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Performance of Limestone as a Multi-Media Filter for Manganese Removal from Groundwater

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ABSTRACT

According to Council Directive 98/83/EC on the quality of water intended for human consumption, concentration of the manganese in the drinking water should not exceed 0.05 mg/l. However, this level of manganese concentration is higher ingroundwaterof a community (Vitia town) in Kosovo. Groundwater is used for drinking supply of some villages and is only chlorified continuing to the reservoir from where is gravitationallydisseminated to the villages. The manganese level of the water is at the range 0.3 to 0.6 mg/l. Limestone has been provenby many researchers to be a very effective filter material in manganese removal for groundwater.A miniature filtration unit was modeled to investigate the removal efficiency of manganese.The unit consists of local limestone, where a single materialis folded in three layers of different grainsizes. In fact, the aim of this paper was to assess whether limestone as a single material acting as a "multi-media filter" can reduce the manganese concentration in groundwater. On the basis of the analysis of the single snapshot sample,the removal of manganese achieved more than 95% in filtered water. Particularly, this study demonstrates that filtering the water through three layers of different grain sizes of limestone ("multi-media limestone filter") can be a good alternative for manganese removal in groundwater.

Keywords: limestone, manganese, multi-media filter, single media filter.

INTRODUCTION

Groundwater is one of the potential natural resources for human consumption in many countries around the world. As groundwater flows through the ground, metal such as manganese - except iron - is dissolved and may later be found in high concentration in the water (USGS 2018). Manganese is a mineral that naturally exists in the Earth's crust. The concentration of manganese in well water can be seasonal and vary with the depth and location of the well and the geology of an area where manganese naturally occurs in groundwater that has little or no oxygen. The presence of manganese in domestic drinking water delivery has become a serious problem, because it changes the taste, color and odor to the water (Dvorak & Schuerman 2021). This can cause staining of clothes and plumbing fixtures, and incrustation of water mains, resulting in black water and debris at the customer's tap (Schneider et al. 2001).

There are many studiesthat contribute to the possibility for manganeseremoval using different filter materials. Several researchers have reported the application of limestone as effective material in removing heavy metals from water and wastewater. According to (Elsheikh et al. 2018), the efficiency of manganese removal can be achieved using: a) potassium permanganate followed by direct filtration; b) direct filtration alone; c) sedimentation after flocculation and then followed by filtration if a high concentration of Mg^{+2} exists. A pilot-scale trickling filter with natural aeration as an alternative method to conventional water treatment plants was developed by (Tekerlekopoulou & Vayenas 2007), in order to show the efficiency of manganese removal from potable water. The support material was silic gravel and the manganese concentration at the outlet of the filter achieved to be under the maximum permitted limit of 0.05 mg/l, even for high feed concentration (up to 4.0 mg/l). (Shafiquzzaman 2017) has worked in manganese removal through the biological arsenic removal using ceramic filter. He used an arsenic removalfilter containing ceramic (clay soil and rice brain) to reduce manganese from groundwater used for drinking supply in three villages of the southwestern region of Bangladesh. The use of a ceramic filter as well as iron setting box, and iron bacterial sludge liquor in a clay pot showed manganese in values of 3.6 times higher than the Bangladesh standard limit of 0.1 mg/l was reduced to less than 0.1 mg/l. (Schneider et al. 2001) assessed through batch test the time required for the removal of manganese by pre-oxidation and microfiltration using different oxidants. It resulted that the preferred oxidant for the oxidation of manganese (to meet the removal manganese goal at 0.5 mg/l) was chlorine dioxide (among chlorine, and hydrogen peroxide). The author also investigated how the membrane system as pilot study with microfiltration will reduce the manganese concentration in raw water which is firstly oxidized with a variety of oxidants (chlorine, chlorine dioxide, and permanganate).The membrane pilot study showed that the concentration of manganese from 0.166 mg/l at the in-filter achieved0.130 mg/l at the outfilter.The use of anthracite or granular activated carbon as media filter for direct biofiltration resulted in the removal of Mn at 91% for surface water source (Granger et al. 2014).The biosorption by biomass of saccharomyces cerevisiae yeast strain showed 83% of Mn removal (Fadel et al. 2015). In these studies, the limestone filtration is followed by the combination withnatural aeration (Tekerlekopoulou & Vayenas 2007; Shafiquzzaman 2017), with cascade aeration (Sanusi et al. 2016), with oxidationusing different chemical oxidants (Schneider et al. 2001; Granger et al. 2014; Elsheikh et al. 2018), with iron-oxidized bacteria (Aziz et al. 2020), and limestone particle alone compared to gravel (Hamidi&Paul 1996). All studies showed that when using limestone as a filter material, the manganese concentration in water will meet themaximum permissible limit according to thestandards of their countries.

