Water Hardness Removal Using Wheat Straw and Rice Husk Ash Properties

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1. Introduction

Presence of dissolved divalent ions, mainly calcium (Ca²⁺) and magnesium (Mg²⁺) acquired through contact with rocks and sediments in the environment, contribute water hardness (Brastad and He 2013). Hard water reduces the cleansing power of soap and thus can affect everyday household works such as laundering, bathing and dishwashing (Suzuki et al. 2002). When hard water is heated, lime scale deposits are formed, which can disrupt the operation of water using appliances as it produces noticeable deposit of precipitates (e.g. insoluble metals, soaps or salts). Hard water also produces scale in hot water lines which may reduce and clog water flow and thus frequent replacement is required (Suzuki et al. 2002). The scale buildup may also reduce the efficiency and performance of water pumps.

Groundwater in different parts of Nepal is contaminated with Ca²⁺ and Mg²⁺, which have contributed for high level of water hardness (Tamrakar and Shakya 2013; Shrestha and Shrestha 2011). Out of 270 water samples collected and analyzed from different intake sources, 60, 20 and 10% of well, stream and spring water samples respectively had hardness above 180 mg/l (Tamrakar and Shakya 2013). Shrestha and Shrestha (2011) also found that 50% of water samples collected from wells in Kathmandu had water hardness greater than 180 mg/l. Like wisely, Pant (2011) reported that groundwater collected from Kathmandu valley contained hardness as high as 800 mg/l (average 220-250 mg/l).

Various advanced technologies are available to remove water hardness such as chemical precipitation, ion-exchange, membrane separation, electro coagulation, solvent extraction, reduction, reverse osmosis (Hell et al. 1998; Schaep et al. 1998; Malakoootianet al. 2010). However, such advanced technologies and materials are not easily accessible and affordable for small scale household level treatments in Nepal. Usage of ashes obtained by burning agricultural waste can be an option as ash contains potassium oxide and other metal oxides, and it can remove hardness making water alkaline (Demeyer et al. 2001) that provides a favorable condition for Ca²⁺ and Mg²⁺ precipitation (Xie et al. 2015). In Nepal, rice husk ash is the most easily available agricultural ashes as rice-mills mostly use rice husk as an energy source. People in Nepal have been traditionally using ash for washing clothes and cleaning utensils. Previous studies have shown that ash from various sources can be used for removal of heavy metals from wastewaters (Bhatnagar and Sillanpää 2010; Prasad et al. 2011). This study was designed to further understand efficacy and usefulness of ash derived from rice husk and wheat straw to remove Ca²⁺ and Mg²⁺ ions in water solution. Rice husk ash and wheat straw ash were selected as they are easily available as agricultural waste in Nepal, and contain different concentrations of potassium and other alkali metals.

2. Materials and Methods

2.1. Collection of raw materials for ash and its properties

Wheat (Triticum aestivum cv Bhrikuti) straw was collected from a local field in Kathmandu and rice (Oryza sativa cv Loktantra) husk was collected from a rice mill. They were burned separately in a muffle furnace at 600°C until a constant weight of ash obtained. The ash content in wheat straw and rice husk were 10.4% and 19.5% of dry matter, respectively. Concentrations of sodium, potassium, calcium and magnesium in the ash were determined by atomic absorption spectrophotometer (AAS) using acid digestion method. Concentrations of these elements in both ash types...
are presented in Table 1.

