REMOVAL OF MANGANESE AND ARSENIC FROM GROUNDWATER USING MANGANESE OXIDE COATED SAND

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Abstract -
Manganese (Mn) and arsenic (As) are common natural groundwater contaminantsin Bangladesh and many other countries. WHO (2004) recommendedhealth-based drinking water guideline values of0.4 mg/l and 0.01 mg/l for Mn and As, respectively. Removal of dissolved Mnby filtration through granular media (sand) could be an effective treatment method forMn removal from drinking water. This research work was focused evaluation of the effectiveness of different Mn-oxide coated media (synthetic media, prepared media, green sand) in removing Mn and As from water.
Laboratory investigations have been carried out to assess removal of Mn and As in three different types of Mn-oxide coated media: (a) "prepared" Mn-oxide coated filter media (prepared by passing Mn-bearing water through filter columns made up of "Sylhet" sand), (b) "synthetic" Mn-oxide coated media (prepared by treating "Sylhet" sand with $MnNO_3$, $H_2O_2$and NaOH), and(c) commercially available Mn-bearing "green sand". The average Mncontentof the "prepared" filter media was about 7,550 mg/kg; average Mn contents of "synthetic" media and "greensand"were 25,250 mg/l and 14,400 mg/kg, respectively.
The three types of Mn-oxide coated filter media have been found to be very effective in removing dissolved Mn from groundwater over a wide range of initial Mn concentration and pH.Results of both column and batch experiments showed that Mn removal efficiency increases with increasing Mn-content of the filter media. Mn removal efficiency also increases with increasing Mn in the influent water and increasing pH (in column experiments). Synthetic Mn-coated media, with the highest Mn content among the 3 media, performed best in removing Mn at higher flow rates. However, the other media ("prepared" media and greensand) also performed wellat slower flow rates. A contact time of about 1.5 minutes was found to be sufficient for almost complete removal of Mn under the experimental conditions employed in this study. Removal of Arsenic [As(III)] in Mn-oxide coated filter media has been found to be strongly dependent on pH and phosphate concentration. Removal of As decreased with increasing pH, especially at pH beyond 7.5.

I. INTRODUCTION

Two major national level surveys, the National Hydro-geochemical Survey [1] and the National Drinking Water Quality Survey (NDWQS) [2] showed that in Bangladesh, large numbers of drinking water wells exceed permissible limits for As, Fe and Mn [3]. The WHO recommends a guideline value of 0.4 mg/l [4] for Mn. About 40 percent of wells in the BGS-DPHE survey exceeded this limit [5]. The NDWQS found that 35 percent exceeded the WHO guideline value [2]. The NDWQS also found that only 60 percent meet the Bangladesh standards for As, Mn and Fe. The WHO [6] eliminated health-based guideline for Mn, noting concentration as high as 0.4 mg/l are rare; obviously this this logic is not valid for Bangladesh.
A number of technologies were developed for Fe removal, but they did not enjoy wide public acceptance. With the discovery of widespread As, community and household-level groundwater treatment units generated renewed attention; different types of treatment plants were developed based on the principle of oxidation, precipitation and filtration. However, recent studies [7, 8] showed variable performance of community As and As-Fe removal plants in removing Fe, As and Mn.
A number of studies showed that Mn is removed effectively from groundwater by oxidation and adsorption processes. Manganese oxide coatings formed on filter media act as good adsorbent for Mn and also play a role in its oxidation [9]. Media coated with synthetic Mn oxides have also been found to have good Mn removal efficiency [10, 11, 12]. Manganese oxide coated filter media could therefore be potentially used for Mn removal from groundwater, although no report of its use in Bangladesh could be gathered. Besides, there is no data on the ability of such media in removing As from water. The present work focuses on evaluation of the effectiveness of Mn and As removal in different types of Mn-oxide coated filter media.

