



## Assessment and optimization of carbonated hard water softening with *Moringa oleifera* seeds

Gustavo Lopes Muniz<sup>a,\*</sup>, Francinete Veloso Duarte<sup>b</sup>, Miroslava Rakocevic<sup>c</sup>

<sup>a</sup>Faculty of Agricultural Engineering, State University of Campinas, Av. Prof. Zeferino Vaz, Campinas-SP, Brazil, Tel. +55 31 995902131; email: gustavo.muniz@feagri.unicamp.br

<sup>b</sup>Institute of Agrarian Sciences, Federal University of Minas Gerais, Av. Montes Claros-MG, Brazil

<sup>c</sup>Embrapa Agricultural Informatics, Av. Dr. André Tosello, 209, Campinas-SP, Brazil, email: mimarako@unicamp.br

Received 4 April 2019; Accepted 24 July 2019

### ABSTRACT

Due to deterioration in the surface water quality and the rainfall scarcity, an increasing demand for groundwater is imposed. Most of groundwaters are characterized as hard water, requiring solutions for water softening, preferably applying environmentally friendly, low-cost and low-energy processes. A new eco-friendly and low-cost method was studied for hard water softening, consisting of the combination of water carbonation followed by application of *Moringa oleifera* seeds. Three hard water samples, characterized by different levels of initial hardness, were pretreated with carbon dioxide. The effects of independent variables, such as stirring, rest time of water after carbon dioxide injection, dosage of *Moringa oleifera* seeds and settling time, had been evaluated. The hard water softening was optimized using a factorial design and a central composite rotational design, in a sequence. Following variables were determined as the optimal for a hardness removal: Water 1 – *M. oleifera* dosage equal to 2,621.4 mg/L; Water 2–2,592.8 mg/L and Water 3–2,478.5 mg/L in 102.4 min of settling time. Developed methodology was efficient in the hard water softening and represents one simple, environmentally friendly and low-cost process, as an alternative to the existing complex methods, proving to be a process of technological innovation.

**Keywords:** Central composite design; CO<sub>2</sub>; Hard water; *Moringa oleifera*; Water softening

### 1. Introduction

Groundwater is the main source of domestic, industrial and agriculture supplies in many regions of Brazil and other part of the world [1–3]. An increasing demand for groundwater is imposed, due to deterioration in the surface water quality and the rainfall scarcity. Most of the available groundwater is classified as hard water, because of the presence of ions, mainly calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) [4].

The use of hard water for supplying can compromise the operation of domestic and industrial devices, because of

the deposition of salts on the surface of appliances. In consequence, this could decrease their efficiency and lifespan and increase energy consumption [5–8].

The currently available water softening methods include chemical precipitation using lime [9], nanofiltration [10], carbon nanotubes [11], capacitive deionization [12], electrochemical precipitation [13], electrocoagulation [14], magnetic field and electrostatic field [15], short pulse plasma application [16]. However, these processes are energy-consuming and expensive for the operation and maintenance of the equipment. In addition, the most commonly used, that

\* Corresponding author.

is chemical precipitation, generates large volumes of sludge, containing chemicals that are required for pH adjustment [17,18]. The electrochemical precipitation has some additional limitations to previously cited, as the requirement of a very large specific area of the electrode; a sacrifice electrode and the necessity of reverse electrode polarity; its drawbacks restrict the allowable current density and shorten the lifetime of electrodes [19–21]. Therefore, a significant need in a search for environmentally friendly, low-cost, and low-energy processes for water softening is imposed.

The presence of carbon dioxide (CO<sub>2</sub>) in water in a greater or lesser amount is a determining factor for the precipitation of calcium carbonate [22–24]. The injection of CO<sub>2</sub> reduces the pH of water by its hydration to carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and contributes to the precipitated dissolution of calcium carbonate [22]. One another alternative for hard water softening is the use of *Moringa oleifera* seeds [25–29].

*M. oleifera* is a native tree of India that grows in the tropics and subtropics of Africa, Asia and the United States. It is well known by various medical benefits of its leaves in prevention and treatments of diabetes [30], cancer and cardiovascular diseases [31]. Seeds of *M. oleifera* are used to remove unwanted coloration [32], turbidity [33,34], microorganisms [26,33] and organic matter [35,36] from water and effluents [37]. *M. oleifera* is known to be a natural cationic polyelectrolyte and flocculant, with a chemical composition of basic polypeptides with molecular weights ranging from 6,000 to 16,000 daltons, containing up to six amino acids of mainly glutamic acid, methionine and arginine [28,38].

To our knowledge, no scientific or technological experience has been reported about the integrated process of carbonated hard water softening with *M. oleifera* seeds. We hypothesized that *M. oleifera* extracts could assist in softening of carbonated water, directed at the development of one simple and sustainable water treatment methodology. We also hypothesized that different parameters such as stirring, rest time of water after CO<sub>2</sub> injection, dosage of *M. oleifera* seeds and settling time would define the success in carbonated hard water softening with *M. oleifera* seeds. It was fundamental to define and optimize those parameters, in order to attain the highest removal efficiencies of hard water hardness. Thus, the aim of this work was to evaluate the efficiency of the *M. oleifera* seed extracts in the carbonated hard water softening and to optimize the complexity of the parameters controlled in the softening process.

## 2. Materials and methods

### 2.1. Sources of groundwater

The groundwater used in the experiment was originated from three sites in the North region of Minas Gerais, Brazil. Waters were collected from tube wells. They were characterized as alkaline with high carbonate hardness. The water with the greatest hardness entitled Water 1, was collected in Janaúba; the intermediate hardness water, Water 2, was collected in Capitão Enéas; the lowest hardness water, Water 3, was collected in Montes Claros. The initial quality of three water samples was characterized (Table 1) using the APHA methodology [39]. The same methodology was used in water characterization after the experimental procedure.

Table 1

Initial quality characteristics of three distinct water samples (hardness reduction from Water 1 to Water 3)

Analyzed variables	Water 1	Water 2	Water 3
Hardness (mg/L as CaCO <sub>3</sub> )	510.00	328.00	233.00
Alkalinity (mg/L as CaCO <sub>3</sub> )	360.00	174.00	248.00
Ca <sup>+2</sup> (mg/L)	174.00	109.00	73.00
Mg <sup>+2</sup> (mg/L)	12.00	10.60	12.00
pH	7.10	7.10	7.50
Chloride (mg/L)	129.00	29.00	3.00
Total iron (mg/L)	<0.10	<0.10	0.46
Total manganese (mg/L)	<0.10	<0.10	0.17
Electric conductivity (μs/cm)	1,172.00	500.00	468.00
Fluoride (mg/L)	0.37	0.27	0.10
Turbidity (NTU)	0.27	1.10	2.40
Sulfates (mg/L)	57.30	3.3	3.00

### 2.2. Experimental procedure

#### 2.2.1. Experimental apparatus

A system for carbonation of water was set up [22]. In this system, CO<sub>2</sub> is injected into a known volume of water (22 L), and the pH is monitored during the gas injection into the container. This stage had as objective to determine the pH CO<sub>2</sub>-saturated water. The experimental apparatus (Fig. 1) used for the optimization of carbonation consisted of a cubic-shaped glass container of 30 L capacity. The container had three upper openings: the first one for gas inlet (made by means of a hose containing a stainless steel gas injector), a second one for the gas circulation and a third for introduction of the pH electrode.

