Column design for groundwater hardness removal using cashew nut shells activated carbon with potential application in low-income communities

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ABSTRACT

In the present study, design parameters for a filter to remove groundwater hardness were investigated. Water hardness has a significant impact on groundwater, especially in arid and semi-arid regions, leading to wasted investments in borehole drilling and worsening accessibility to potable water. In many developing countries, groundwater is the main source of drinking water. In this study, low cost and readily available cashew nut shells activated carbons (CNSAC) were used to remove hardness from groundwater in a column setting. The recommended design parameters for the packed-bed column were as follows: area \( (A) \) of 265.0 cm\(^2\) and diameter \( (d) \) of 18.4 cm, at a flow rate \( (Q) \) of 75.0 cm\(^3\) min\(^{-1}\). For the field hard water at a flow rate of 2.0 mL min\(^{-1}\), the recommended empty bed contact time was 70.7 min whereas the breakthrough time was about 430.0 min. Also for field hard water, the results showed that competing ions in the groundwater lowered the materials adsorption capacity. Results from this study indicated that CNSAC may be used to adequately remove groundwater hardness. Using these results, a filter was designed. The designed water hardness filter, which will be scaled up for point-of-use applications, may provide the much-needed solution to many people in most developing countries where similar field conditions prevail.

Keywords: Activated carbon; Cashew nut shells; Column design; Groundwater; Hardness removal; Water filter

1. Introduction

Accessibility to adequate and potable water for all is among the key goals of the World Health Organization (WHO) and Sustainable Development Goals (SDGs) [1]. It is approximated that 1.1 billion people around the world do not have access to potable water. A large proportion of this population is from the rural and peri-urban areas of developing countries [2,3]. The use of unsafe water contributes to about 80.0% of water-related diseases and kills around 10 million people annually [4–7].

Poor access to potable water is attributable to a lack of expertise in water supply operation and maintenance as well as the lack of skills in water quality improvement. This, coupled with the prevalence of geological and anthropogenic contaminant levels, may lead to contamination of rural water supply systems and expose the rural communities various risks [8,9].

In areas with limited surface water resources, communities depend largely on groundwater. For example, in rural areas of Tanzania, where this study was conducted, 42.0% of the population depends on groundwater as their sole source of drinking water [10]. Furthermore, in the central and coastal areas of Tanzania, groundwater is reported to be highly contaminated with hardness-causing ions, making the water unsuitable for domestic use [11]. As can be seen in Fig. 1, a total of 43.0 groundwater boreholes in the Tanzanian capital, Dodoma, was recorded with water hardness well

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Above the acceptable standards. Mg and Ca ions are known to contribute to water hardness. When present at very high levels, these ions cause a salty taste in water [12]. Mg- and Ca-rich sedimentary rocks are the main sources of water hardness in the groundwater systems of Tanzania [13].

The levels of Ca and Mg salts in groundwater in some parts of Tanzania have been reported to be as high as 1,300.0 mg L\(^{-1}\) as CaCO\(_3\). The Tanzanian Bureau of Standards (TBS) and WHO recommended a level of hardness in water are 600.0 and 500.0 mg L\(^{-1}\) as CaCO\(_3\), respectively (Fig. 1). Thus, the hardness burden in these water sources is costly because it leads to damages in water supply infrastructure, renders groundwater unsuitable for irrigation, and leads to poor access to potable water. Infrastructure damages caused by water hardness include clogging of water pipes, sinks and other appurtenances [12,14–16].

Many conventional hardness removal methods have been developed. These include, but are not limited to membrane filtration, ion exchange, and electron-based techniques [17]. However, in most developing countries such as Tanzania, high installation, operation, and maintenance costs hinder the applicability of these techniques.

Adsorption of contaminants onto activated carbons has increasingly become the industry standard when it comes to ionic decontamination of aqueous solutions. Adsorption is a process of enriching chemical species from a fluid phase onto solids. It is efficient removal of a variety of solutes from aqueous solutions. Usually, molecules or ions are removed from the aqueous solution by adsorption onto a solid surface known as an adsorbent [18]. Adsorption using activated carbons made from agro-wastes has been proven to be efficient in water and wastewater treatment [19]. Cashew nut shells, which are among the abundant agro-wastes, are usually disposed of after extraction of the endosperm. When converted into activated carbons, the once-waste cashew nut shells can be used to reduce the levels of ionic contaminants in groundwater, hence softening the once-hard water.

