RW13
Assessment of Manganese Removal from Groundwater Using Adsorptive Filtration Media

Kazi Mahmuda Tasneem[1] and M. Ashraf Ali[2]
[1]*Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA, USA.*
[2]*Department of Civil Engineering, Environmental Engineering Division, Bangladesh University of Engineering & Technology (BUET), Dhaka, Bangladesh*

***Abstract*— Adsorption and formation of Manganese (Mn) oxide coatings on filter media are thought to be responsible for Mn removal from groundwater; however limited information is available on factors affecting formation of such coatings. In this study, manganese oxide coated sand bed was prepared and factors affecting formation of Mn oxide coating on sand was assessed. The experiments were carried out at natural pH of groundwater (7±0.1), without addition of any chemical (e.g., oxidant), for filter run time varied from 180 to 220 hours; this time is required for Mn Oxide coatings formation on filter media, which then acts as an effective adsorbent for aqueous Mn. Good Mn removal was recorded even after few minutes of filter operation especially for higher initial Mn concentrations, and the removal efficiency improved with filter run time and flow rate up to 5ml/min has little impact on Mn removal efficiency. Efficiency of iron (Fe) oxide coated sand bed in removing manganese was also assessed. Iron coated sand bed did not show satisfactory performance (only about 20% removal) for manganese removal.**

INTRODUCTION

Manganese is a common natural groundwater contaminant in Bangladesh. Although groundwater quality problems in Bangladesh include mainly the excessive concentrations of Arsenic and Iron, available data suggest that excessive concentration of Manganese is also a significant problem in many areas. The National Hydro-geochemical Survey conducted by the British Geological Survey [1] showed that in Bangladesh, large numbers of wells (both deep and shallow) exceed permissible limits for Iron (Fe) and Manganese (Mn). The National Hydro-geochemical Survey found that three quarters of the 3,534 wells surveyed in 61 out of 64 districts exceeded the Bangladesh drinking water standard (0.1 mg/l) for Manganese (Mn). Some of the reported Mn concentrations are very high, over ten times the permissible limit. Average Mn concentration in the surveyed wells has been reported to be 0.5 mg/l (median 0.3 mg/l) [2].

Water with a high concentration of iron or manganese may cause the staining of plumbing fixtures or laundry. Manganese solids may form deposits within pipes and break off as black particles that give water an unpleasant appearance and taste. High intakes of manganese through both inhalational exposures and drinking water have been shown to be toxic [3]. Manganese is best characterized as a neurotoxin; occupational exposures are associated with a characteristic syndrome called manganism, which involves both psychiatric symptoms and Parkinsonian features [4]-[6]. For high intake Manganese having adverse neurotoxic health effect, WHO recommends guideline value of 0.4 mg/L [7] to protect against neurological damage; drinking water standard from aesthetic considerations is even more stringent, 0.1 mg/L.

The Manganese issue however has attracted relatively less attention in Bangladesh. Manganese can be removed using the same processes of oxidation, precipitation and filtration as in Fe removal. Conventionally, a strong oxidant such as chlorine or potassium permanganate is used for oxidation of Mn (II) rather than oxygen alone [8]. Mn (II) oxidation can lead to precipitation of Mn (III, IV) oxides which are in turn good adsorbents and oxidants [9]. Some studies [10], [11] revealed that Mn removal is significant in some types of community arsenic-iron removal plants currently being used in some arsenic affected areas, while Mn removal is insignificant in other removal plants. While Iron and Arsenic are removed in these plants primarily by adsorptive filtration, the mechanism of Mn removal is not clearly understood. Adsorption of Mn on filter media and formation of Mn oxides coatings on the media are thought to be responsible for Mn removal and formation of Mn oxide coatings on filter media is a slow process and only limited information is available on factors affecting formation of such coatings, it is important of understand the chemistry of Manganese oxidation and adsorption of the commonly used filter media. Hence, research on formation of Manganese Oxide coatings on sand bed and the performance of Manganese removal in commonly used filter media under different parametric condition will improve our understanding of Manganese removal. It is expected that information and data generated from such a research work will provide knowledge on developing design criteria for optimum Manganese removal from natural groundwater in a treatment process.

