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LEUCOBRYUM GLAUCULUM MOSS AS A BIOSORBENT FOR REMOVAL OF WATER HARDNESS

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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 the purpose of water softening and preventing the 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, there is a need to develop adequate alternative methods. The potential of the method using biosorbents such as moss *Leucobryum glaucum* and *Spaghnum peat moss* for the purpose of removing water hardness has recently become the subject of intensive research with growing interest. In this study, the method using *Leucobryum glaucum* as a biosorbent was tested and a comparison was made with the conventional method and previously conducted studies that used other biosorbents.

Keywords: Ca^{2+}, Mg^{2+}, total hardness, water softening, alternative softening methods, biosorbent

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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 households. The most common problems in 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 [1]. Scale deposition is a common problem that occurs in heat exchangers in industrial recirculating cooling water systems [2,3]. Scale deposits on the heat exchanger surface are mostly made up of concentrated hardness ions such as Ca^{2+} and Mg^{2+}, which reduce the flow rate and increase energy consumption [4-6].

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 [7].

In recent considerable attention has been focused on the development and use of low-cost biosorbents based on renewable or waste materials [8-10]. Mosses appear to have great potential in terms of the biosorption of metal ions. However, the exact mechanism of metal ion binding to moss is not well understood. The process of cation sorption, based on the ion exchange between the moss thallus and a solution that wets the thallus, is the most known. The ion-exchange process involves several functional groups, including carboxyl groups (–COOH), aldehyde groups (–CHO), hydroxyl groups (–OH) and amino groups (–NH_2), that form part of cell wall-forming compounds, such as lignin-like phenolic compounds [11]. Some authors also point to the possibility of complexing metal ions and physical adsorption [12].

It has been known that *Leucobryum glaucum* from the family of Bryophyta (mosses), has a physical structure that efficiently absorbs metal ions, most notably Zn^{2+} and Cd^{2+} from water [13]. Furthermore, *L. Glaucum* has applications in removing pollutants from wastewater through phytodegradation. Therefore, it is used as an active filtering and adsorption agent for the COD and BOD treatment of wastewater [14].

The aim of this study was to evaluate the ability of the biosorption method using *L. glaucum* to remove Ca^{2+} and Mg^{2+} from water in order to analyze its efficiency in removing water hardness compared to the conventional ion exchange method and previously conducted research using the biosorption method.

2. MATERIALS AND METHODS

2.1. Materials

In all water softening experiments, water from the Tuzla water supply system was used as raw water. For the needs of the experiment of softening water with moss biosorbent, the moss *Leucobryum glaucum* was harvested.

2.2. Methods

2.2.1. Determination of pH value

Electrometric pH measurement was performed by direct measurement of the pH meter METTLER TOLEDO FE 20/EL 20 [15].

2.2.2. Determination of electrical conductivity

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

2.2.3. Determination and calculation of total hardness

The analysis of total hardness was measured using EDTA titrimetric method [16].

2.2.4. Determination of calcium hardness and calculation of calcium content

Determination of calcium hardness was performed using the volumetric titration method with standard solution EDTA. The solution was buffered with 0.1 M NaOH and 0.5 g of Murexid indicator was used. Ca^{2+} concentration was calculated using equation 1:

$$C_{Ca^{2+}} = \frac{560 \cdot V_{EDTA}}{V_S} \quad (1)$$

where is:

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

Calculation of magnesium content

The concentration of Mg^{2+} has been calculated using equation (2):

$$C_{Mg^{2+}} = \frac{TH - C_{Ca^{2+}}}{7.19} \quad (2)$$

Where is:

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

TH – total hardness (°N)

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

2.2.5. Determination of alkalinity

The analyzed alkalinity parameter was determined by adding four drops of phenophthalein to the sample. If the addition changed the color of the sample to pink, the sample was titrated with 0.1 M hydrochloric acid solution until discoloration. If no discoloration occurs, two drops of methyl orange are added to the same sample. It would then be titrated with 0.1 M hydrochloric acid solution until the color turned orange. The results were expressed in ml of 0.1 M hydrochloric acid required for neutralization per liter of water, and the calculation was performed using equation (3) and equation (4):

$$P\ alkalinity = A_{phph} \cdot 10 \quad (3)$$
$$M\ alkalinity = A_{mo} \cdot 10 \quad (4)$$

Where:
A_{phph} - 0.1 M hydrochloric acid solution used for titration with phenophthalein (ml)
A_{mo} - 0.1 M hydrochloric acid solution used for titration with methyl orange (ml)

2.3. Experimental design

2.3.1. Water softening using ion exchange method

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

2.3.2. Water softening experiment using *L. glaucum* as a biosorbent

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, 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, 30 g of moss was weighed and put in 1500 mL (0.02 g/mL) of water. The rest of the procedure was 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.

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 percentages for different methods and their mass concentrations were calculated and shown in Table 2.