II. METHODOLOGY

Laboratory investigations have been carried out to assess removal of As and Mn in three different types of Mn-oxide coated media: (a) "prepared" Mn-oxide coated filter media (prepared by passing Mn-bearing water through filter columns made up of Sylhet sand), (b) "synthetic" Mn-oxide coated media (prepared by treating Sylhet sand with $MnNO_3$, H_2O_2 and NaOH), and (c) commercially available Mn-bearing "green sand". The average Mn content of the "prepared" filter media was about 7,550 mg/kg; average Mn contents of "synthetic" media and "greensand" were 25,250 mg/l and 14,400 mg/kg, respectively.Figure 1 shows the experimental set up for assessment of the performance of different Mn-oxide coated media in removing Mn and As from groundwater. The filter

beds were set in transparent acrylic glass filter column with x-sectional area of 28.2 cm^2 (for "prepared" media and "synthetic" media) or 26.5 cm^2 (for "green sand"), fitted with flow control arrangements.

For the "prepared Mn-oxide coated media", the total depth of filter media in the column was 40 cm; the "prepared media" consisted of the top 5 to 6 cm (approximately) of the column, while Sylhet sand consisted of the rest of the column. For the "synthetic Mn-oxide coated media", total depth of media in the filter column was 40 cm; top 6 cm (approximately) consisting of the "synthetic media" and bottom 30 cm consisting of Sylhet sand. For "green sand", the total depth of filter media in the filter columns was 40 cm, consisting of "green sand" and Sylhet sand. The depths of "green sand" and Sylhet sand media were varied as follows: (i) Column 1: top 10 cm "green sand", bottom 30 cm Sylhet sand; (ii) Column 2: top 20 cm "green sand", bottom 20 cm Sylhet sand; (iii) Column 3: top 30 cm "green sand", bottom 10 cm Sylhet sand.

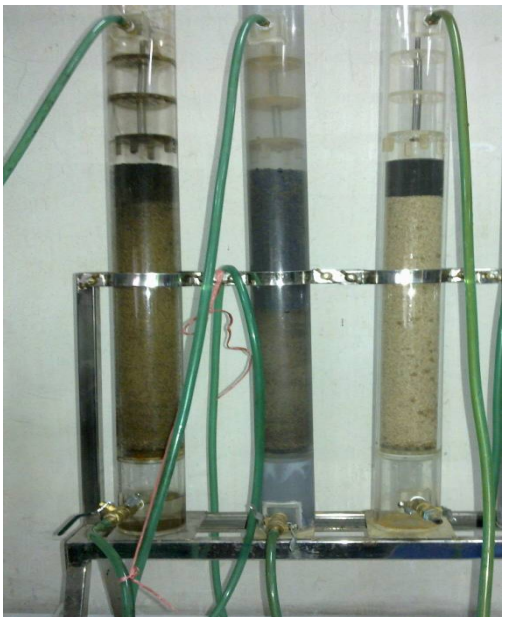


Figure 1: Experimental set up for assessing performance of different Mn-coated media in removing Mn and As from groundwater; from left to right: (a) "prepared" Mn-oxide coated media; (b) Green Sand (20 cm; Column 2); (c) Synthetic Mn-coated sand media

For assessment of removal efficiency, manganese concentration in the influent water (prepared by amending natural groundwater) was varied from 0.5 to 10.0 mg/l; while arsenic concentration was varied from 100 to 1,000 µg/l. No effort was made to adjust the pH of the influent water; pH of influent water was close to the pH of natural groundwater, 7± 0.1. However, during the experiment the pH of the influent water gradually increased to about 7.55 due to gradual release/escape of CO_2 from groundwater (used for preparing the influent water). Apart from initial Mn and As concentrations, effect of a number of water quality parameters (pH, Phosphate) and process variables (flow rate) on removal was evaluated. The surface overflow rate through the filter media was varied from 0.5 to 8.0 ml/min/cm^2 (i.e., flow rate through the filter column was varied from 14.1 ml/min to 225.6 ml/min) to assess its impact on removal of Mn.

III. RESULTS AND DISCUSSION

Mn and As Removal in "Prepared Mn-oxide Coated Media"

Figure 2 shows average Mn removal in the "prepared Mn-oxide coated media" as a function of flow rate. It shows that flow rate or contact time has a significant impact on Mn removal; removal increased as flow rate decreased or contact time increased. Figure 2 also shows that Mn-content of media also has an impact on Mn removal, with removal efficiency increasing with increasing Mn-content of filter media. Initial Mn concentration and initial phosphate concentration did not have much influence on removal efficiency.