The chemical composition of limestone differs according to its origin (from rock-forming organisms in seas, fresh waters, lakes rivers, and caves), and its main conditions for the formation (climate and the absence of clay or sandy material) (Šiler et al. 2018). Generally, the chemical analysis of limestone from different works shows that limestones are rocks predominantly made by minerals of calcite. The calcium carbonate content is often above 95% (Nath & Dutta 2010; Akbar et al. 2015; Abdullahi et al. 2018; Šiler et al. 2018). According to (Akbar et al. 2015), the removal efficiency of manganese is higher when using limestone with high concentration of Ca. Limestone contains calcium carbonate that increases the pH to the level at which manganese became insoluble and precipitate in the form of metal carbonate.Other benefits of using limestone for water quality control are because it is economically affordable as well as locally available.

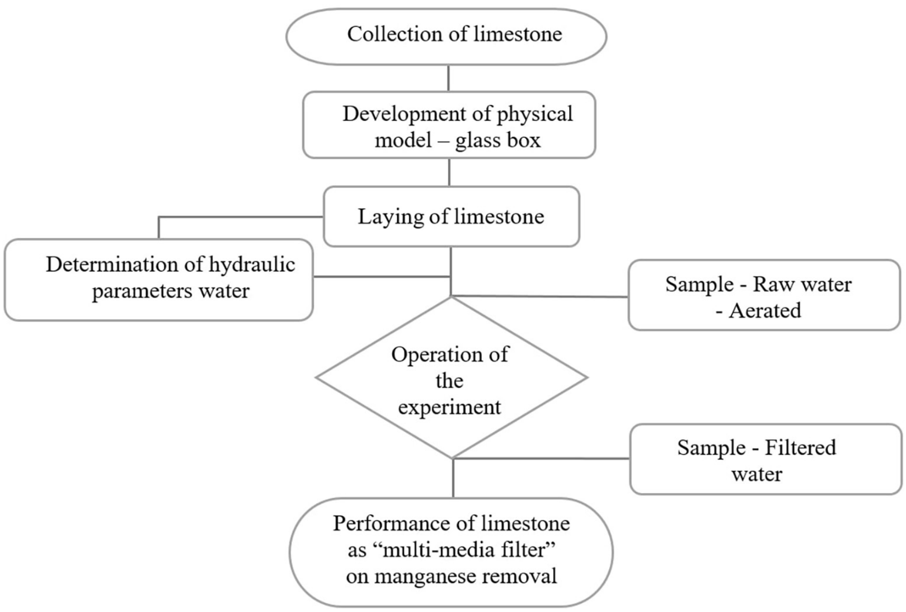

Figure 1. Scheme of the entire steps for this research

MATERIAL AND METHODS

To investigate the behavior of a single material folded in three layers of different grain sizes, acting as a "multi-media filter"comprised of local limestonein the light of manganese removal in groundwater, an experiment is developed in a physical model. The physical modelserves as a filter through which the raw water flows verticaly. The raw water which is to be treated in this filterexceeds the limited standard range of manganese concentration.The scheme shown in Figure 1 simply illustrates all steps of this research.

A detailed description of the filter material modelled and used, the physical model, as well as the whole experiment development for the treatment performance is provided next.