METHODOLOGY

Preparation and development of filter bed (Column) using locally available sand

Filter bed was prepared with sand using glass burettes with a cross sectional area of 1sq cm (column height 43 cm). In this study, locally available Sylhet sand passing through #40 sieve and retaining on #50 sieve were used. The experimental set ups was consist of a sand filter bed in a burette, buckets with tap for holding raw water, flow control arrangement, and collector buckets. Groundwater, collected from a deep tubewell pump station at BUET with Manganese concentration of around 0.2 ppm, were spiked with Mn stock solution to prepare influent water with different concentrations of Mn (0.5 to 5.0 ppm). (II) Stock solution was prepared by adding known quantity of 98% pure $MnCl_2.4H_2O$ in distilled water. The influent waters

with known concentration of Mn were allowed to pass through the filter columns and residual Manganese concentrations were measured with the passage of time. Total times were recorded to assess the time required for obtaining the maturity of filter bed for optimum Manganese removal. At the same time, Manganese oxide coating formed on the media was observed visually. pH variation was also measured during Bed preparation.

Assessment of effect of various parameters (initial concentration, flow rate) on the removal of Mn in Mn oxide coated sand bed

Manganese concentration in the influent water was fixed at 0.25, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L. For these experiments, flow rate of water through the columns were maintained at about 5 mL/min. Similar experiments were carried out for assessing the effect flow rate (or contact time) on Mn removal by keeping the Mn concentration of influent water constant and varying the flow rate from 1 to 5 mL/min. No effort was made to adjust the pH of the influent water; pH of influent water close to the pH of natural groundwater, that is 7±0.1. Manganese concentration of water samples were measured using AAS-Flame (Shimadzu, AA-6800) and pH was measured using pH meter (HAC 11d). pH was varied using HCl or NaOH solution. All chemicals to be used in this research work are of reagent grade.

Assessment of Manganese Removal using Iron Oxide Coated Sand Bed

In this study, manganese removal efficiency of iron-oxide coated sand bed was evaluated. Iron coated sand bed was prepared as described by [12], [13]. Efficiency of iron coated sand bed in removing Mn (II) was evaluated in glass burettes having cross sectional area of 1 sq. cm with a column height of 43 cm.

Manganese removal efficiency was assessed following similar procedure described in previous section. Natural groundwater spiked with Manganese (II) at concentrations of 0.25, 0.5, 1, 2, 3, 4 and 5.0 mg/L were passed through the iron coated sand filter bed at natural pH of pH (7±0.1); flow rate was maintained at 5ml/min and residual Manganese concentrations were measured. The experiment with the lowest initial Mn concentration (0.25 mg/L) was carried out first, which was followed by experiments with next higher initial Mn concentration (0.5 mg/L), and so on. For each initial Mn concentration, the filter run time was about 240 to 300 minutes.

RESULTS AND DISCUSSIONS

Effect of pH on formation of Mn oxide coating on the sand filter

Batch experiments similar to those described above were carried out where the pH of influent water was varied from about 6 to 10. Manganese concentration of the influent water was maintained at 1 mg/L (Fig 1).

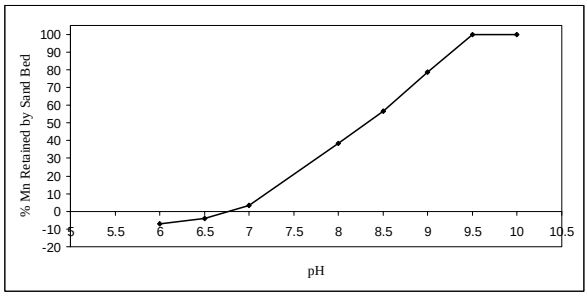

Fig.1: Effect of pH on Manganese coating formation on a sand filter bed

Fig 1 shows effect of Mn retention by the sand filter media as a function of pH of influent water. 100% of Mn was removed when pH of influent water was above 9.5. Fig 1 also indicates negative percentage of Mn retained below pH of 7 which possibly implies leaching out of the Mn content from the previously prepared bed, which results in more Mn content in effluent than that in influent Mn-bearing water.