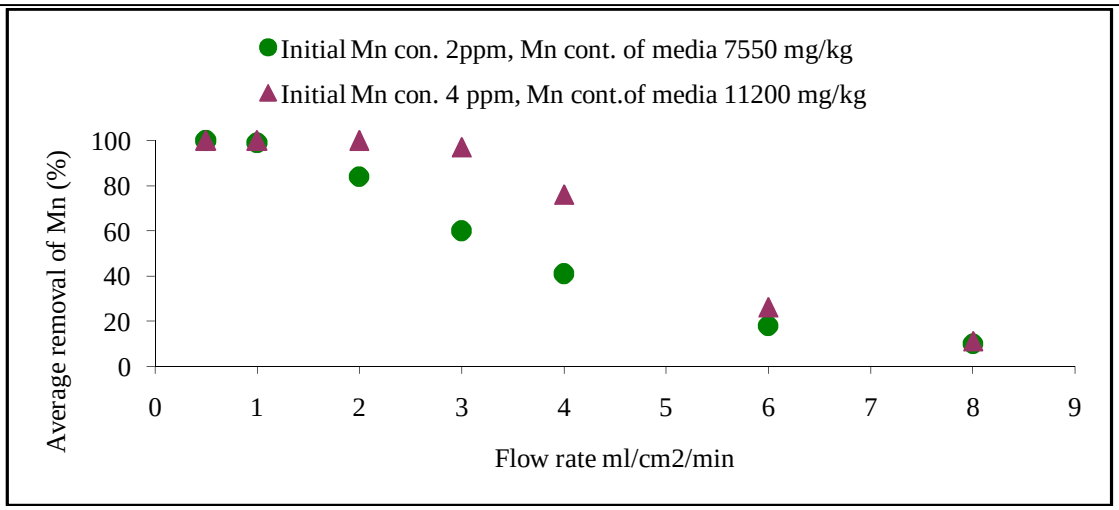


Figure 2: Mn removal in prepared Mn-oxide coated media as a function of flow rate

The removal of As in the prepared Mn-oxide coated media has been found to be a strong function pH and phosphate. Figure 3 shows removal of As(III) (initial concentration 300 □g/l) from groundwater in the prepared Mn-oxide coated media as a function of pH; Figure 4 shows average removal (up to 150 minutes filter run time) of Arsenic as a function phosphate concentration.

