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MANGANESE REMOVAL FROM DRINKING WATER USING ROUGHING FILTRATION

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Abstract

Manganese can be removed using the processes of oxidation, precipitation and filtration as in iron removal. Conventionally, a strong oxidant such as chlorine or potassium permanganate is used for oxidation of Mn(II) rather than oxygen alone.Naturally present DO and other constituents (e.g., bicarbonate) in water can promote removal of Mn in a filter media (by sorption and oxidation) without the addition of an oxidant. Two multistage filtration units (MSFU) have been constructed in Sirajgonj to investigate the effectiveness in removing manganese from groundwater adopting the technique of adsorption and co-precipitation of manganese onto the flocs of ferric hydroxide, making use of the naturally occurring iron of groundwater. Observed results indicate that manganese removal is a function of raw water manganese concentration. Higher the Mn concentration, greater is the removal performance. 80-89% manganese removal performance was achieved through this filtration process. Contribution of Down-flow roughing filter (DRF) alone in removing manganese was observed very significant (around 37%). Contribution of aeration, flocculation and sedimentation in removing manganese is around 33%. Contribution of Up-flow roughing filter (URF) in removing manganese is moderate (around15%).

Keywords: *Concentration, DRF, effect, filtration, manganese, performance, removal, URF*

Introduction

Manganese is one of the most abundant metals in Earth's crust, usually occurring with iron. It is a component of over 100 minerals but is not found naturally in its pure (elemental) form (ATSDR, 2000). Manganese is an element essential to the proper functioning of both humans and animals, as it is required for the functioning of many cellular enzymes (e.g. manganese superoxide dismutase, pyruvate carboxylase) and can serve to activate many others (e.g. kinases, decarboxylases, transferases, hydrolases) (IPCS, 2002). Manganese can exist in 11 oxidative states; the most environmentally and biologically important manganese compounds are those that contain Mn2+, Mn4+ or Mn7+ (USEPA, 1994).

At excessive concentrations, manganese can be detrimental to health. Evidence from occupational exposure indicates that manganese can affect neurological function. Miners and welders exposed through airborne contamination for long periods have eveloped neurological disorders such as Parkinson's disease (Takeda, 2003).Some links have been made between exposure to manganese and a form of motor neuron disease found in the Pacific region, known as Guamian amyotrophic lateral sclerosis (Foster, 1992). Iwami et al. (1994) found correlations between the concentrations of manganese in food and the prevalence of motor neuron disease in the Kii Peninsula of Japan. Cawte et al. (1987) also reported neurological symptoms in manganese ore miners from Australia. Occupational exposure to manganese has also been linked with liver, kidney and lung damage.

Groundwater is abundant in Bangladesh and the aquifers are highly productive. 90% of Bangladeshi depends on ground water for drinking purpose because much of surface water of Bangladesh is microbially unsafe to drink (Ahsan and Del Valls,2011). Unfortunately, the vast area of Bangladesh's groundwater is naturally contaminated with arsenic, iron and manganese concentrations above the World Health Organization (WHO) drinking water guideline and even the Bangladesh drinking water guideline (BGS and DPHE 2001; Smedley 2003; Anawar et al., 2003).Presence of excessive manganese in potable water may cause significant adverse health impacts. It may also causes problems related to aesthetics and may cause precipitation in the water distribution system. The World Health Organization (WHO) has a provisional health based guideline value of 0.4 mg/l for manganese in drinking water (WHO, 2004) forprotect against neurological damage. The WHO guideline value from consumer acceptability consideration is 0.10 mg/l (WHO, 993). Bangladesh Standard for manganese in drinking water is also 0.10 mg/1. At levels exceeding O.1 mg/, manganese in water supplies stains sanitary ware and laundry and causes undesirable taste in beverages. The presence of manganese in

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drinking water may lead to accumulation of deposits in the distribution system. Even at a concentration of 0.02 mg/I, manganese may form coating on distribution pipes, which may slough off as a black precipitate(Hoque,2006).