Filter material

The limestone used in this research as a filter material is gathered from a local stone quarry"GURI" in a village in Kosovo. For the experiment, three different size ranges of limestone are used: (0 – 2 mm); (2 – 5 mm); and (8 – 11 mm) (Figure 1), with porosities: 33%; 42%; and 50% (Figure 2. a, b, and c), respectively.

Figure 2. Limestone grain sizes used for filter media

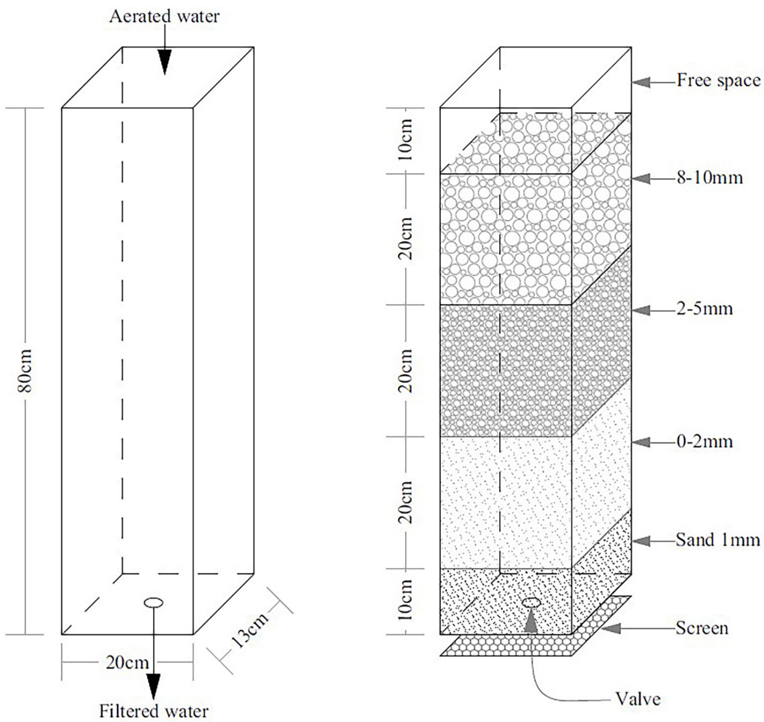

Figure 3. Physical model for experiment: (a) Model dimensions, (b) Layers of material in the model

The main benefits of using limestone for filtering are its easy availability, low cost, andeasy maintenance. Another incentive of using limestone is its high content of $CaCO_3$ (at about 95-97%), as noticed by (Akbar et al. 2015).

Physical model

A simple physical model constructed for this research is a unit with the vertical flow, as ilustrated in Figure 3a. It is a miniature filter model which consists of a glass box with a height of 80 cm, a length of 20 cm, and a width of 13 cm. The upper 60 cm of the box height (below 10 cm of free surface) is filled with filter material (Figure 3b). The filter material ranging from the smallest to the largest grain sizes of limestoneis placed on the 10 cm drainage layer as sandconsisting of 1 mm grains. The drainage material is used under the media filter to prevent the entry of any impurities of limestone (since it is not washed initially). In the bottom part of the model, a valve to collect a smaple of filtered water is placed under the screen, laid at the end of the model.

Sample collection

The water used for the experiment, gathered as a first sample and hereinafterreferred to asraw water, is collected from a closed reservoir which is filled with groundwater of a community in Kosovo. The second sample is gathered at the exit point of media filter and is hereinafterreferred to as filtered water. The gathered samplesare collected in order to measure the manganese concentration particularly, and hence are compared with the Kosovo drinking water standard limits (0.05 mg/l) for manganese (Kosovo 2021). The samples are analyzed by the Regional Water Company of the served community.