White Martins CO<sub>2</sub> of 99.5% purity was used. The gas was supplied from the 4.5 kg CO<sub>2</sub> cylinder containing pressure regulator and flowmeter to control the CO<sub>2</sub> flow rate. The cylinder was calibrated to a pressure of 3.5 kgf cm<sup>-2</sup>. The used CO<sub>2</sub> flow rate was 6 L min<sup>-1</sup>.

#### 2.2.2. Determination of the pH CO<sub>2</sub>-saturated water (pHs CO<sub>2</sub>)

Curves of pH values vs. time of application of CO<sub>2</sub> were plotted measuring the pH of the water at each 5 s during CO<sub>2</sub> injection, by using a bench pH meter with a combined electrode of pH (model PH-21, Hanna Instruments, Italy). The curves were drawn to obtain the pHs CO<sub>2</sub>, which represented the value at which the pH of the water is stabilized even under the continuous CO<sub>2</sub> addition.

### 2.3. Carbonation

After obtaining the pHs CO<sub>2</sub> and the necessary time of CO<sub>2</sub> injection for pHs CO<sub>2</sub> had been reached, the carbonation tests were carried out for each studied water. The container (Fig. 1) was filled with 22 L of hard water, and CO<sub>2</sub> was injected in water for as long as necessary to reach pHs CO<sub>2</sub>. After this time, the CO<sub>2</sub> inlet valve was closed in the water and the vents at the top of the vessel were properly sealed with rubber caps. The influence of the rest time of

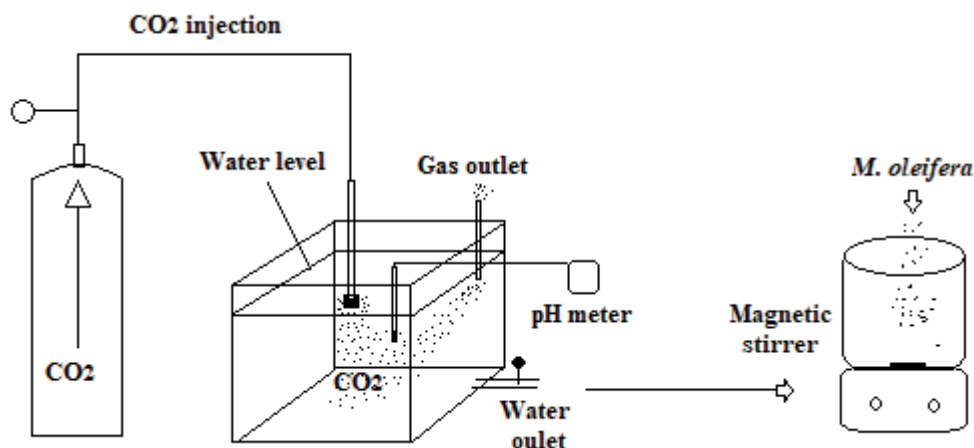


Fig. 1. Experimental sequence scheme for hard water softening, using carbonation and treatments with extracts of *Moringa oleifera* seeds.

the water after CO<sub>2</sub> injection was evaluated and the following times were studied: 0, 24 and 48 h. After the rest time, 1 L of carbonated water was collected and used in the next step in developing methodology, the test with *M. oleifera* seeds.

#### 2.4. *Moringa oleifera* tests

The *M. oleifera* seeds used in this experiment were collected from trees located in the park of Institute of Agricultural Sciences in Montes Claros, Minas Gerais, Brazil. The dried seeds were removed from the pod and ground in a household blender. The particulate material was sieved to standardize particle size. Particles smaller than 0.3 mm were used. *M. oleifera* extract was used on the same day of preparation, following recommendations of Ndabigengesere et al. [40], the desired dry mass of the extract (Table 2) was weighed on an analytical balance and added in 1 L of carbonated water to be treated. In the first design, the following dosages of *M. oleifera* extract were studied: 0, 1,000 and 2,000 mg/L of carbonated water. The beaker containing the *M. oleifera* extract and water was brought into a magnetic stirrer (Q261, Quimis), which was set to speed determined during the experiment (Table 2). It was stirred for 15 min at room temperature. After the stirring time, the equipment was turned off and each sample rested for settling time, to deposit the sediments. When the settling time was reached, samples of the supernatant were collected for residual hardness analysis.

#### 2.5. Experimental design

The experiment was divided into two stages, using two different statistical designs in a sequence: fractional factorial ( $2^{4-1}$ ) and central composite rotational design (CCRD).

The fractional factorial design had the exploratory aims, as a selection of factors with a significant effect on softening and an evaluation of the ranges (levels) of tested values. Four factors (independent variables) were studied: *M. oleifera* dosage, water rest time after CO<sub>2</sub> injection, agitation of carbonated water after addition of *M. oleifera* seeds and settling

Table 2

Coded and uncoded levels of the independent variables on factorial design ( $2^{4-1}$ )

Variables	Levels		
	-1	0	1
<i>Moringa oleifera</i> dosage (mg/L)	0	1,000.0	2,000.0
Rest time (h)	0	24.0	48.0
Stirring (rpm)	0	150.0	300.0
Settling time (min)	0	30.0	60.0

time. The removed hardness was the used variable response. The ranges of variation between the lower and the upper limits (levels) of each independent variable were established based on preliminary tests (Table 2).

A CCRD design was carried out with the aim to optimize the factors with a significant effect on softening and determining the optimal treatments. In CCRD, the stirring was fixed at the upper level (+1), since in the factorial design was determined that the best results in hardness removal were obtained when the system was submitted to 300 rpm. The rest time of the water after CO<sub>2</sub> injection was not statistically significant. Therefore, in CCRD design the water was collected immediately after CO<sub>2</sub> injection for the tests with *M. oleifera*. The *M. oleifera* dosage and sedimentation time varied. CCRD design consisted of a factorial  $2^2$  with four axial points and five central points, totaling 13 runs, performed in a random sequence, attaining following values of the coded and real levels of the independent variables (Table 3).

The value of  $\alpha$  was dependent of the number of independent variables ( $k = 2$ ) and was calculated using Eq. (1):

$$\alpha = (2^k)^{1/4} = 1.414 \quad (1)$$

The variation ranges between the lower and the upper limits of each independent variable in CCRD design were established based on the results obtained by the factorial design and using data from the literature [26,28].