Table 1. Concentrations of metal elements (g/kg) in ashes

<table>
<thead>
<tr>
<th>Element</th>
<th>Rice husk ash (RHA) (g/kg)</th>
<th>Wheat straw ash (WSA) (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>0.08</td>
<td>0.68</td>
</tr>
<tr>
<td>Potassium</td>
<td>9.3</td>
<td>32.2</td>
</tr>
<tr>
<td>Calcium</td>
<td>2.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>5.7</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Table 2. Characteristics and sampling locations of water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description of the sample</th>
<th>Initial hardness (mg/l)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Well water of Tripureswor, Kathmandu</td>
<td>320</td>
<td>7.47</td>
</tr>
<tr>
<td>2</td>
<td>Tap water of Pulchowk campus, Lalitpur</td>
<td>236</td>
<td>7.60</td>
</tr>
<tr>
<td>3</td>
<td>Synthetic water of Ca$^{2+}$</td>
<td>400</td>
<td>6.48</td>
</tr>
<tr>
<td>4</td>
<td>Synthetic water Mg$^{2+}$</td>
<td>340</td>
<td>6.22</td>
</tr>
<tr>
<td>5</td>
<td>Synthetic water of combined Ca$^{2+}$ and Mg$^{2+}$</td>
<td>370</td>
<td>6.35</td>
</tr>
<tr>
<td>6</td>
<td>Synthetic water of Ca$^{2+}$</td>
<td>580</td>
<td>6.50</td>
</tr>
<tr>
<td>7</td>
<td>Synthetic water of Mg$^{2+}$</td>
<td>520</td>
<td>6.25</td>
</tr>
<tr>
<td>8</td>
<td>Synthetic water of combined Ca$^{2+}$ and Mg$^{2+}$</td>
<td>550</td>
<td>6.36</td>
</tr>
</tbody>
</table>

2.2. Preparation of water samples

The experiment included 2 groundwater and 6 artificially hardness enriched synthetic water samples. Sources and properties of the water samples used in this study are presented in Table 2. Synthetic water samples 3, 4 and 5 were prepared to make initial hardness <500 mg/l, which is normally found in water in Kathmandu. Water samples 6, 7 and 8 were prepared to make initial hardness >500 mg/l as Ca$^{2+}$, Mg$^{2+}$ and Ca$^{2+}$ + Mg$^{2+}$ hardness, respectively. The stock solutions for synthetic Ca$^{2+}$ and Mg$^{2+}$ hard water were prepared by adding 0.52 g of hydrated calcium chloride (CaCl$_2$·2H$_2$O) and 0.82 g of hydrated magnesium sulphate (MgSO$_4$·7H$_2$O) to 1 l of distilled water, respectively. Both stock solutions contained Ca$^{2+}$ and Mg$^{2+}$ hardness of about 400 mg/l.

2.3. Hardness removal experiment

For each analysis, 200 ml of water sample was put into a 500 ml beaker with a paddle jar to mix ash in water. The mixing speed was set at 100 rpm using a portable electronic tachometer. Thereafter, ashes were added and followed by stirring for 10 min. The residual hardness in treated water was measured using standard methods (APHA 1992) after one hour of settling time. Light flocks were formed in the mixture, which were filtered prior to water hardness and pH measurements.

All 8 types of water samples (Table 2) were treated with 10 different doses (2.5-25.0 g ash l$^{-1}$) at regular increment of 2.5 g) of both ash types (wheat straw ash and rich husk ash, referred as WSA and RHA, respectively hereafter). Also, each type water sample was included as control (no ash addition).

Water hardness was measured using ethylene diamine tetraacetic acid (EDTA) method (Clesceri et al. 1998). In brief, total hardness was measured by titrating the water sample against EDTA or its sodium salt so as to form a stable complex ion with Ca$^{2+}$ or Mg$^{2+}$ ions in water. In the titration, Eriochrome Black T was used as an indicator to confirm all ions contributing for hardness were complexed. At first, 50 ml of hard water was taken in a 250 ml titration flask, and then 2 ml of NH$_4$NH$_4$Cl buffer and three drops of Eriochrome Black T indicator were added, which changed the color of solution to wine red. The standard M/100 EDTA solution was titrated against water samples running from the burette until the color was changed from wine red to blue. The titration was repeated until two concurrent readings were obtained. Hardness was measured when all ions were complexed. Also, pH of the filtrates was measured using Chemiline digital pH meter (The Science House, Chennai, India).

