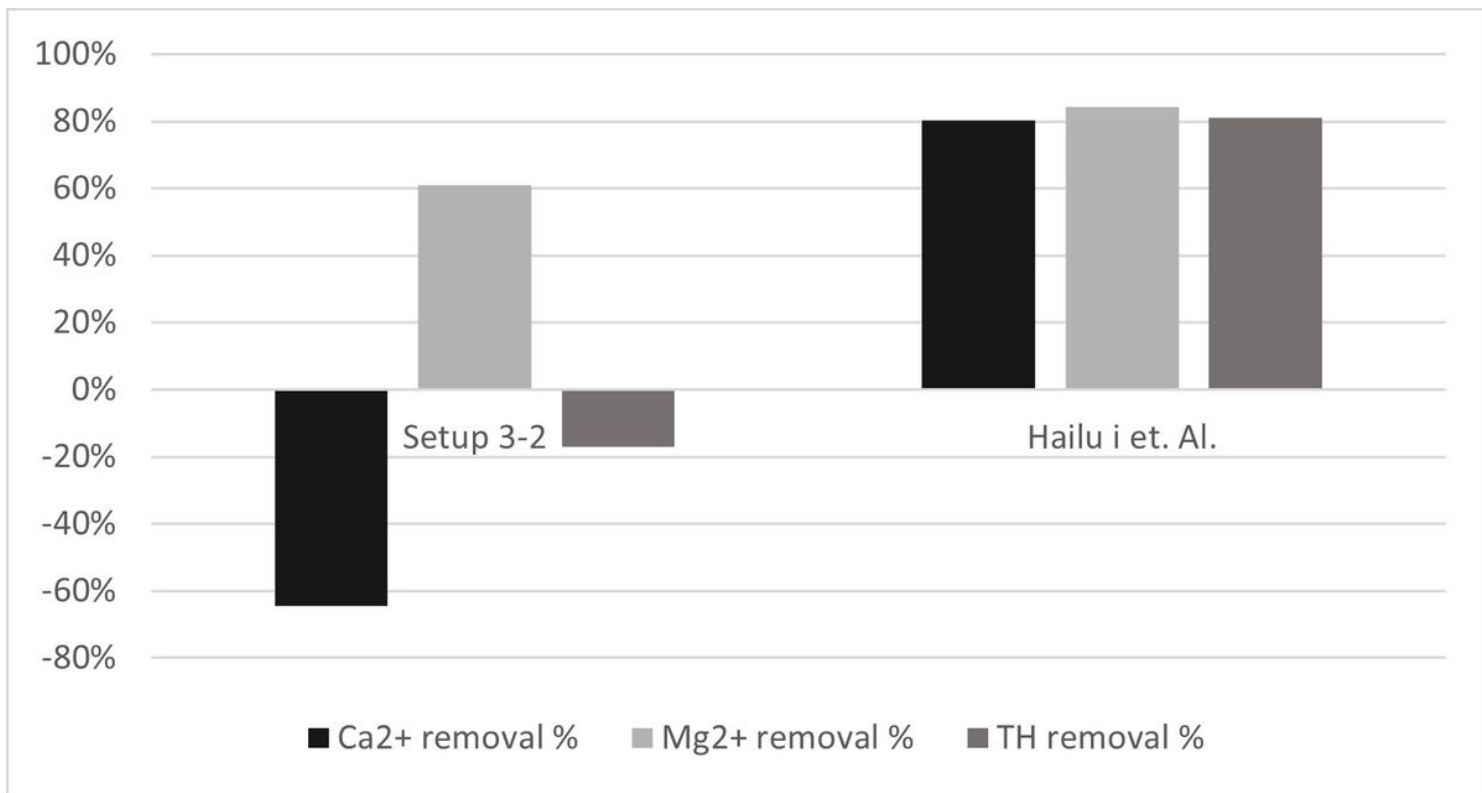


Figure 7

Comparison of the percentage reduction in Ca^{2+} , Mg^{2+} and total hardness of setup 3-2-2 and the Hailu et al. study