Table 3  
Coded and real levels of the independent variables in central composite rotational design

Independent variables	Coded and real levels of independent variables				
	$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
<i>M. oleifera</i> dosage (mg/L)	1,293.0	1,500.0	2,000.0	2,500.0	2,707.0
Settling time (min)	17.6	30.0	60.0	90.0	102.4

### 2.6. Statistical analysis

The analysis of variance (ANOVA) was performed at a 95% confidence level. Modeling and analysis of experimental data were performed by using the Minitab v.17. Experimental results were fitted to a second-order polynomial model by using the least square method to optimize the variables in the softening process. The quadratic equation model for predicting the optimal conditions can be expressed as Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} x_i x_j \quad (2)$$

where  $Y$ ,  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ ,  $\beta_{ij}$  are the predicted response, the regression constant coefficient, the linear coefficient, the quadratic coefficient and the interaction coefficient, respectively, and  $x_i$  and  $x_j$  are the coded values of the variables [41]. The linear and quadratic coefficients and the interactions between the factors in the mathematical model were obtained for the response of water hardness. Contour plots for the removed hardness were obtained. The residual concentrations of calcium, magnesium, alkalinity and the final pH of the water treated were analyzed in the optimum conditions obtained for the removal of hardness, using the obtained mathematical model (Eq. (2)) and the desirability function, available in the statistical program.

## 3. Results and discussion

### 3.1. pHs $\text{CO}_2$

The pHs  $\text{CO}_2$  for Water 1, Water 2 and Water 3 were 5.8, 5.6 and 5.7, respectively (Fig. 2). The times taken to reach pHs  $\text{CO}_2$  were 290.0, 325.0 and 335.0 seconds for Water 1, 2 and 3, respectively.

Three studied hard waters were naturally saturated with carbonate, thus would not express pH below 6.0. However, due to the injection of  $\text{CO}_2$  into the water, the pH was reduced to values below 6.0, since the dissolved  $\text{CO}_2$  reacted with the water forming carbonic acid, which had been rapidly dissociated to hydrogen ions and bicarbonate ions, resulting in an increased concentration of these ions in water (Eqs. (3) and (4)):



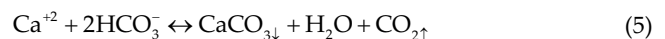
The obtained pHs  $\text{CO}_2$  values (Fig. 2) could be explained by the different alkalinities of the studied waters (Table 1). However, pHs  $\text{CO}_2$  would never fell below the point where

the equilibrium between carbonic acid ( $\text{H}_2\text{CO}_3$ ) and bicarbonate ions ( $\text{HCO}_3^-$ ) predominates (Eq. (4)). Thus, the increase of the total carbonate species, promoted by the addition of  $\text{CO}_2$  to the water, promoted the reduction of the pH of equilibrium between the carbonic acid and bicarbonate species until the pH saturation. In one closed system, this provokes the increases in  $\text{Ca}^{+2}$  saturation concentrations in the water [22], and  $\text{Ca}^{+2}$  is susceptible to adsorption by the *M. oleifera* seeds [28,42].

### 3.2. Fractional factorial design

In the significance test of the main effects of coagulant dosage, settling time, rest time and stirring in removal of water hardness, Pareto graphs were generated (Fig. 3). The coagulant dosage, settling time and stirring were significant on the removal of water hardness ( $p < 0.05$ ). On the other hand, the rest time after the  $\text{CO}_2$  injection did not show the significant effect on the studied softening process ( $t_{\text{cal}} < t_{\text{tab}}$ ).

The stirring promoted the removal of dissolved  $\text{CO}_2$  in water [43]. The decreased concentration of carbonic gas in water promoted by the stirring is explained by Le Chatelier's principle, because the calcocarbon equilibrium of the reaction (Eq. (5)) is displaced towards the formation of the calcium carbonate precipitates and, consequently, the water hardness decreases.



The increased water-softening efficiency as response to the increased stirring speed to about 80.0 rpm is observed when *M. oleifera* seeds are used as softening agent [44]. Above this value, due to the brittleness of the flake, a slight

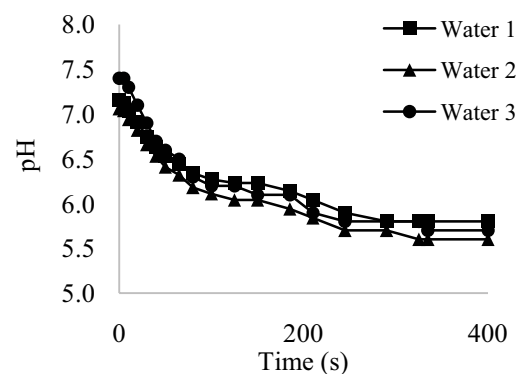


Fig. 2. Water pH as a function of  $\text{CO}_2$  injection time in three distinct hard water samples.