3. Results and Discussion

The residual hardness decreased when treated with WSA and RHA (Fig. 1). In all water samples, maximum removal was achieved with lower dose of WSA (around 17.5-20.0 g/l) than RHA (~ 22.5 g/l). Removal efficiency of WSA was always higher than RHA (Fig. 2). On average, maximum removal efficiency of WSA was 76% (range 69-81%), whereas it was only 55% for RHA (range 49-58%). Maximum hardness removal efficiency of tap water (sample 2) with WSA (68%) was considerably lower than average efficiency achieved for other water samples (81%) with same ash type, which may be due to lower initial hardness of the sample (Table 2). The higher removal efficiency of WSA than RHA may be due to higher concentrations of potassium and other oxides present in the ash (Table 1). The results clearly indicate that both ash types have potentials to use as water softening materials. However, the results contradicted with the findings from Prasad et al. (2011) who reported that fly ash obtained from burning of coal increased total hardness of the mine water. The contrasting results might be related to different sources of ash, as the fly ash used in Prasad et al. (2011) study contained much lesser concentration of K (1.0%) compared to the concentrations K in RHA (9.3%) and WSA (32.2%) used this study (Table 1). Prasad et al. (2011), however, found that zeolite prepared from fly ash decreased hardness with increasing concentrations from 5 to 40 g/l. Prasad et al. (2011) also reported that zeolite rapidly removed hardness for the first but slowed down after 30 min and reached to steady state within 4 hrs. As contact time is an important aspect to remove hardness with adsorption method, further studies are needed to find saturation of the ion exchange capacity of different ash types.

For all water samples, pH increased with increased doses of ash (Fig. 3). Maximum pH of 11.2 and 10.2 were reached respectively for WHA and RSA at the highest dose of ash (25 g/l). Generally, large increase of pH of synthetic water samples was observed even at small doses of ash additions, which reached to saturation at higher doses. Such increase was also observed for natural water samples, but increasing rate was more gradual than synthetic water samples. In agreement with removal efficiency, WSA treated water samples had consistently higher pH than RHA treated samples.

Demeyer et al. (2001) reviewed pH of ashes from different sources and found a range from 8.9 to 13.19 (extracted in water). Such high alkaline nature of ash may have contributed for increased pH. Oxides in ash are hydrated in water solutions to form hydroxides, which can later react with CO$_2$ in order to form carbonates ions (CO$_3$–2) that contribute to such a rapid pH increase (Meiwes 1995; Eriksson 1998). The metal oxide concentrations in WSA were considerably higher than RHA (Table 1), and therefore, WSA might have been more efficient than RHA to increase water pH. The rapid increase in pH however decreased the removal efficiency as maximal Ca and Mg adsorption capacity may be achieved in neutral pH (Sephehr et al. 2013). Although both ash types were effective to remove water hardness, results in this study suggest that water softening by the use of agricultural ash
Fig. 1. Removal of total hardness from different water samples using different doses of wheat straw ash (WSA) and rice husk ash (RHA). Description about the water samples used is presented in Table 2.
Fig. 2. Removal efficiency of total hardness from different water samples using different doses of wheat straw ash (WSA) and rice husk ash (RHA). Description about the water samples used is presented in Table 2.
Fig. 3. pH changes of different water samples using addition of different doses of wheat straw ash (WSA) and rice husk ash (RHA). Description about the water samples used is presented in Table 2.
may not be suitable option for drinking purpose due to the high level of alkalinity in the treated water. However, this simple water softening method can be used for other usages, such as cleaning and laundering, where hard water is a major problem.

4. Conclusion

In this study, we compared wheat straw ash (WSA) and rice husk ash (RHA) for their hardness removal efficiency from water. Two water samples from natural sources and 6 synthetic water samples, with hardness ranging from 236 to 580 mg/l were included. Each water sample was treated with 10 different doses of both types of ashes ranging from 2.5 to 25 g ash l$^{-1}$. Across all studied water samples, WSA showed higher hardness removal efficiency (average 76%) than RHA (average 55%) as the hardness removal reached saturation at lower dose (17.5-20.0 g/l) of WSA addition than RHA (22.5 g/l). Although both ash sources were effective for hardness removal, it also created undesired consequence as pH of water samples increased even at small doses of ash addition which reached up to 11.2 and 10.2 for WSA and RHA treated samples, respectively at the highest dose. Thus, the results suggest that ash treatment is not useful for softening of drinking water but the technique can be used for other usages which require soft water.

References