However, a pH adjustment with addition of acid/base is a problematic operation for household or community water treatment units. Hence efforts are always made to avoid operations involving chemicals and to develop treatment systems that operate at natural pH of water. Therefore it is important to develop/prepare media that would remove significant Mn in the neutral pH range which is demonstrated in the following sections.

Effect of Initial Mn Concentration and Time on Formation of Mn Oxide Coating on Sand

The objective was the assess the time required for the filter media to achieve "maturation", that is, to reach a condition when all Mn in the influent water would be removed (or retained) by the media at natural pH.

Formation of Mn oxide coating was assessed for different initial concentrations. Groundwater spiked with Manganese (II) at concentrations of 0.5, 1.0, 2.5 and 5.0 mg/L were passed through the bed at natural groundwater pH (7±0.1) and residual Mn concentrations were measured (Fig 2).

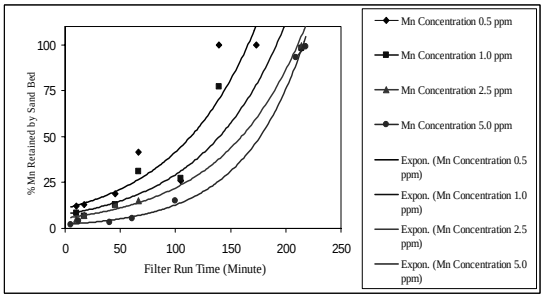

Fig. 2: Manganese removal on sand bed with different concentration of Manganese at pH (7±0.1)

Fig 2 shows Mn retention by the sand filter media as a function of "filter run time". It shows increasing rate of Mn retention with time, possibly implying autocatalytic effect of Mn oxidation, whereby previously formed Mn coating promotes further oxidation and precipitation of Mn. It shows that filter run time varied from 180 to 220 hours,

depending on the Mn concentration in influent water. In general, the media achieved maturation faster, when Mn concentration in the influent water was lower.

Effect of initial Mn concentration on Manganese removal using Mn oxide coated sand bed

In order to assess the effect of initial concentration of manganese on Manganese removal, influent groundwater with Manganese (II) concentrations of 0.25, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L were passed through the bed at natural pH of groundwater (7±0.1) and at constant flow rate 5ml/min, and residual Manganese concentrations were measured (Fig 3).

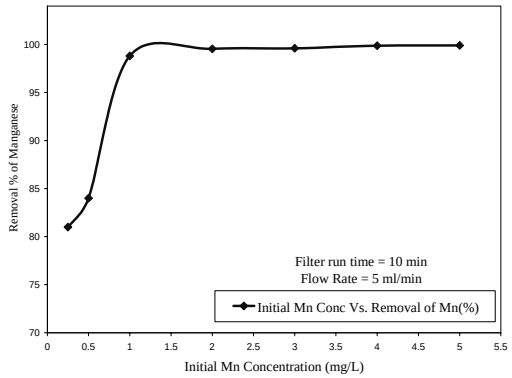

Fig. 3: Manganese removal on Mn oxide coated sand bed with different initial concentration of Mn after 10 min filter run time at pH (7±0.1) and constant flow rate 5 ml/min.

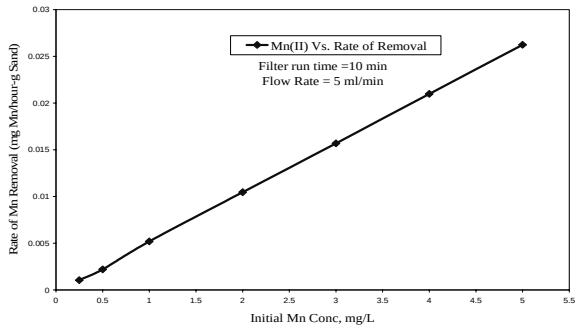

Fig. 4: Rate of manganese removal with different initial concentration of Manganese after 10 minute filter run time (at pH (7±0.1) and constant flow rate 5 ml/ min).