The national hydro-chemical survey (BGS and DPHE, 2001) have shown that in Bangladesh, large numbers of wells exceed permissible limits for iron (Fe) and manganese (Mn). This is true of shallow tubewells, and also to some extent for deep tubewells and ring-wells, which are common water supply options in arsenic-affected areas. The national hydro-chemical survey found that half of the wells surveyed exceeded the Bangladesh drinking water standard for iron (I mg/I) and three quarters exceeded the standard for Mn (0.1 mg/I). Both of these limits are based on aesthetic considerations; above these levels, people may be unwilling to drink the water, and turn instead to a better-tasting, but microbiologically less safe water sources. About 40% of wells were found to exceed the WHO health-based guide value (0.4 mg/I). Some of iron and manganese concentrations reported .in the national hydro-chemical survey (BGS and DPHE, 2001) are very high, over ten times the permissible limit. Iron and manganese concentration as high as 25 mg/l and 10 mg/l, respectively have been reported. Average iron concentration has been reported to be 3 mg/l (median 1 mg/l) and average manganese concentration 0.5 mg/l (median 0.3 mg/l) (BGS andWaterAid,2001).

Unlike the distribution of arsenic, which has a distinct regional pattern with highest contamination in the south, south-west, and north-eastern regions of Bangladesh, high concentrations of manganese are found in most areas, but relatively high concentrations are seen in the current Brahmaputra and Ganges floodplains. The distribution generally does not correspond to that of arsenic (BGS and WaterAid, 2001). This means that groundwater with acceptable concentration of arsenic may not have acceptable concentration of manganese (Hoque,2006).

Manganese can be removed using the same processes of oxidation, precipitation and filtration as in iron removal (Fair et al., 1968). Conventionally, a strong oxidant such as chlorine or potassium permanganate is used for oxidation of Mn(II) rather than oxygen alone (Hartmann, 2002) .However, some studies (e.g., ITN-BUET, 2011) reported that naturally present DO and other constituents (e.g., bicarbonate) in water could promote removal of Mn in a filter media (by sorption and oxidation) without the addition of an oxidant. This phenomenon needs to be investigated in more detail through laboratory experiments (Habib,2013). Mn(II) oxidation can lead to precipitation of Mn(III, IV) oxides which are in turn good adsorbents and oxidants (Hem, 1978) . A number of studies (Kanet a l., 2012; Buamah, 2009; Afsana, 2004) showed that Mn is removed effectively from groundwater by oxidation and adsorption processes. Media coated with synthetic Mn oxides have also been found to have good Mn removal efficiency (Merkle et al., 1997; NMSU, 1999; Dhiman and Chaudhuri, 2007; Maliyekkal et al., 2009). 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 (Habib,2013.Oxidation precipitation is by far the most widely used technique for manganese removal from water. A number of water quality parameters such as pH,eH ,iron, organic matter etc. can affect the efficiency of manganese removal from water (Seeling et al., 1992; Lemley et al., 1999). Manganese oxide coatings formed on filter media in filtration beds have been found to act as good adsorbent for Mn and also plays a role in its oxidation (Eley and Nicholson, 1993; Tasneem, 2010; ITN-BUET, 2011).

The iron problem has long been recognized in Bangladesh, and many technologies have been developed for iron removal at municipal, community and household levels. Municipal Iron Removal Plants (IRPs) were first installed in Bangladesh during the early 1980s. After the detection of arsenic in ground water, many municipal IRPs are now being designed and used for removal of both iron and arsenic. In the backdrop of the discovery of arsenic in many areas of the country, community treatment units designed for removal of both arsenic and iron are becoming popular. Many NGOs are now installing different types of such community-based iron/ arsenic removal plants. However, most of the plants have been constructed without following any technical design parameters (BRTC, 2006). So it is important to see whether Mn is removed significantly in the currently operational iron and/or Fe-As removal plants, which have been designed primarily for removal of iron and/or arsenic.