The average annual production of cashew nuts in Tanzania stands at 300,000 tons, and it is expected to increase due to the recent government interventions. Tanzania is the leading cashew nuts grower after Nigeria and Côte d’Ivoire and is the eighth largest producer of cashew nuts in the world [20]. Water softening using cashew nutshell activated carbon (CNSAC) has been reported to have 90% efficiency in the softening of hard water in batch tests [22]. Activated carbons from cashew nut shells have high carbon content and possess great adsorption capacity mainly due to their porosity [23].

Although batch laboratory studies provide useful information on the use of CNSAC-based adsorbents for the removal of specific constituents in water, continuous column studies give the most realistic application of the processes involved in water treatment. This is attributable to the higher adsorption abilities in equilibrium with the influent concentration rather than the effluent concentration [24]. Batch tests are known to provide a simple experimental setup. However, these tests have limitations including environmental concerns on the disposal of the sludge remaining after filtration. Also, batch tests are useful when the material used is in powder form with particle sizes <40 μm [25]. Furthermore, in a batch setup, the sorbate-sorbent mixture needs to be agitated at a predetermined rate, followed by sedimentation and filtration. In a column setup, these additional steps are usually not necessary. Moreover, in batch tests, it is relatively difficult to recover the biosorbents after
use. That is why this study uses a fixed-bed column set up for the removal of hardness from groundwater.

In many rural areas in developing countries, functioning centralized water treatment systems are inexistent. In such places of the world, low-cost point-of-use (PoU) treatment systems are important [26]. However, most of the available PoU water treatment technologies on the market target other things such as heavy metal ions and microbial contaminants and do not deal with the removal of water hardness to improve the taste and applicability potential of water. There are no devices on the market that specifically target water hardness. Therefore, this study aims at examining the fixed-bed adsorption column of water hardness using CNSAC to form the basis for design of a full-scale water filtration system that removes hardness from groundwater.

2. Materials and methods

2.1. Materials

The CNSAC was prepared as reported in a previous study [22]. The CNSAC of 0.4 to 1.2 mm particle size range was used. Synthetic hard water was prepared as reported by Rolence et al. [22] where 1.2 g of CaCl₂ and 1.0 g of MgSO₄ were dissolved in 1.0 L of deionized water to make hard water with 1,278.5 mg L⁻¹ as CaCO₃ hardness concentration and this solution was stocked.

Field hard water with hardness concentration of 2,172.0 mg L⁻¹ as CaCO₃ was collected from a borehole in Dodoma, central Tanzania. This sample was stored below 4°C temperature to avoid microbial activities. All reagents used for this study were of analytical grade. Other water sampling procedures were followed as stipulated in the guidelines by the American Public Health Association [27].

2.2. Experiments

Fixed-bed column studies were carried out by using a glass column with an internal diameter of 30.0 mm and a length of 600.0 mm. The CNSAC having 0.4–1.2 mm particle size range was used. The activated carbon was packed in the column sandwiched in a layer of glass wool (bottom) and glass balls (top) as seen in Fig. 2.

The column was equipped with rubber stoppers at both ends to avoid bed lifting. A constant column bed height of 200.0 mm was used. To minimize a possibility of wall and axial dispersion effects in the column, the ratio between bed length and particle size diameter of more than 20 is usually recommended [28]. The container with synthetic hard water was placed at a higher elevation to allow for gravity flow through the column. The container at a higher elevation delivered the solution to the lower container at a constant predetermined flowrate. The lower container was fitted with a pipe to maintain a constant level of the hard water in

![Fig. 2. Schematic diagram of the experimental setup for laboratory packed-bed column adsorption studies.](image)
the container to avoid flow fluctuations during the passage of water through the column. The containers were equipped with gate valves to control the flow.

The following variables were monitored: the flowrate (Q), bed depth (H), the influent concentration (C₀) and the bed diameter. The values obtained from the optimization experiments were as is shown in Table 1.