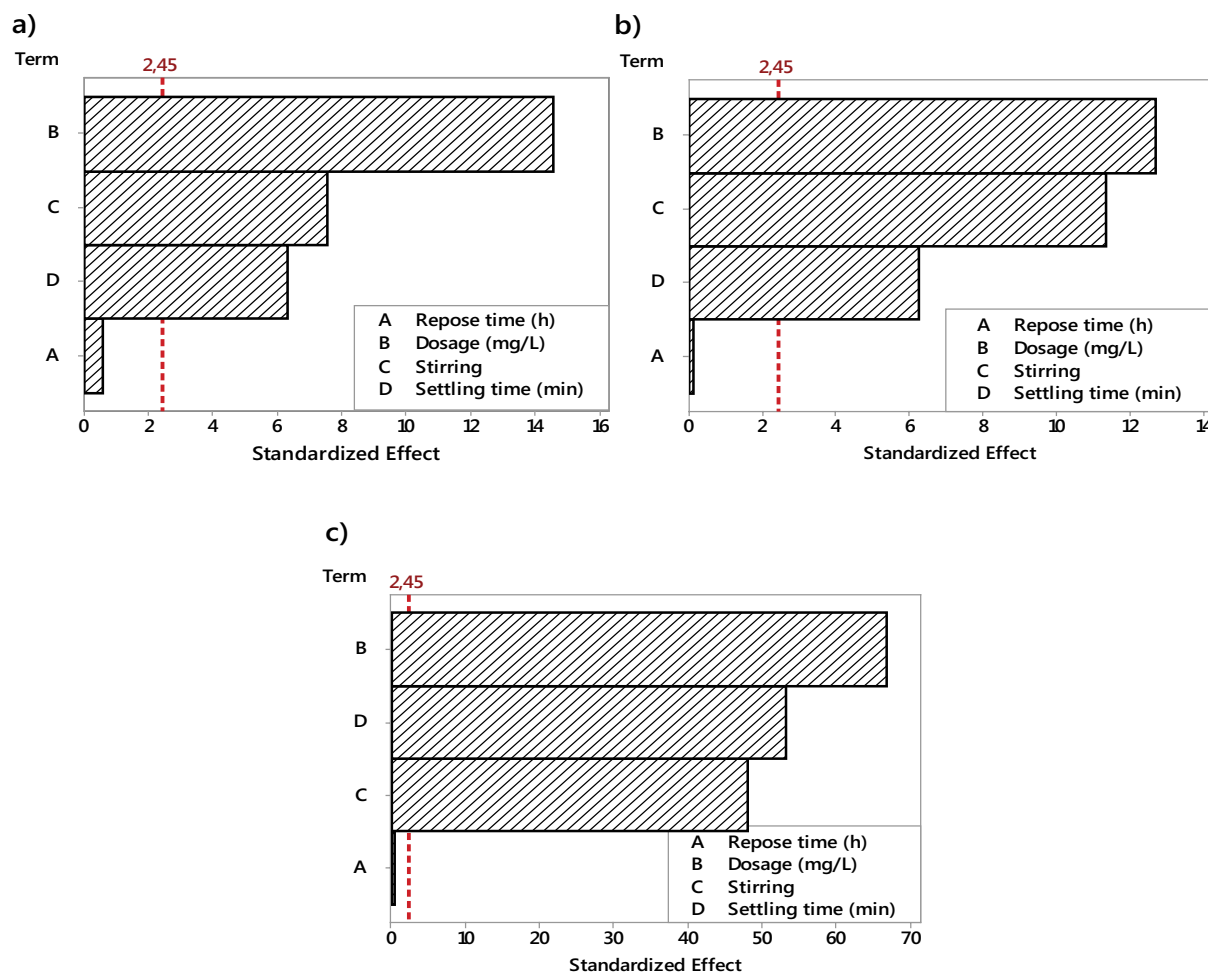


Fig. 3. Pareto plot of effects of rest time, dosage of *M. oleifera* seeds extracts, stirring and settling time evaluated for (a) Water 1, (b) Water 2 and (c) Water 3.

loss of efficiency is noticed, certainly due to the breaking of the flakes and the dispersion of the colloidal material. It is noteworthy that Sánchez-Martín et al. [44] employed the stirring only as a mechanism to increase the flocculation efficiency, different from our experiment, in which the stirring provided, in addition to the flocculation, the aggressive CO<sub>2</sub> removal. Thus, the optimum stirring speed found in our work (300.0 rpm) was much higher than determined by Sánchez-Martín et al. [44].

### 3.3. Optimization using CCRD

In the CCRD design, we choose to fix the stirring variable at the maximum studied value, that is, 300.0 rpm (Table 2), since at this speed the hardness removal was the most efficient. Values above 300 rpm could cause shear stresses that lead to the breaking of the formed flakes, not being common in the literature [28]. Thus, the *M. oleifera* dosage and the settling time varied from 1,293.0 to 2,707.0 mg/L and 17.5 to 102.4 min, respectively (Table 4).

The best results of removal efficiencies of water hardness were attributed to runs 7 and 12, where high doses of coagulant (points +1 and + $\alpha$ ) with high settling time (points

+1 and + $\alpha$ ) were used (Table 3). The removal efficiency of water hardness attained the values higher than 40%, in three hard water samples, regardless of their initial hardness. The reduction of the *M. oleifera* dosage resulted in a decrease in the removal efficiency of the water hardness (Table 4), as the previously observed relation [45].

In statistical analysis of variance of the model for removed hardness, the non-significant effects were neglected (i.e., interaction dosage x settling time) in the three studied waters, leaving only the significant variables (Table 5). Variables that show low contribution to the explanation of the results can be removed from the complete model, generating simple models without prejudice to the final adjustments [46]. The higher *F*-values and lower *p*-values than 0.05 show significant factor effects on response [41]. To accomplish the predictive demand, the ratio between the calculated and measured *F*-values must be greater than 3 [47]. In our study, this ratio had the following values: 17.47, 18.05 and 15.54 for Water 1, Water 2 and Water 3, respectively, well above the expected ratio. In order to create a reliable model, the difference between the measured *R*<sup>2</sup> and adjusted *R*<sup>2</sup> should be less than 0.2 [48]. In our experiment, this difference was found in the three studied waters, indicating

Table 4  
Removal efficiencies of water hardness considering the dosage of *M. oleifera* seeds extracts and settling time in three distinct hard water samples

Run	<i>Moringa oleifera</i> dosage (mg/L)	Settling time (min)	Water 1		Water 2		Water 3	
			Removed hardness (mg/L as CaCO <sub>3</sub> )	% Hardness removal	Removed hardness (mg/L as CaCO <sub>3</sub> )	% Hardness removal	Removed hardness (mg/L as CaCO <sub>3</sub> )	% Hardness removal
1	1,500.0	30.0	138.36	27.13%	86.26	26.30%	58.72	25.20%
2	1,500.0	90.0	171.46	33.62%	113.16	34.50%	75.86	32.56%
3	2,000.0	60.0	201.76	39.56%	125.30	38.20%	86.75	37.23%
4	2,500.0	30.0	183.50	35.98%	107.39	32.74%	74.14	31.82%
5	2,000.0	60.0	193.60	37.96%	116.90	35.64%	81.78	35.10%
6	2,000.0	60.0	209.10	41.00%	126.28	38.50%	85.98	36.90%
7	2,000.0	102.4	226.44	44.40%	140.38	42.80%	96.02	41.21%
8	1,293.0	60.0	141.47	27.74%	86.33	26.32%	58.95	25.30%
9	2,000.0	60.0	198.90	39.00%	124.84	38.06%	81.55	35.00%
10	2,707.0	60.0	212.67	41.70%	133.17	40.60%	90.73	38.94%
11	2,000.0	17.5	150.96	29.60%	85.61	26.10%	56.62	24.30%
12	2,500.0	90.0	223.58	43.84%	147.17	44.87%	101.68	43.64%
13	2,000.0	60.0	201.76	39.56%	126.05	38.43%	81.78	35.10%

excellent reliability of the models (Table 5). It can also be observed that the lack of adjustment was not significant at the 5% probability level ( $F_{\text{calculated}} < F_{\text{measured}}$ ), which is the desirable level for when obtaining a regression model [41].