Results of the laboratory experiments suggest that Mn removal in the Mn-oxide coated filter media increases with filter run time and quickly approaches 100% removal. Fig 3 shows removal of Mn after 10 minutes of filter run as a function of initial Mn concentration. It shows that in general Mn removal efficiency increases with increasing Mn concentration in the raw water. For initial Mn concentration of 0.5 mg/L, Mn removal after 10 min of filter run was slightly above 80%; however, for initial Mn concentration exceeding 1 mg/L, Mn removal after 10 min of filter run approached about 100%. It should be noted the Mn removal efficiency of the filter increased with filter run time, even for influent water with low Mn concentration, and eventually approached 100% removal (see Fig. 3).

Fig 4 shows rate of removal of Mn in the filter media during the first 10 minutes of filter run time. It shows that rate of removal of Mn in the filter media was much higher when initial Mn concentration was higher. As explained earlier, this is possibly due to autocatalytic effect of Mn oxidation, whereby previously formed Mn coating promotes further oxidation and precipitation of Mn.

Effect of Flow Rate on Manganese removal using Mn oxide coated sand bed

Fig 5 shows removal of Mn in Mn-oxide coated sand filter bed for different flow rates.

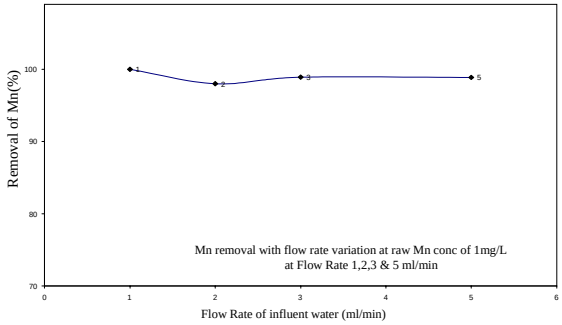

Fig. 5: Manganese removal on Manganese oxide coated sand bed with different flow rate at pH (7±0.1) and constant initial Mn concentration of 1 mg/L.

Fig 5 shows that flow rate has little impact on Mn removal efficiency of the prepared filter bed under the experimental conditions. Ideally slower flow rates should promote better Mn removal by increasing the time of contact between the aqueous Mn and the filter media. However, this effect was not apparent from these experimental results. This is probably because the "contact time" corresponding to the highest flow rate (5 ml/min) employed in these experiments was enough for the removal of almost the entire Mn present in water. However, a negative impact on Mn removal is expected at higher flow rate. The results from these experiments suggest that a flow rate of 5 ml/min (corresponding to a contact time of 2.58 minutes) will not produce any adverse effect on Mn removal in the prepared media.

Manganese Removal on Iron Oxide Coated Sand Bed

In this study, manganese removal using iron coated sand bed was assessed. Fig 6 shows removal of Mn in Fe-oxide coated sand filter for different initial Mn concentrations. For each initial Mn concentration, the treated water samples were collected after 300 minute of filter-run. It shows relatively poor Mn removal in the Fe-oxide coated sand filter. Manganese removal varied from about 16 to 23% for all initial Mn concentrations used in the laboratory experiments.

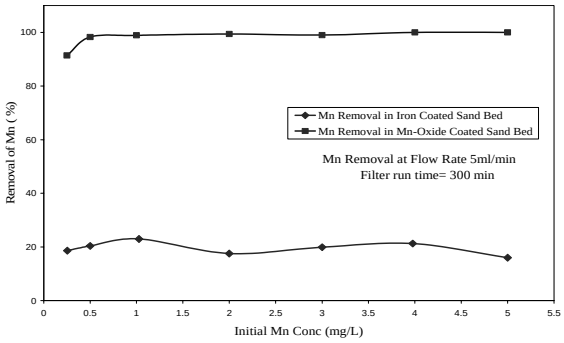

Fig. 6: Manganese removal on Mn oxide coated sand bed and Iron oxide coated sand bed with different concentration of Manganese at pH (7±0.1) and constant flow rate 5 ml/L.