Table 1. Measured experimental results (EC – electroconductivity, TH – total hardness, Ca^{2+}, and Mg^{2+}- Ca^{2+} and Mg^{2+}concentrations, P and M – P and M alkalinity)

Parameter		pH	EC	TH	Ca^{2+}	Mg^{2+}	P	M
Unit		-	(µS/cm)	(°N)	(mg/L)	(mg/L)	-	-
Tap water		7.2	499.6	14	86.9	38.2	40.7	40.6
Ion exchange method		2.7	507	3.6	18.6	12.9	0	0
Softening method using	0.01 g/mL	6.8	443	10.8	63.8	32.2	33.6	33.6
L. glaucum biosorbent	0.02 g/mL	6.6	284.3	5.7	41.8	11.1	34.6	34.6

Table 2. Total hardness, Ca^{2+} and Mg^{2+} removal percentage obtained in the study

Parameter		TH	Ca^{2+}	Mg^{2+}
Unit		(Removal %)	(Removal %)	(Removal %)
Ion exchange method		74%	79%	66%
Softening method using	0.01 g/mL	23%	27%	16%
Leucobryum glaucum biosorbent	0.02 g/mL	59%	52%	71%

The methods that showed the greatest ability to remove the total hardness of the entire study are the ion exchange method (74% removal). Softening method using 0.02 g/mL moss showed also the ability to significantly remove the total hardness with 59% removal. The method of water softening using 0.01 moss showed the ability to soften water with a moderate reduction in total hardness where the hardness was reduced by 23%. 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 (79% removal). From the methods of water softening using moss, a significant percentage of Ca^{2+} removal had a setup using a mass concentration of 0.02 g/mL biosorbent in water with 25% removal. The method of water softening using 0.01 moss again showed the ability to soften water with moderate reduction (27% removal). Softening method using 0.02 g/mL moss proved to be particularly effective in removing Mg^{2+} from water, and more efficient than the ion exchange method with a percentage reduction in Mg^{2+} content of 71%. From the 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 ion exchange method showed a reduction in Mg^{2+} content of 66%. The method of water softening using 0.01 moss was performed with poor efficiency of reduction Mg^{2+} (16% removal). A significant decrease in pH value was observed in the ion exchange method where the pH was reduced to 2.68 value compared to raw water where the pH has 7.2 value, while neither of the moss softening method setups showed a significant effect on the pH value. Softening method using 0.02 g/mL moss showed a significant reduction in electrical conductivity with a reduction percentage of 43.1% while softening method using 0.01 g/mL moss and the ion exchange method showed an insignificant impact on the electrical conductivity parameter.

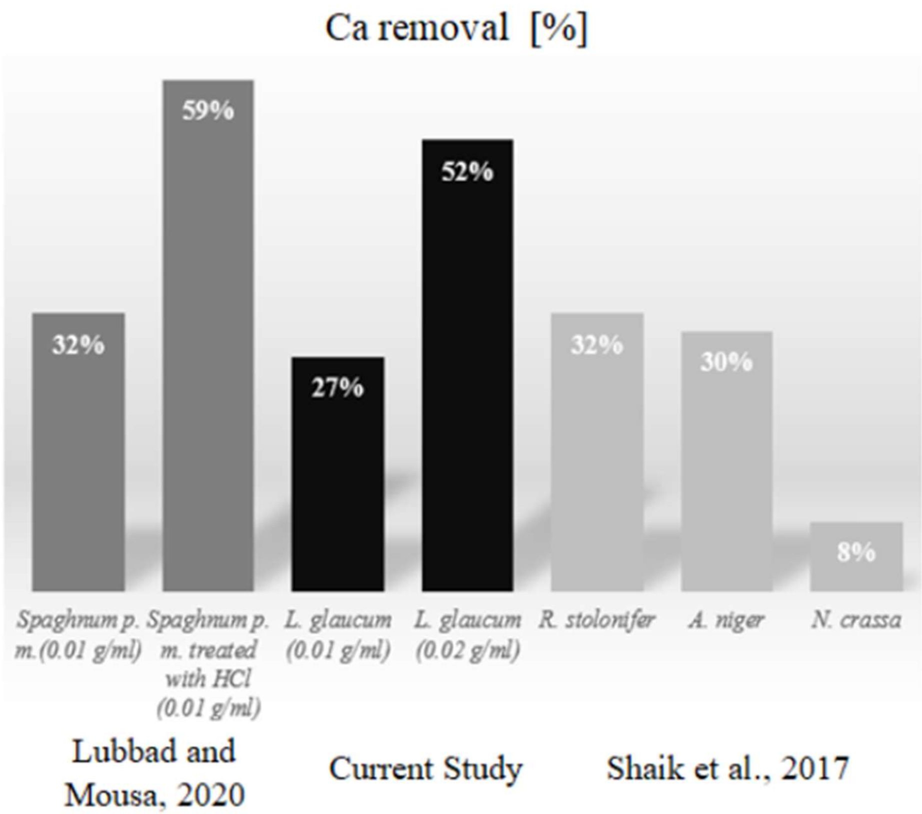

Figure 1. Percentage reduction Ca^{2+} biosorption method using *L. glaucum* compared to biosorbents used in previous studies [17,18]

Compared to the previous study [17], 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 of 5 minutes, the moss softening method using *L. glaucum* 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 Sphagnum is 59%, which is a significant increase. The study [18] also conducted research 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 stolonifera* with 32% (120 minutes sample preparation time). The results of Ca^{2+} removal using *L. glaucum* as a biosorbent in relation to other studies, in which other biosorbents were used in order to assess the efficiency of water softening, are shown in Figure 1.

4. CONCLUSIONS

During the laboratory tests, the ion exchange method, used as a reference method, showed the highest efficiency of hardness removal and Ca^{2+}, while the biosorption method where the moss content was 0.02 g/mL significantly removed the total hardness and Ca^{2+} as well. The method of water softening using 0.01 g/mL moss showed the ability to soften water with moderate to low reduction in total hardness, Ca^{2+}, and Mg^{2+}. Softening method using 0.02 g/mL moss proved to be particularly effective in removing Mg^{2+} from water, and more efficient than the ion exchange method.

The content of biosorbent (*L. 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.

Compared to the previous study [17] softening method using *L. Glaucum* with 0.02 g/mL content of biosorbent showed a relatively small difference in terms of Ca^{2+} removal.

Conflicts of Interest

The authors declare no conflict of interest.

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