The adjustment indicators of the model indicated a good fit of the chosen model (Table 5). Higher is the  $R^2$  (closer to 1.0), better is the model and smaller is the error. Models with  $R^2$  values greater than 0.60 can be used for predictive

purposes [49]. The second-order polynomial equations modeled the removed hardness as a function of *M. oleifera* dosage and of the settling time (Eqs. (6)–(8) for Water 1, 2 and 3, respectively:

$$Y_1 = 177.5 + 0.2558 A + 16.93 B - 0.000052 A^2 - 0.786 B^2 \quad (6)$$

$$Y_2 = -95.6 + 0.1336 A + 12.45 B - 0.000026 A^2 - 0.537 B^2 \quad (7)$$

Table 5  
Analysis of variance (ANOVA) of the regression models for the removed hardness in Water 1, 2 and 3

Source	Df	Water 1		Water 2		Water 3	
		F-value	p-value	F-value	p-value	F-value	p-value
Model	4	67.09	<0.001*	69.30	<0.001*	59.68	<0.001*
Linear	2	116.46	<0.001*	127.07	<0.001*	111.61	<0.001*
Dosage	1	127.54	<0.001*	105.45	<0.001*	94.70	<0.001*
Settling time	1	105.38	<0.001*	148.69	<0.001*	128.53	<0.001*
Square	2	17.73	0.001*	11.53	0.004*	7.75	0.007*
Dosage <sup>2</sup>	1	30.10	0.001*	16.60	0.004*	10.56	0.007*
Settling time <sup>2</sup>	1	9.07	0.017*	9.31	0.016*	6.90	0.017*
Error	8	–	–	–	–	–	–
Lack of fit	4	1.44	0.367 <sup>NS</sup>	1.36	0.388 <sup>NS</sup>	1.98	0.285 <sup>NS</sup>
Pure error	4	–	–	–	–	–	–
Total	12	–	–	–	–	–	–

	Water 1			Water 2			Water 3		
	$R^2$	$R^2_{\text{adj.}}$	$R^2_{\text{pred}}$	$R^2$	$R^2_{\text{adj.}}$	$R^2_{\text{pred}}$	$R^2$	$R^2_{\text{adj.}}$	$R^2_{\text{pred}}$
Fit estimators	0.971	0.957	0.902	0.972	0.958	0.922	0.967	0.951	0.905

\*Significant ( $p < 0.05$ ); NS: no significant ( $p > 0.05$ ); Df: degrees of freedom;  $R^2$ : R-squared;  $R^2_{\text{adj.}}$ : adjusted R-squared;  $R^2_{\text{pred}}$ : predicted R-squared; F tabulated for regression: 3.84; F tabulated for lack of fit: 6.39.

$$Y_3 = -67.8 + 0.0912 A + 9.00 B - 0.000017 A^2 - 0.402 B^2 \quad (8)$$

where  $Y_1$ ,  $Y_2$  and  $Y_3$  are the removed hardness (mg/L as  $\text{CaCO}_3$ ) from Water 1, 2 and 3, respectively;  $A$  is the *M. oleifera* dosage (mg/L) and  $B$  is the settling time (min). From mathematical models (Eqs. (6)–(8)), the contour graphs were generated for relation between the removing hardness and *M. oleifera* dosage/settling time (Fig. 4).

The removal of hardness increased with increasing of the *M. oleifera* dosage and the settling time (Fig. 4). This can be proven because these two variables showed negative quadratic coefficients  $-A^2$  and  $-B^2$  (Eqs. (6)–(8)), indicating that with the increasing of the *M. oleifera* dosage and settling time, the removal efficiency of the hardness would increase. Dosages of about 2,500.0 mg/L at a settling time over 90.0 min provided for removals of nearby 45% of hardness in the Water 1, Water 2 and Water 3.

The efficiency of *M. oleifera* seeds in the removal of water hardness was higher when the water was previously carbonated (Fig. 4) when compared with the non-carbonated waters [50]. The effect of carbonation of the water on hardness removal can be explained by the equilibrium of the carbonate system.  $\text{CO}_2$  injection into water increases the total concentration of the carbonate species (law of mass action), and as a consequence, this increases, in the closed system, the saturation concentration of calcium, which induces the precipitation of  $\text{CaCO}_3$ . High concentration of calcium in the water is required to occur the precipitation of  $\text{CaCO}_3$  [22,24,42]. When free  $\text{CO}_2$  is released from the water, promoted in this work by stirring the mixture, precipitation of  $\text{CaCO}_3$  is favored by increasing pH [24].

The presence of bicarbonate in a solution, or the presence of carbonates precipitated in water, depends on the presence of a carbon dioxide in high or low amounts in water,