Experimental setup

For the experiment, the filter boxis fed by the pipe with the raw water containing manganese-which flows vertically, from the top to the bottom of the filter. The water flow is provided uniformly to the filter and no pond occured. The filtration unit operates with a capacity of 3.0 l/d. First thehydraulic loading rate (HLR) is calculated, then the hydraulic aplication rate (HAR) given the dosing frequency of flow is 24 doses per 24 hours, and finally the quantity of flow (Q) per dose with which the filter operates, and results presented in Table 1.

Table 1. Calculated flow parameters before filter operation

HLR	HAR	Q
11.53 cm/d	0.480 cm/dose	2.08 ml/min

The box is not fully filled, nor it is filled with same size grains of a single filter materials. Hence, the volume occupied by each of the three individual layers of the filter materialis calculated asintroduced next:

- Volume of limestone: (0 – 2 mm), (2 – 5 mm), and (5 – 11 mm): $V = 5200$ cm³.
- Volume of the drainage material (dm): $V = 2600$ cm³.
  Since the water is absorbed by filter materials, the effective volume is also calculated (Ahmedi & Pelivanoski 2016) accounting the porosity of limestone grain sizes in each layerused in the media.
- The effective volume of limestone (0 – 2 mm): $V = 1716$ cm³.
- The effective volume of limestone (2–5 mm): $V = 1965.6$ cm³.
- The effective volume of limestone (8 – 11 mm): $V = 2600$ cm³.
- The effective volume of drainage material (dm): $V = 1066$ cm³.
- The total effective volume: $V_e = 7347.6$ cm³.

The hydraulic retention time (HRT) is:

$$HRT = \frac{7347.6\ cm^3}{3000\ \frac{cm^3}{d}} = 2.44\ d \approx 58.5\ hours \quad (1)$$

Figure 4. Operation of the experiment: (a) aeration of raw water, (b) filtration of aerated water

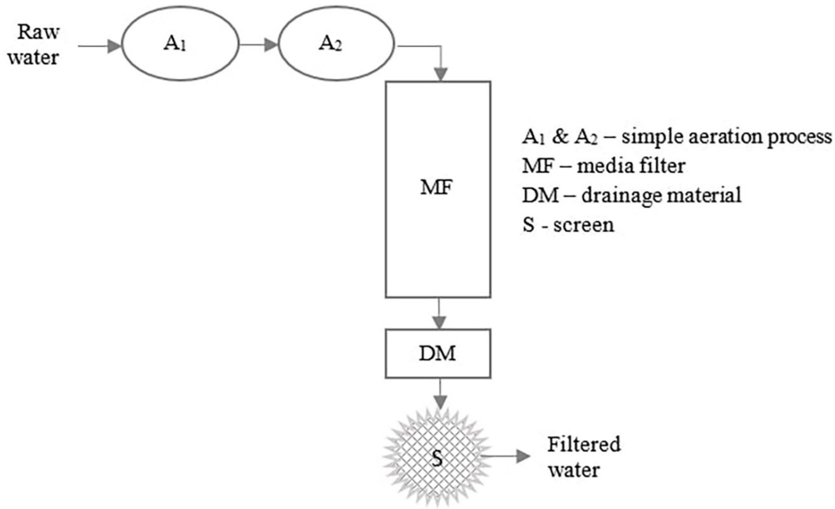

Figure 5. Schematic diagram of the water path

In order to oxidize the manganese, the water is aerated prior to filtration (as used by many researchers as an oxidation proces. See the introduction part of the paper). The simple aeration is realized using two buckets (Figure 4a), passing the water from one to another bucket (Shafiquzzaman 2021). This action is repeated six times, and then the aerated water runs uniformly to the media filter (Figure 4b). A schematic diagram of the water paths to be treated for manganese removal is presented in Figure 4. After the aeration (A_1& A_2), aerated water started to flow through the media filter (MF) to the drainage material (DM), and finally through a screen (S) before it is collected as a filtered water sample (Figure 5).