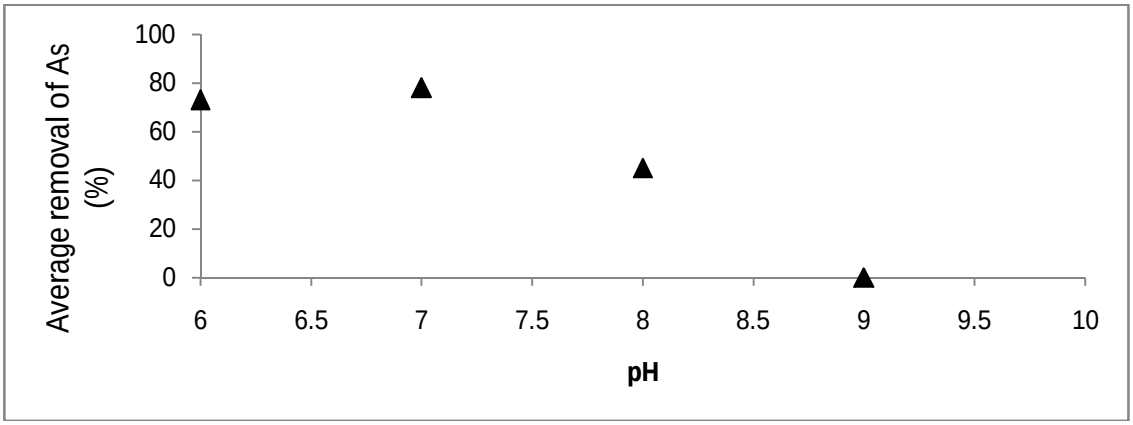


Figure 3: Removal of As(III) in Mn-oxide coated media as a function of pH

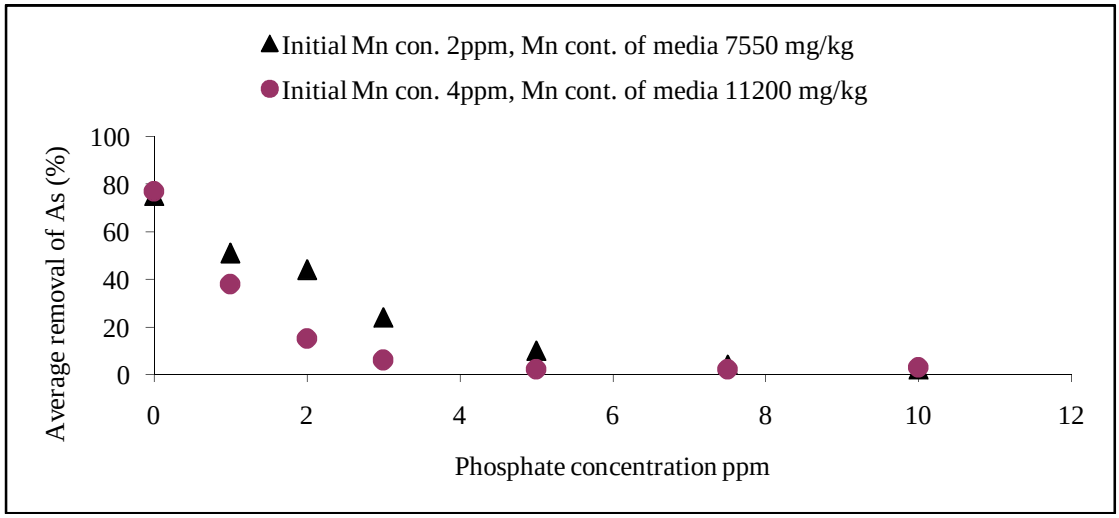


Figure 4: Average removal of As as a function of phosphate concentration

Mn and As Removal in "Synthetic Mn-oxide Coated Media"

Figure 5 shows average Mn removal in synthetic Mn-oxide coated media as a function of flow rate. As was observed for prepared Mn-oxide coated media, flow rate or contact time has a significant impact on Mn

removal; removal increased as flow rate decreased or contact time increased. As before, initial Mn and phosphate concentrations did not have much influence on Mn removal.