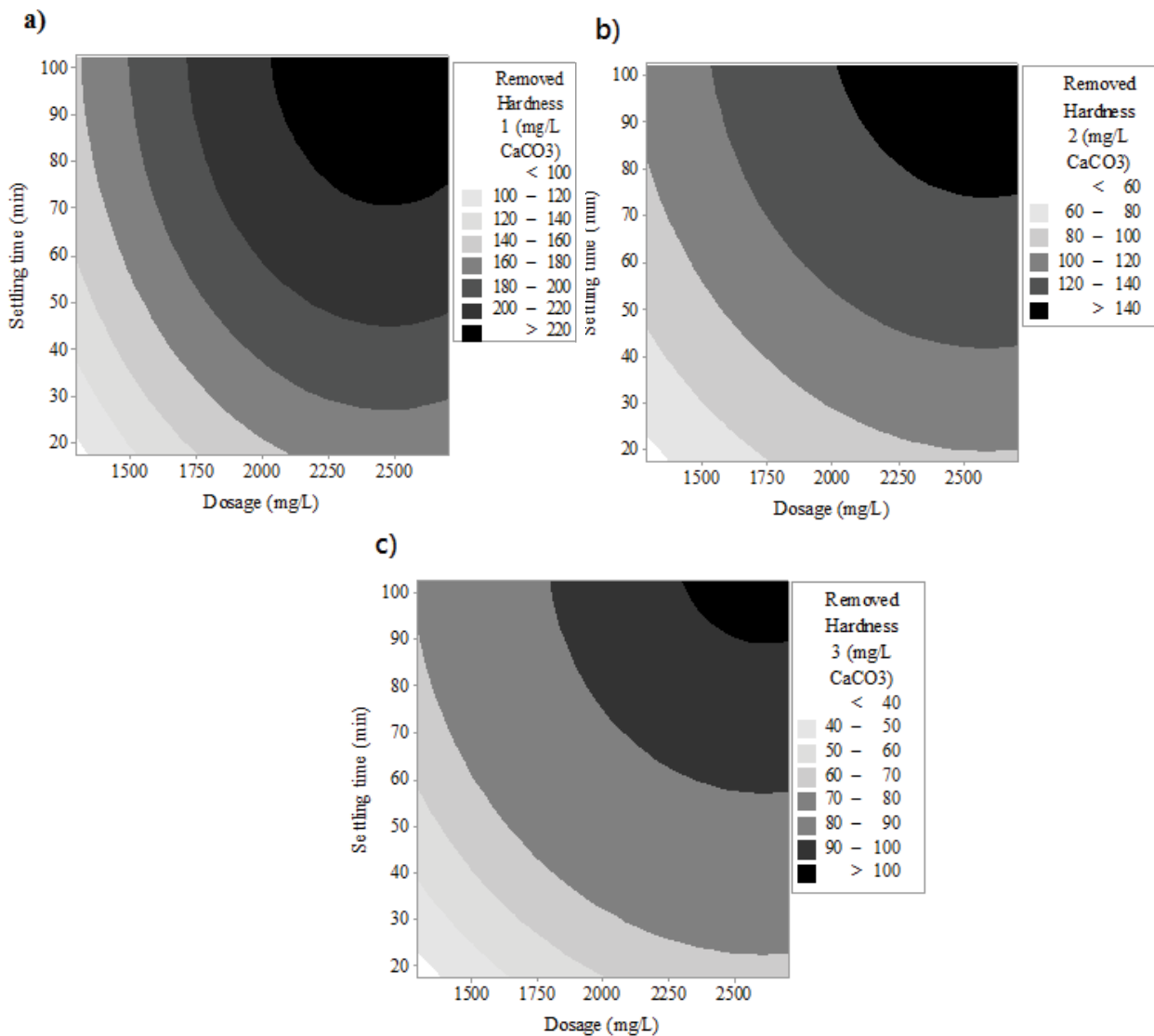


Fig. 4. Contour plots relating the removed hardness (mg/L as  $\text{CaCO}_3$ ) as a function of the *M. oleifera* dosage (mg/L) for Water 1 (a), Water 2 (b) and Water 3.



which increases all carbonate species ( $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) [22]. The precipitation of calcium carbonate from aqueous solutions can occur simply by the addition of a soluble carbonate to a solution containing a soluble calcium salt, or also by the solubilization of  $\text{CaCO}_3$  in water saturated with  $\text{CO}_2$ , forming calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$ . When carbon dioxide is released from this solution into the atmosphere, the reaction is reversed with  $\text{CaCO}_3$  and then precipitated again [22].

The residual hardness, after carbonation, is removed by *M. oleifera* seeds, which promotes the adsorption of calcium and magnesium ions [28]. As a polyelectrolyte, it may, therefore, be postulated that *M. oleifera* removes hardness in water through adsorption and inter-particle bridging [51]. Thus, the mechanism of removal of hardness by *M. oleifera* seeds can be attributed to a strong adsorption by the protein, which has previously been identified as low mass (about 7 k daltons), in combination with the tendency for the protein to associate in chains that will promote the removal of ions from water [28,52,53]. The adsorption isotherms are tending to be the Langmuir type and the conversion of soluble hardness-causing substances to insoluble products happens by precipitation [28,45].

When the *M. oleifera* seeds are used as a coagulant in the treatment of groundwater characterized by the initial hardness of 190.0 mg/L as  $\text{CaCO}_3$ , the water hardness decreases as the coagulant dosage increases, reaching 100.0 mg/L [26]. Thus, the residual hardness is consistent with the results found in our study (Table 4). When the concentration of *M. oleifera* seeds as a coagulant increases in a treatment of underground from wells characterized by the initial hardness of 496.5 mg/L  $\text{CaCO}_3$ , the water hardness will decrease [28]. At the maximum dosage studied by these authors (2,400.0 mg/L), the observed residual hardness is 232.2 mg/L as  $\text{CaCO}_3$ , similar to the values observed in our study (Fig. 2a). *M. oleifera* seeds extracted with 1.0 M sodium chloride solution (MO-NaCl) were used in surface water treatment [45]. These authors observed hardness removal efficiency of up to 80% in waters with initial hardness of 300.0 mg/L. The hard water softening with *M. oleifera* seeds was also studied by other authors [53]. According to the results, higher concentrations of the *M. oleifera* were required to soften hardness due to Ca and Mg ions than for hardness due to Ca ions alone. It took between 1,000.0 and 2,000.0 mg/L of the *M. oleifera* to reduce the Ca and Mg hardness to 200.0 mg/L  $\text{CaCO}_3$ , compared with 800.0–1,200.0 mg/L needed for Ca hardness alone.

Optimal operating parameters for hardness removal in this work were obtained using the proposed mathematical models (Eqs. (6)–(8)) and the desirability functions. The following points were determined as optimal points for removal of hardness: Water 1: coagulant dosage 2,621.4 mg/L, Water 2: 2,592.8 mg/L and Water 3: 2,478.5 mg/L, in 102.4 min of settling time. In Brazil, the Ministerial Ordinance number 2914 of the Ministry of Health [54] establishes that the maximum water hardness value for human consumption should not exceed 500 mg/L as  $\text{CaCO}_3$ . In its raw state, the Water 1 did not meet this exigency (Table 1). However, it was observed that the applied methodology for water softening promoted the reduction of hardness of Water 1 to the values lower than 500 mg/L as  $\text{CaCO}_3$  (Table 6), which placed it within the standards required by the Ordinance number 2914 [54].

#### 3.4. Characterization of water at the optimum point

The residual concentrations of calcium, magnesium, the alkalinity and final pH of the studied water were analyzed under the obtained optimal condition (Table 6). Under the optimal conditions, the pH of the water remained within the range indicated for human consumption. The low alkalinity variation was due to the absorption and/or detachment of the  $\text{CO}_2$  in the water when applied. In terms of water treatment for human consumption, the variation can be considered irrelevant.

High residual hardness values are observed due to the presence of permanent carbonates and bicarbonates present in the water, since not all carbonate present in the water will precipitate [22]. In water treatment systems, the removing of all hardness from the water is not desirable, since it may become aggressive due to low alkalinity. In addition, the ideal value of water hardness varies according to the purpose of its use [55].

The future studies can investigate the impact of aeration of carbonated waters, since it may be more efficient in the control of the species that govern the equilibrium of the carbonate system, favoring greater efficiency of precipitation and shorter reaction time.

## 4. Conclusions

The efficiency of *M. oleifera* seeds in the softening of previously carbonated water was studied, as an environmentally friendly and low-cost method. As the coagulant dosage and the settling time increased, the residual hardness

Table 6  
Water characteristics in optimum condition

Analyzed variables	Water 1		Water 2		Water 3	
	Before	After	Before	After	Before	After
Hardness (mg/L as $\text{CaCO}_3$ )	510.0	283.0	328.0	180.0	233.0	135.2
Alkalinity (mg/L as $\text{CaCO}_3$ )	360.0	356.0	174.0	168.0	248.0	243.0
$\text{Ca}^{+2}$ (mg/L)	174.0	90.0	109.0	60.6	73.0	37.6
$\text{Mg}^{+2}$ (mg/L)	12.0	10.1	10.6	13.0	12.0	10.1
pH	7.1	7.6	7.1	7.5	7.5	7.8



decreased. The following points were determined as the optimal points for removal of hardness: Water 1: coagulant dosage equal to 2,621.4 mg/L, Water 2: 2,592.8 mg/L and Water 3: 2,478.5 mg/L in 102.4 min of settling time. The obtained mathematical model indicated excellent reliability and can be used for predictive purposes. Our results showed that this methodology has potential to be used both in water softening for supply and for irrigation, as technological process in the future. The adopted methodology is simple, low cost, environmentally sustainable and ideal for decentralized water treatment systems, as in small communities in semi-arid regions that have problems with highly calcareous waters and do not have access to conventional water treatment.