Objective of the study are (a) to investigate the effectiveness of roughing filtration in removing manganese from groundwater adopting the technique of adsorption and co-precipitation of manganese onto the flocs of ferric hydroxide, making use of the naturally occurring iron of groundwater, (b) Manganese Removal Performance of Different Treatment Unit Processes (c) Effect of initial manganese concentration on manganese removal performance.

Methodology

Selection of study area

Two study area Kodda and Chala in Sirajgonj district were selected on the basis of iron and manganese concentration in ground water. Department of Public Health Engineering (DPHE) were contacted and requested to extend their co-operation for this research work. The field sites were identified by direct co-operation of the Department of Public Health Engineering (DPHE) staffs. The water quality characteristics of the study area and plant location have been shown in Table 1.

Table 1. Water quality characteristics of the study area and plant location

Location of Filtration Units	pH	Alkalinity (mg/lSO as $CaCO_3$)	Iron (mg/l)	Manganese (mg/l)
Kodda, Sirajgonj	7.1	174	16	1.625
Chala, Sirajgonj	7.0	134	15	0.720

Selection of kinetics of manganese oxidation, precipitation & removal

Manganese is much more slowly oxidised through aeration than iron. In fact, the rate is negligible at pH levels below 9.0.Chemical oxidation of Mn requires a pH level above 8.5 and 1.0 mg of chlorine can oxidise 1.3 mg of Mn. Mn oxidation through chlorine requires 2-4 hours to react completely.Both hydrous $Fe(OH)_3$ & MnO_2, tend to sorb Fe++ & Mn++ ions.Removal of iron and manganese is generally hastened and made more efficient (swifter) by letting water trickle downward or rise upward through gravel or other relatively coarse heavy materials coated with hydrous oxides of Fe(III) and Mn(IV) precipitates by sorption.If Fe(II) > Mn(II) rather than Mn(II) alone, removal than becomes predominantly a matter of sorption of Mn++ on incipient ppt. of iron

Selection of the unit process for the MSFU

Multistage filtration units (MSFU) considered under the study comprised of three units :1st chamber (aerator plus down-flow flocculator), 2nd chamber (sedimentation plus up-flow roughing filter) and 3rd chamber (down-flow roughing filter).

Functions of individual unit

The functions of the individual units have been shown in the following table.

Table 2. The functions of the individual units of roughing filter

Unit	Functions
Aerator	Water entering the first chamber is distributed uniformly over the whole bed of course media through a porous thin ferro-cement plate placed on the top, resulting strip out of CO_2 and increase of pH value for the oxidation of soluble iron.
Down flow Flocculator	Oxidation and subsequent precipitation of iron oxy hydroxides occurs respectively on the top and within the interstices of coarse media which adsorbs manganese oxy anions. Sinusoidal flow across the coarse media enhance collisions for the flocculation of precipitated particles.
sedimentation chamber	Comparatively larger flocculated precipitates settle at the bottom of the 2nd chamber
up-flow roughing filter	Maximum removal of precipitated particles occurs by sorption on to iron oxy hydroxides and mechanical straining during up-flow through the comparatively finer coarse media bed in the 2nd chamber.
down-flow roughing filter	Final removal of precipitated particles occurs through sorption on iron flocs and other metal oxy-hydroxides during down-flow through the comparatively finer coarse media bed than the 2nd chamber

Design Parameter of multistage filtration units

Following design parameters have been considered for multistage filtration units.

Table 3. Design parameters for multistage filtration units.