The experiments were conducted by varying the flow rate and influent concentration of the solution while keeping the bed height of the column constant. Flowrates of 2.0 and 2.5 mL min⁻¹ were used with 1,278.5 and 2,172.0 mg L⁻¹ as CaCO₃ influent concentrations for synthetic and field hard water, respectively. Effluent samples were collected at specified intervals and analyzed for residue hardness concentration by titration using a DIT 50 Behrotest® titrator. The ethylenediaminetetraacetic acid (EDTA)-titration-titration method was used; Ca and Mg ions were titrated using a standardized solution of EDTA. The endpoint was denoted by the color change of the Eriochrome Black T (EBT) indicator from red to deep blue. The experiments were terminated upon saturation of adsorbents in the column bed. Adsorption capacity (𝑞ₑ) was determined by using the following equation [18]:

\[
𝑞ₑ = \frac{(V \times (C₀ - Cₑ))}{S}
\]

where \(V\) is volume, \(L\); \(C₀\) is initial hardness, mg L⁻¹; \(Cₑ\) is effluent hardness, mg L⁻¹; and \(S\) is the CNSAC's weight, g.

### 2.3. Design methods

To predict the behavior of breakthrough curves in fixed-bed adsorption, various mathematical tools have been developed and applied. These tools are divided into two major groups, scale-up method and breakthrough curve models [25]. For this study, the scale-up method was selected. This method requires to determine the breakthrough curves from laboratory-scale experiments as the basis for predicting the behavior of breakthrough curves in full-scale applications in field conditions. Furthermore, this method is based on the fundamental relationships among the operational parameters. However, the scale-up method does not give a deeper insight into the adsorption process mechanisms. The applicability of the scale-up methods is restricted to conditions such as specific similarity criteria, where results of the laboratory-scale experiments should match the conditions in the field [25].

The breakthrough curve model, on the other hand, utilizes mathematical models that are based on equilibrium relationships and mass transfer equations. The models offer more flexibility in application. In principle, the behavior of breakthrough curves can be predicted from separately determined isotherm and kinetic parameters. However, due to the complex nature of adsorption mechanisms, more or fewer simplifications are necessary. Thus, it is important to validate any selected model using experimental data. The validation steps makes it difficult and tedious to apply the breakthrough curve models [25]. This is the reason these models were not applied for this study.

### 3. Results and discussion

#### 3.1. Adsorption mechanisms onto the CNSAC

Adsorption is a phenomenon whereby the adsorbate molecules are accumulated onto a porous solid surface known as an adsorbent [18]. Activated carbon is one of the most widely used adsorbents in the removal of both inorganic and organic micropollutants. This is due to its highly porous nature, high adsorption capacity and high affinity to hydrophobic organic contaminants. Ca and Mg ions migrate into the CNSAC micropores through intraparticle diffusional along the concentration gradient. The adsorbents in the column bed start to get saturated, the speed with which Mg and Ca ions are captured begin to decrease. In the present study, the rate of mass transfer was affected by both the influent adsorbate concentration and the hard water flow rate.

#### 3.2. Breakthrough point

At the start of the experiment, the hardness level in the effluent was low compared to the influent concentration. This was due to the initial high efficiency of the CNSAC material in the column. As time progressed, the effluent hardness kept increasing proportionally to the decreasing adsorption capacity of the CNSAC. In the end, the effluent hardness level was equal to that of the influent. This endpoint means that the adsorption efficiency in the column was zero. At this point, the CNSAC was fully saturated with Ca and Mg ions [29]. The breakthrough point is the time at which the effluent concentration reaches a specific concentration of interest [24]. In this case, the breakthrough was reached when the effluent concentration reached Tanzania hardness standard in drinking water, that is, 600.0 mg L⁻¹ as CaCO₃.

Two types of breakthrough curves were plotted: (1) effluent concentration (Cₑ) vs. time (Fig. 3a) for the synthetic hard water and (2) effluent concentration (Cₑ) vs. time for the field hard water (Fig. 3b).

#### 3.3. Effect of synthetic hard water flowrate on the breakthrough time

The effect of flowrate on hardness removal by CNSAC was studied by varying the flow rate between 2.0 and 2.5 mL min⁻¹ while maintaining a constant column height of 200.0 mm and an influent concentration of 1,278.5 mg L⁻¹ as CaCO₃.

Fig. 3a indicates that there was a substantial time (420.0 and 360.0 min) spent to reach breakthrough for synthetic hard water compared to field hard water (240.0 and 180.0 min) in

### Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (mL min⁻¹)</td>
<td>2.0–2.5</td>
</tr>
<tr>
<td>Bed/column depth (mm)</td>
<td>200.0</td>
</tr>
<tr>
<td>Influent hardness (mg L⁻¹ as CaCO₃)</td>
<td>1,278.5</td>
</tr>
<tr>
<td>Bed diameter (mm)</td>
<td>30.0</td>
</tr>
</tbody>
</table>
Fig. 3b for both 2.0 and 2.5 mL min\(^{-1}\) flow rates respectively. This may be attributed to the fact that for the synthetic hard water (Fig. 3a), there was no much competition for the binding sites because the water was spiked with only one contaminant. The initial hardness level for the synthetic hard water was low compared to that of the field hard water.