RESULTS AND DISCUSSION

The aim of this paper was to evaluate if the local limestone acting as a ”multi-media filter” can reduce the manganese from the grounwater. Flow parameters: hydraulic loading rate (HLR) hydraulic aplication rate (HAR), and the quantity of flow (Q) per doseare calculated before the operation of the filter. Further,the effective volume, considering the porosity of limestone grain size in each layers was calculated, in order to determine the hydraulic retention time (HRT). To understand the efficiency ofmanganese reduction by limestone asa single material folded in three layers with different grain sizes, as a “multi media

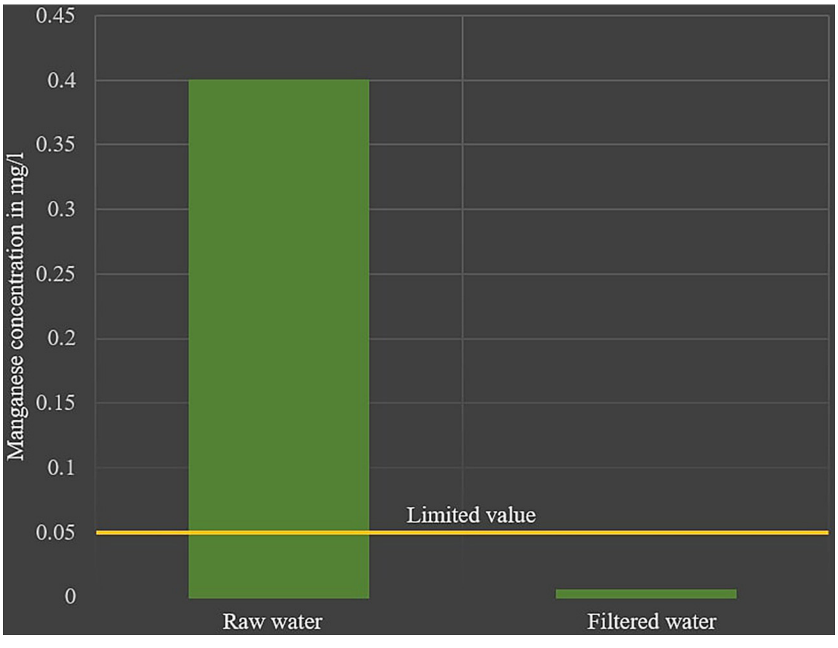

Figure 6. Manganese removal through limestone filter of different grain sizes

limestone filter", a single sample was collected for each raw water and filtered water and then the samples were analyzed for the manganese concentration. The results of analysis over this single sample present a single snapshot sample of filter media performance at the moment the sample was taken, for the sake of the experiment. An analyzedsingle snapshot sample of raw water indicated that the manganese concentration is 0.4mg/l. For filtered water, the result of a single snapshot sample collected in a glass bottleafter the filtration process indicated that the managnese removal is achieved. The results derived for raw and filtered waterare presented in Figure 6.

It is obvious from the results obtained that the manganese content in filtered water through the limestone is reduced to 98.75%. In fact, using laboratory physical model, this study shows that "multi-media limestone filter" providesremoval of manganese up to 0.005 mg/l (Figure 6). Furthermore, results show that the concentration of manganese in filtered water is within the limited valuedetermined by Kosovo drinking water standard limit (Kosovo 2021). It should be noted that data yield from only a single snapshot is not a complete picture of manganese reduction, and cannot be over-interpreted, since changes may occur over time.

CONCLUSIONS

The results prove that limestone having high content of $CaCO_3$, which has previously been introduced by many researchers, enhances the removal of manganese in groundwater at a rate of more than 95%. The filtration results of this study show that filtering groundwater through three limestone layers with different grain sizes, folded one on top of the other, can remove manganese below the 0.05 mg/l, i.e. more than 95%.

In practice, the "multi-media limestone filter" presented in this paper, given its manganese removal affinity and its characterics of being low cost and locally available, may be considered for use by water authorities like in Kosovo as a potential source of manganese removal in groundwater targeted for domestic purposes in community.Further studies on the manganese removal presented in this paper, as well as on the long-term performance of filter media in the context of clogging are still needed to provide promising results in continuous manganese removal.

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