Unit	Parameter		
Down flow Flocculator	Face velocity =3.24-4.05 m/hr	Detention time =4.5 – 6 min	Flow =16 - 20 L/min
Sedimentation Chamber	Surface Over Flow Rate=9.7-12.9 m^3/m^2-day	Detention Time = 28 - 35 min	
Up-flow Roughing Filter	Face Velocity = 0.32 – 0.40 m/hr	Detention Time = 28 - 35 min	Flow = 12 – 15 L/min
down-flow roughing filter	Face Velocity = 0.22 – 0.27 m/hr	Detention Time = 66 - 82 min	Flow = 2 – 2.5 L/min

Sampling and analytical methods of testing

Water quality analysis of this study was conducted at the laboratory of Environmental Engineering Laboratory, Department of Civil Engineering, BUET, Dhaka.The pH and Iron contents of the water samples were determined in the field regularly. In this process iron concentrations were determined using HACH field kit and pH were determined by field pH meter. At each treatment plant location, raw and treated water samples were collected for subsequent analysis of iron, manganese and other selected water quality parameters in the laboratory. Samples were collected in pre-washed 500 ml plastic bottles and were acidified with 1 ml concentration Nitric acid, which were later used for analysis of dissolved manganese and iron. In the laboratory iron and manganese concentrations were determined using HACH spectrophotometer as well as Flame-AAS(Atomic Absorption Spectrophotometer).

Result and discussions

Performance analysis of the filtration units on the basis of collected field data and laboratory test results have been analyzed and presented in the following articles.

MSFU-1 (Kodda,Sirajgonj)

The variation of average manganese concentration with operation period in different treatment unit processes of the MSFU-1 have been explained in Fig. 1. The initial concentration of manganese in the effluent of URF and DRF were found to be 0.7 and 0.29 mg/L indicating removal efficiency of 57 % and 82% respectively. With the passage of time the manganese concentration in the effluent of URF and DRF decreased upto 0.58 mg/L and 0.11 mg/L indicating removal efficiency of 64 % and respectively 93%. This was because there were gradually adsorption of precipitated iron flocs on the coarse media surfaces and gradually deposition of the same in the interstices and these iron particles along with other metal oxy-hydroxides provided increased adsorption surfaces for the manganese ions to be adsorbed. However, after 3 to 4 weeks of run the manganese concentrations in the effluent of DRF again started to increase. This was because when the coarse media pores were clogged the increased pore velocities caused shearing / sloughing of precipitated iron particles which resulted less adsorption site available for arsenic ions and ultimately appeared with the effluent water.

From the beginning of the filter run a continuous increasing trend of arsenic concentration in the effluent of sedimentation chamber have been observed .Because with the passage of time gradually accumulated iron flocs at the bottom of sedimentation chamber along with adsorbed manganese ions were carried over and ultimately appeared in the effluent of this chamber.

This figure indicates that DRF process have significant effect on manganese removal. Manganese concentrations in the effluent of sedimentation chamber and URF chamber were much above the WHO health based guideline value for manganese (0.4 mg/L) to protect against neurological damage.

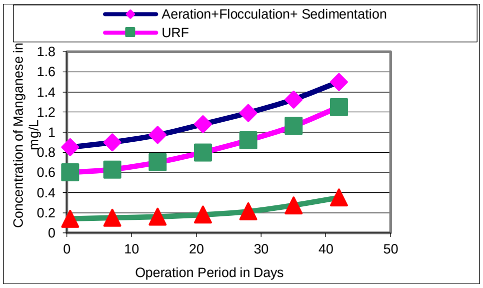

Fig. 1. Variation of average manganese concentration with operation period in different treatment unit process of Kodda

On the other hand,manganese concentration in the effluent of DRF was observed less than 0.4 mg/L. This was due to the fact that detention time of pre-DRF chamber did not meet the time requirement of manganese oxidation-because manganese is much more slowly oxidised through aeration than iron and not only that Mn oxidation through chlorine requires 2-4 hours to react completely.