3.4. Effect of field hard water flowrate on the breakthrough time

As Fig. 3b indicates the breakthrough time decreased from 430.0 to 360.0 min as flowrate increased from 2.0 to 2.5 mL min\(^{-1}\), respectively. As can be seen in Fig. 3a, when the flow rate was low, it took a long time to reach the breakthrough point. This phenomenon may be attributable to the fact that at lower flowrates, the movement of Ca\(^{2+}\) and Mg\(^{2+}\) into the pores of the CNSAC is slow; the CNSAC required more time to capture and bind the ions.

Moreover, it was noted that as the flow rate increased, the breakthrough time was decreased. The curve became steeper with increased flowrate and reached the breakthrough point faster. This implies that the mass transfer zone was shortened indicating effective intraparticle diffusion effects [30]. When the hard water flow rate was increased, it led to the reduced rate of adsorption which is due to the limited residence time of the hard water in the column [31]. Increasing flowrate reduced the lifespan of the CNSAC in the column and hence a quick saturation of the column bed.

Also, Fig. 3b indicates how changes in the influent hardness concentration of the field water influenced the breakthrough time. Field hard water with a total hardness of 2,172.0 mg L\(^{-1}\) as CaCO\(_3\) was used for this experiment. The column height, as well as the inlet flow rates were the same as the ones used in the previous experiment.

When compared to the results from the synthetic hard water, it is clear that breakthrough curves for the field hard water became steeper (Fig. 3b) and breakthrough time became shorter as seen in Table 2.

This change in both the breakthrough curves and time could be attributed to the higher initial hardness in the field of hard water compared to the initial hardness of the synthetic hard water. The steeper breakthrough curves and reduction in breakthrough time may also be attributable to low mass transfer flux from the solution onto the particle surface because of weak driving forces [32,33].

High water hardness meant that the abundance and availability of hardness-causing ions also increased and quickly populated the binding sites [34]. Another reason for the steeper curve and shorter breakthrough time could be the fact that unlike the synthetic hard water, the field hard water had other contaminants that were competing with hardness-causing ions for the binding sites.

3.5. Hardness removal capacity vs. time

Figs. 4a and b show the adsorption capacity vs. time at different influent flowrates for both synthetic hard water and field hard water. At a lower flow rate, the synthetic hard water reached a maximum sorption capacity (70.0 mg g\(^{-1}\)) at around 100 min. The field hard water with a lower flowrate reached maximum sorption capacity (125.0 mg g\(^{-1}\)) at around the 80 min. This difference may be attributed to the lower influent hardness levels in the synthetic hard water.
water compared to the higher initial hardness level in the field water. Furthermore, in the field of hard water, there were other pollutants apart from the hardness-causing ions. These other pollutants may have contributed to the fast achieving of the maximum sorption capacity by the field hard water [35].

On the other hand, increasing the flowrate does not cause a notable difference in synthetic hard water. But for the field hard water, at a faster flow rate, the time is taken to reach maximum sorption slightly increased. This slight increase in the time needed to reach saturation may be attributed to the reduced retention time of the hard water in the column. Furthermore, faster flowrates would mean that the rate of mixing in the column also increases. With increased mixing, it would require slightly more time for the CNSAC particles to reach saturation. This also means that if the influent concentration entering a column is high, increasing the flowrate would also cause a slight increase in the time needed to reach maximum adsorption capacity [35].

3.6. Pilot column design

The laboratory-scale column tests were used to get parameters for the full-scale design of the packed bed column for field application. The same filtration rate (FR) and bed depth which were used in the pilot laboratory experiments were also used in designs for field application.