Fig 6 shows Mn removal performance by the sand filter made of manganese oxide coated and Iron oxide coated sand bed. It shows that manganese removal through iron coated sand bed was not significant as compared to that on Manganese oxide coated sand bed. It shows that while Fe-coated sand bed was very effective in removing Arsenic from water [13], it has very limited capacity to remove Manganese from groundwater.

CONCLUSION

Results obtained from the experiments demonstrated that Manganese oxide coated filter media can be prepared by passing Mn-bearing groundwater through filter bed made of locally available natural sand, such as Sylhet sand, where the overall time requirement of about 220 hours under experimental condition.

The prepared manganese oxide coated sand filter bed have significant capacity of manganese removal from groundwater at natural pH of groundwater (7±0.1), without addition of any chemical (e.g., oxidant) and flow rate up to 5 ml/min has little impact on Mn removal efficiency of the prepared filter bed under the experimental conditions. This prepared bed was effective in removing Mn, satisfying national standard (0.1 mg/L) and WHO standard (0.4 mg/L), for a wide range of initial Mn concentrations.

Iron coated sand bed did not show satisfactory performance for manganese removal; only about 20% removal was achieved under the experimental conditions.

ACKNOWLEDGMENT

This research work was financially aided by Bangladesh University of Engineering and Technology for undertaking the Masters Thesis work as the requirement of Masters Degree.

REFERENCES

[1] BGS and DPHE 2001 *Arsenic contamination of groundwater in Bangladesh*, Final report, British Geological Survey and Department of Public Health Engineering, February.

[2] BGS and WaterAid 2001 *Groundwater quality: Bangladesh*, British Geological Survey and WaterAid Bangladesh.

[3] Institute of Medicine Food and Nutrition Board. 2002 *Dietary Reference Intakes: Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium and Zinc.* Washington DC: National Academy Press.

[4] Calne DB, Chu NS, Huang CC, Lu CS, Olanow W. 1994 *Manganism and idiopathic parkinsonism: similarities and differences*. Neurology. ;44(9):1583–1586.

[5] Dobson AW, Erikson KM, Aschner M. 2004 *Manganese neurotoxicity*. Ann NY Acad Sci.; 1012:115–128.

[6] Yamada M, Ohno S, Okayasu I, Okeda R, Hatakeyama S, Watanabe H, et al. 1986, *Chronic manganese poisoning: a neuropathological study with determination of manganese distribution in the brain*. Acta Neuropathol (Berl).;70(3–4):273–278.

[7] WHO 2004 Guideline for Drinking Water Quality, *Health Criteria and Other Supporting Information*, 3rd Edition, WHO, Geneva.

[8] Hartmann, P. 2002 *Iron and Manganese Removal: Simple Methods for Drinking Water*, Working Papers on Water Supply and Environmental Sanitation, The Swiss Centre for Development Cooperation in Technology Management (SKAT).

[9] Hem J.D. 1978 *Redox processes at surfaces of manganese oxide and their effects on aqueous metal ions.* Chemical Geology 21, 199-218

[10] BRTC-Unicef 2006 *Assessment of iron and manganese removal technologies for drinking water supplies in Bangladesh*, report prepared for Unicef, United Nations Children's Fund, Dhaka, by the Bureau of Research Testing and Consultation, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh.

[11] Hoque, A. 2006, *Assessment of iron, manganese and arsenic removal efficiencies of conventional iron removal plants*, M.Sc. Engineering Thesis, Department of Civil Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh.

[12] Joshi, A. and Chaudhuri, M. 1996, *Removal of Arsenic from Ground Water by Iron Oxide- Coated Sand*, ASCE Journal of Environmental Engineering, 122(8), p.769-771.

[13] Ali, M. A., Badruzzaman, A.B.M., Jalil, M. A., Hossain, M. D., Hussainuzzaman, M. M., Badruzzaman, M., Mohammad, O. I. and Akter, N. 2001, *Development of Low-cost Technologies for Removal of Arsenic from Groundwater*, Proceedings of the International Workshop on Technologies for Arsenic Removal from Groundwater, May 5-7, Dhaka, Bangladesh, p. 99-120.