### Acknowledgment

G. L. M., F. V. D. and M. R. are thankful to UFMG and COPASA for financial support.

### References

- [1] M.J. Brandt, K.M. Johnson, A.J. Elphinston, D.D. Ratnayaka, Groundwater Supplies, Twort's Water Supply, 2017, pp. 117–158.
- [2] V.G. Gude, Desalination of deep groundwater aquifers for freshwater supplies – challenges and strategies, *Groundwater Sustain. Dev.*, 6 (2018) 87–92.
- [3] R. Hirata, B.P. Conicelli, Groundwater resources in Brazil: a review of possible impacts caused by climate change, *An. Acad. Bras. Cienc.*, 84 (2012) 297–312.
- [4] N.N.A. Kadir, M. Shahadat, S. Ismail, Formulation study for softening of hard water using surfactant modified bentonite adsorbent coating, *Appl. Clay Sci.*, 137 (2017) 168–175.
- [5] B. Van der Bruggen, H. Goossens, P.A. Everard, K. Stemgée, W. Rogge, Cost-benefit analysis of central softening for production of drinking water, *J. Environ. Manage.*, 91 (2009) 541–549.
- [6] D. Hasson, G. Sidorenko, R. Semiat, Low electrode area electrochemical scale removal system, *Desal. Wat. Treat.*, 31 (2011) 35–41.
- [7] J. Wang, Y. Liang, Anti-fouling effect of axial alternating electromagnetic field on calcium carbonate fouling in U-shaped circulating cooling water heat exchange tube, *Int. J. Heat Mass Transf.*, 115 (2017) 774–781.
- [8] Y. Yu, H. Jin, P. Meng, Y. Guan, S. Shao, X. Chen, Electrochemical water softening using air-scoured washing for scale detachment, *Sep. Purif. Technol.*, 191 (2018) 216–224.
- [9] V. Gitis, N. Hankins, Water treatment chemicals: trends and challenges, *J. Water Process Eng.*, 25 (2018) 34–38.
- [10] A.A. Izadpanah, A. Javidnia, The ability of a nanofiltration membrane to remove hardness and ions from diluted seawater, *Water*, 4 (2012) 283–294.
- [11] M.A. Tofighty, T. Mohammadi, Permanent hard water softening using carbon nanotube sheets, *Desalination*, 268 (2011) 208–213.
- [12] C. Kim, J. Lee, S. Kim, J. Yoon, Electrochemical softening using capacitive deionization (CDI) with zeolite modified carbon electrode (ZMCE), *Desal. Wat. Treat.*, 57 (2016) 24682–24687.
- [13] S. Zhi, S. Zhang, A novel combined electrochemical system for hardness removal, *Desalination*, 349 (2014) 68–72.
- [14] J.N. Hakizimana, B. Gourich, C. Vial, P. Drogui, A. Oumani, J. Naja, L. Hilali, Assessment of hardness, microorganism and organic matter removal from seawater by electrocoagulation as a pretreatment of desalination by reverse osmosis, *Desalination*, 393 (2016) 90–101.
- [15] J. Sohaili, H.S. Shi, Lavania-Baloo, N.H. Zardari, N. Ahmad, S.K. Muniyandi, Removal of scale deposition on pipe walls by using magnetic field treatment and the effects of magnetic strength, *J. Cleaner Prod.*, 139 (2016) 1393–1399.
- [16] Y. Yang, A. Gutsol, A. Fridman, Y.I. Cho, Removal of CaCO<sub>3</sub> scales on a filter membrane using plasma discharge in water, *Int. J. Heat Mass Transf.*, 52 (2009) 4901–4906.
- [17] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, *J. Hazard. Mater.*, 170 (2009) 530–551.
- [18] K.S. Brastad, Z. He, Water softening using microbial desalination cell technology, *Desalination*, 309 (2013) 32–37.
- [19] D. Hasson, V. Lumelsky, G. Greenberg, Y. Pinhas, R. Semiat, Development of the electrochemical scale removal technique for desalination applications, *Desalination*, 230 (2008) 329–342.
- [20] D. Hasson, G. Sidorenko, R. Semiat, Calcium carbonate hardness removal by a novel electrochemical seeds system, *Desalination*, 263 (2010) 285–289.
- [21] B.A. Kraft, Electrochemical water disinfection: a short review, *Platinum Met. Rev.*, 52 (2008) 177–185.
- [22] F.V. Duarte, Influência da aplicação de gás carbônico na redução de precipitação de carbonatos em sistema de irrigação localizada, UFMG, 2010.
- [23] R. Menzri, S. Ghizellaoui, M. Tlili, Calcium carbonate inhibition by green inhibitors: thiamine and pyridoxine, *Desalination*, 404 (2017) 147–154.
- [24] S. Smith, F. Mackenzie, The role of CaCO reactions in the contemporary oceanic CO Cycle, *Aquat. Geochem.*, 22 (2016) 23.
- [25] J.W. Fahey, *Moringa oleifera*: a review of the medical evidence for its nutritional, therapeutic, and prophylactic properties. Part 1., *Trees Life J.*, 1 (2005) 1–33.
- [26] S.M. Mangale, S.G. Chonde, P.D. Raut, Use of *Moringa oleifera* (Drumstick) seed as natural absorbent and an antimicrobial agent for ground water treatment, 1 (2012) 31–40.
- [27] J.F. Morton, The horseradish tree, *Moringa pterygosperma* (Moringaceae)—a boon to Arid Lands?, *Econ. Bot.*, 45 (1991) 318–333.
- [28] S.A. Muyibi, L.M. Evison, *Moringa oleifera* seeds for softening hardwater, *Water Res.*, 29 (1995) 1099–1104.
- [29] J.T.A. Oliveira, S.B. Silveira, I.M. Vasconcelos, B.S. Cavada, R.A. Moreira, Compositional and nutritional attributes of seeds from the multiple purpose tree *Moringa oleifera* Lamarck, *J. Sci. Food Agric.*, 79 (1999) 815–820.
- [30] R. Gupta, M. Mathur, V.K. Bajaj, P. Katariya, S. Yadav, R. Kamal, R.S. Gupta, Evaluation of antidiabetic and antioxidant activity of *Moringa oleifera* in experimental diabetes, *J. Diabetes*, 4 (2012) 164–171.
- [31] M. Vergara-Jimenez, M. Almatrafi, M. Fernandez, Bioactive components in *Moringa oleifera* leaves protect against chronic disease, *Antioxidants*, 6 (2017) 91.
- [32] V. López-Grimau, M. Vilaseca, C. Gutiérrez-Bouzán, Comparison of different wastewater treatments for colour removal of reactive dye baths, *Desal. Wat. Treat.*, 57 (2016) 2685–2692.
- [33] B. Bina, M.H. Mehdinejad, G. Dalhammer, G. Rajarao, M. Nikaeen, H.M. Attar, Effectiveness of *Moringa oleifera* coagulant protein as natural coagulant aid in removal of turbidity and bacteria from turbid waters, *World Acad. Sci. Eng. Technol. Int. J. Environ. Ecol. Eng.*, 4 (2010) 261–263.
- [34] G.L. Muniz, F.V. Duarte, S.B. de Oliveira, Use of *Moringa oleifera* seeds for the removal of turbidity of water supply, *Revista Ambiente e Água, Ambient. e Água - An Interdiscip. J. Appl. Sci.* 10 (2015) 454–463. Available at: <http://www.ambi-agua.net/seer/index.php/ambi-agua/article/view/1439> (Accessed 26 February 2019).
- [35] J.P. Francisco, J.B.G. Silva, O.C.C. Roque, A.L. Nascentes, L.D.B. Silva, Evaluation of the effect of the seed extract of *Moringa oleifera* lam over the efficiency of organic filters in wastewater treatment of dairy cattle breeding, *Eng. Agríc.*, 34 (2014) 143–152. Available at: <http://www.scielo.br/pdf/eagri/v34n1/v34n1a15.pdf> (Accessed 26 February 2019).
- [36] A.F.S. Santos, P.M.G. Paiva, J.A.C. Teixeira, A.G. Brito, L.C.B.B. Coelho, R. Nogueira, Coagulant properties of *Moringa oleifera* protein preparations: application to humic acid removal, *Environ. Technol.*, 33 (2012) 69–75.
- [37] A. Srivastava, D. Mittal, I. Sinha, I. Chakravarty, R.B. Raja, Study of adsorption isotherms for the reduction of basic dyes