Data used from the laboratory pilot column tests included: the flow rate (Q) of 2.0 mL min⁻¹, column diameter (D) of 30.0 mm, column bed depth (H) of 200.0 mm, the density of CNSAC of 0.5 g mL⁻¹. Other information used in the design was the breakthrough volume from the breakthrough curve of 560.0 mL and the volume at capacity exhaustion of 1,200.0 mL. To determine the required FR, the following equations were employed:

\[
\text{Filtration rate (FR)} = \frac{Q(\text{flow rate})}{A(\text{cross-sectional area})} \tag{2}
\]

where:

\[
\text{Area (A)} = \frac{\pi d^2}{4} \tag{3}
\]

Data used for the determination of FR included: the diameter (d) of the laboratory test column of 3.0 cm which yielded an area of 7.1 cm². Since the flow rate was 2.0 cm³ min⁻¹ and area (A) = 7.1 cm²; the FR obtained was 0.3 cm³ min⁻¹, applicable for the field packed-bed column. To determine the area of the packed-bed column to be used onsite, the following equation was used:

\[
\text{Area} = \frac{Q(\text{Flow rate})}{FR(\text{filtration rate})} \tag{4}
\]

Taking into consideration the onsite conditions, the assumed flow rate of the packed bed column design was 75.0 cm³ min⁻¹; therefore the obtained area (A) was 265.0 cm². Since Area (A) = \(\frac{\pi d^2}{4}\), the column diameter obtained, d, was equal to 18.4 cm.  

In this study, the time between a treatment cycle and the next cycle, that is, the empty bed contact time (EBCT) (Eq. (5)) was also estimated. For this estimation, the assumption was that the fluid used the same flow rate across the CNSAC from entry to exit.

\[
\tau(\text{Empty bed contact time}) = \frac{\text{Volume of bed}}{Q(\text{flow rate})} \tag{5}
\]

The volume of bed = A (cross-sectional area) × bed height = 141.4 cm³. EBCT = 70.7 min. Thus, the estimated EBCT was 70.7 min.

The column bed height was computed by using the EBCT and the FR where the height (H) = EBCT × FR = 70.7 × 0.3 = 20.0 cm. This height is the same as the height of the laboratory test column because the height of the column is set
Table 3
Summary of a filtration system design parameters

<table>
<thead>
<tr>
<th>Design parameters</th>
<th>Values</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate, mL min⁻¹</td>
<td>2.0</td>
<td>Same flow rate used in the laboratory to be used in field application</td>
</tr>
<tr>
<td>Column diameter, cm</td>
<td>18.4</td>
<td>–</td>
</tr>
<tr>
<td>EBCT, min</td>
<td>70.7</td>
<td>–</td>
</tr>
<tr>
<td>Bed depth, cm</td>
<td>20.0</td>
<td>Same bed depth used in the laboratory to be used in field application</td>
</tr>
<tr>
<td>Quantity of adsorbent per cycle of experiment, kg</td>
<td>2.5</td>
<td>–</td>
</tr>
</tbody>
</table>

by EBCT (τ) and FR and these are the same for both laboratory test column and the field packed-bed column.

The mass of the CNSAC needed to complete one cycle of hardness treatment was computed by using the volume of packed column = Cross-sectional area \( A \) × Height \( H \).

Volume of packed column = \( \frac{3.142 \times 18.37 \times 18.37 \times 20.0}{4} = 5301.5 \text{ cm}^3 \) \( (6) \)

Thus, mass of the adsorbent = Density of adsorbent × volume = 0.47 × 5,301.45 = 2,491.68 g = 2.5 kg

The mass of 2.5 kg of CNSAC is required to treat approx. 5.0 L of hard water in one treatment cycle. With these measurements, a user at the PoU can filter approximately four liters of drinking water of 60 min. Considering that in many rural settings in sub-Saharan Africa, a person uses approximately 25.0 L of water per day; the above design is appropriate for such rural settings. A summary of all the design parameters used in this study is provided in Table 3.

4. Conclusions

- Granular activated carbons (GACs) have been applied in many previous studies to decontaminate water. However, most of the previous studies used the GACs to remove other contaminants e.g. heavy metals, odor, and fluoride. This study used the GACs to successfully remove hardness from both synthetic hard water and field groundwater.

- Additionally, most of the previous studies that attempted to remove water hardness used batch settings. In this study, we successfully removed hardness from both synthetic hard water and real field groundwater using a column setting. The results show that the CNSAC may be applied as the filter-medium in the fabrication of filters for hardness removal. The effects of flow rate and initial hardness concentration from groundwater on breakthrough curves and adsorption capacity were also examined. For synthetic hard water, it was revealed by the present study that the adsorption capacity and breakthrough time declined with increasing flowrate. However, for the field groundwater, the breakthrough curves were steeper and the breakthrough time was quickly reached.

- In the present study, we developed and tested various filtration parameters and the results indicated that these parameters can be used for designing a hard water filter that can be affordably used in rural settings in most developing countries. However, further studies on the regeneration of the biosorbents are recommended.

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References