MSFU-2 (Chala, Sirajgonj)

Fig.2 represents the variation of average manganese concentration with operation period in different treatment unit processes of the MSFU-2.The initial concentration of manganese in the effluent of URF and DRF were found to be 0.35 and 0.16 mg/L indicating removal efficiency of 52% and 77% respectively. With the passage of time manganese concentration in the effluent of URF and DRF decreased upto 0.288 mg/L and 0.1 mg/L indicating removal efficiency of 60% and respectively 86%. The figure 4.11.1 and 4.11.2 shows that manganese removal efficiency of MSFU-2 was not as effective as MSFU-1. One reason is manganese removal is a function of raw water manganese concentration .i.e. higher the Mn concentration, greater is the removal performance .Since tube well water manganese concentration of MSFU-2 is less than MSFU-1,so manganese removal efficiency of MSFU-2 was<MSFU-1. Another reason is total number of users of MSFU-2 > total number of users of MSFU-1.So detention time available for manganese oxidation in all the chambers of MSFU-2 was less than that of MSFU-1. This figure indicates that residual manganese concentration in the effluent of DRF successfully satisfied the WHO health based guideline value (0.4 mg/L) to protect against neurological damage. Due to less detention time and more use of the plant, pre DRF processes was unable to maintain the WHO health based guideline value for manganese (0.4 mg/L) in the effluent.

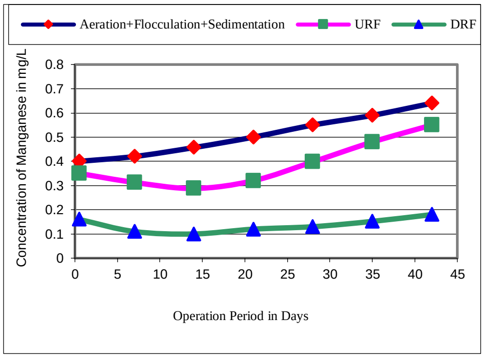

Fig.2. Variation of average manganese Concentration with operation period in different treatment unit process of Chala

Manganese Removal Performance of Different Treatment Unit Processes

Following Fig. 3 elaborates the average manganese removal performance of the different Treatment unit processes of the Multi-stage Filtration Units. Appreciable amount of manganese reduction have been occurred through Aeration cum Flocculation cum Sedimentation Processes (33%).

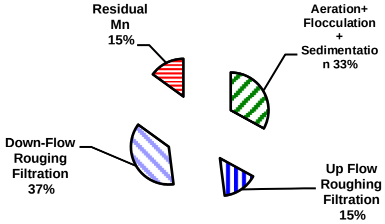

Fig.3. Manganese removal performance of different treatment unit processes (average of Kodda and Chala)

Effect of DRF process alone in removing manganese was found very significant (37%).Role of URF process in reducing manganese was observed moderate (15%).

Effect of initial manganese concentration on manganese removal performance

Effect of initial manganese concentration on manganese removal performance of the MSFUs of Kodda and Chala have been furnished in fig.4.

It indicates that in Kodda, where manganese concentration was 1.625 mg/L and iron concentration was 16 mg/L, then residual manganese concentration was detected around 11% (0.178 mg/L) in the treated water and in Chala, where manganese concentration was 0.72 mg/L and iron concentration was 15 mg/L, then residual manganese concentration was detected around 20% (0.144 mg/L) in the treated water. From this it can be concluded manganese removal performance was observed to be a function of raw water manganese concentration. Higher was the manganese concentration, greater was the removal performance.

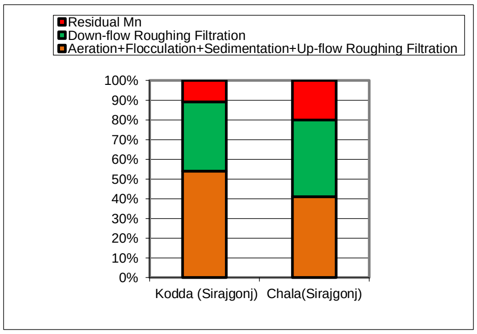

Fig. 4. Effect of initial manganese concentration on manganese removal performance of the MSFUs of Kodda & Chala

Conclusions

(1)Multistage filtration can be used effectively in removing manganese from groundwater.

(2) Around 33%,15% and 37% manganese removal have been occurred through pre-URF (aeration + flocculation + sedimentation),URF and DRF (post URF) processes respectively

(3) Manganese removal performance was observed to be a function of raw water manganese concentration. Higher was the manganese concentration, greater was the removal performance.

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