- in effluent water using *Moringa oleifera* seeds, *Ann. Biol. Res.*, 2 (2011) 227.
- [38] S. al A. Jahn, Proper use of African natural coagulants for rural water supplies: research in the Sudan and a guide for new projects, Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH, Eschborn, Germany, 1986.
- [39] APHA, Standard Methods for the Examination of Water and Wastewater, 22nd ed., 2012. Available at: <https://store.awwa.org/store/productdetail.aspx?productid=28493774> (Accessed 26 February 2019).
- [40] A. Ndabigengesere, K.S. Narasiah, B.G. Talbot, Active agents and mechanism of coagulation of turbid waters using *Moringa oleifera*, *Water Res.*, 29 (1995) 703–710.
- [41] M.M. Momeni, D. Kahforoushan, F. Abbasi, S. Ghanbarian, Using Chitosan/CHPATC as coagulant to remove color and turbidity of industrial wastewater: optimization through RSM design, *J. Environ. Manage.*, 211 (2018) 347–355.
- [42] P.L. McCarty, C.N. Sawyer, G.F. Parkin, *Chemistry for Environmental Engineering* (McGraw-Hill series in water resources and environmental engineering), Amazon.com: Books, New York, 1994.
- [43] A. Maruscak, C.G.J. Baker, M.A. Bergougou, Calcium carbonate precipitation in a continuous stirred tank reactor, *Can. J. Chem. Eng.*, 49 (1971) 819–824.
- [44] J. Sánchez-Martín, K. Ghebremichael, J. Beltrán-Heredia, Comparison of single-step and two-step purified coagulants from *Moringa oleifera* seed for turbidity and DOC removal, *Bioresour. Technol.*, 101 (2010) 6259–6261.
- [45] M.R. Fahmi, N.W.A. Zainon Naj, P.C. Ping, N. Hamidin, Mechanism of turbidity and hardness removal in hard water sources by using *Moringa oleifera*, *J. Appl. Sci.*, 11 (2011) 2947–2953.
- [46] G.L. Muniz, A.C. Borges, D.V. Souza, T.C.F. da Silva, R.O. Batista, Comparison of the central composite rotatable design with doehlert matrix on the optimization of the synthetic dairy effluent treatment, *Water Air Soil Pollut.*, 229 (2018) 306.
- [47] G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for experimenters: an introduction to design, data analysis, and model building*, John Wiley & Sons, Chichester, UK, 1978.
- [48] Z. Sabeti, M. Alimohammadi, S. Yousefzadeh, H. Aslani, M. Ghani, R. Nabizadeh, Application of response surface methodology for modeling and optimization of *Bacillus subtilis* spores inactivation by the UV/persulfate process, *Water Sci. Technol. Water Supply*, 17 (2016) 342–351.
- [49] B. Barros Neto, I.S. Scarminio, R.E. Bruns, Como fazer experimentos: pesquisa e desenvolvimento na ciência e na indústria, Bookman, Campinas, Brazil, 2010.
- [50] G. Lopes Muniz, F.V. Duarte, P.R. Vieira, *Revista de engenharia e tecnologia, Rev. Eng. E Technol.*, 9 (2017) 20–33. Available at: <http://revistas2.uepg.br/index.php/ret/article/view/11951> (Accessed 26 February 2019).
- [51] T.W. Healy, *Adsorption-flocculation Reactions of Macromolecules at the Solid-liquid* - Thomas William Healy - Google Livros, 1963.
- [52] H.M. Kwaambwa, M. Helling, A.R. Rennie, Adsorption of a water treatment protein from *Moringa oleifera* seeds to a silicon oxide surface studied by neutron reflection, *Langmuir*, 26 (2010) 3902–3910.
- [53] S.A. Muyibi, C.A. Okuofu, Softening hard wellwaters with *Moringa oleifera* seed extracts, *Int. J. Environ. Stud.*, 50 (1996) 247–257.
- [54] Brasil, PORTARIA Nº 2.914, DE 12 DE DEZEMBRO DE 2011, 2011, pp. 1–38. Available at: [http://bvsms.saude.gov.br/bvs/saudelegis/gm/2011/prt2914\\_12\\_12\\_2011.html](http://bvsms.saude.gov.br/bvs/saudelegis/gm/2011/prt2914_12_12_2011.html) (Accessed 26 February 2019).
- [55] C.A. Richter, *Água: métodos e tecnologias de tratamento*, Edgar Blucher, São Paulo, 2009.