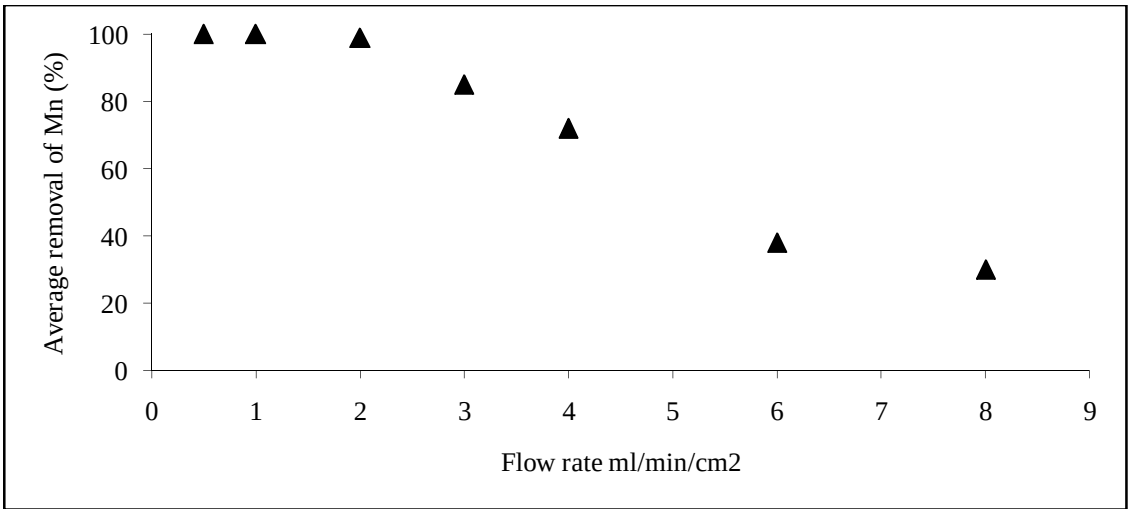
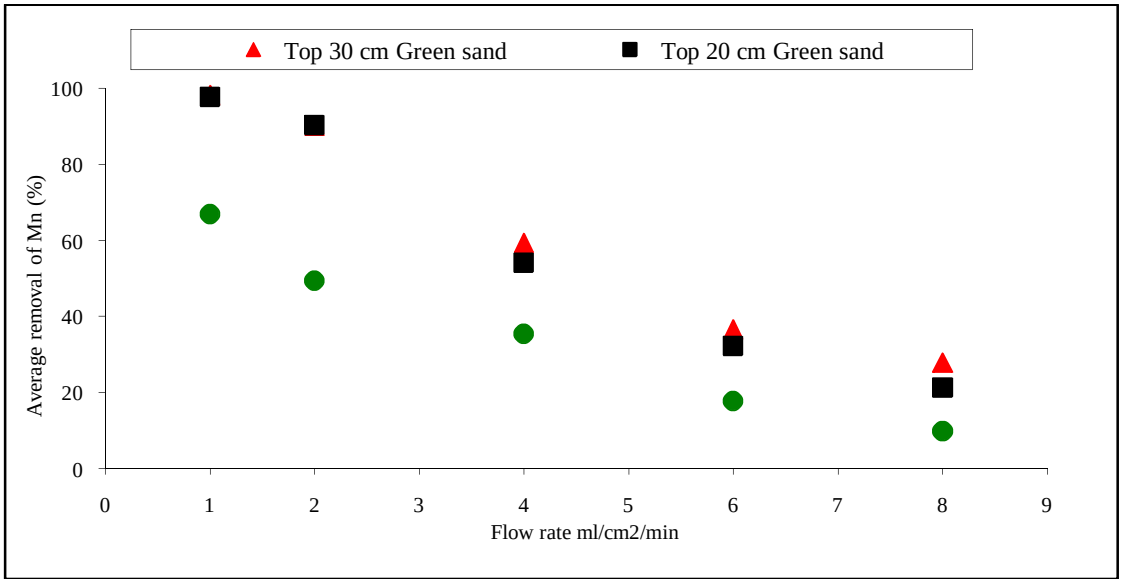


Figure 5: Mn removal in Mn-coated synthetic media as a function of flow rate

Phosphate was found to have very significant influence on Arsenic removal; Arsenic removal came down from about 60% in the absence of phosphate to about 0% at a phosphate concentration exceeding 7.5 mg/l due to competitive adsorption.

Mn and As Removal in "Green Sand"

Figure 4.19 shows average Mn removal in three different green sand columns as a function of flow rate. clearly shows that removal of Mn depends on both flow rate and depth of "green sand" (that is, depends on contact time between water and "green sand"). Removal increased as flow rate decreased or depth of green sand increased (i.e., as contact time increased). As before, initial Mn and phosphate concentrations did not have much influence on Mn removal; while Arsenic removal by the media was found to be strongly influenced in phosphate concentration.



CONCLUSIONS

Synthetic Mn-coated media with Mn content of about 25,250 mg/kg, the highest Mn content among the 3 media, performed best in removing Mn at higher flow rates. However, at slower flow rates, other media also performed well. A contact time of about 1.5 minutes was found to be sufficient for almost complete removal of Mn under the experimental conditions employed in this work.

Removal of Arsenic [As(III)] in Mn-oxide coated filter media has been found to be strongly dependent on pH. Removal of As decreased with increasing pH, especially at pH beyond 7.5 and virtually no As

removal takes place at pH 9 and beyond. Arsenic removal increased with increasing Mn-content of the filter media. Presence of phosphate significantly reduced arsenic removal due to competitive adsorption.

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