REMOVAL OF MANGANESE FROM GROUNDWATER USING SORPTIVE FILTRATION

By

Kazi Mahmuda Tasneem

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

DEPARTMENT OF CIVIL ENGINEERING
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Kazi Mahmuda Tasneem

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Kazi Mahmuda Tasneem

Dedicated
to
My Family & Friends

ABSTRACT

Manganese is a common natural groundwater contaminant in Bangladesh. The WHO recommends a guideline value of 0.4 mg/L (WHO, 2004) to protect against neurological damage; drinking water standard from aesthetic considerations is even more stringent, 0.1 mg/L. But, available data show that large numbers of wells in Bangladesh exceed these permissible limits for Manganese (Mn). Adsorption and formation of Mn-oxide coatings on filter media are thought to be effective for Mn removal; however limited information is available on factors affecting formation of such coatings. In this study, laboratory batch experiments were carried out for preparation of manganese oxide coated sand bed and assessment of factors affecting formation of Mn oxide coating on sand. Ability of prepared Mn-coated and Fe-coated sand filter beds in removing both Mn and Arsenic (As) was then assessed for evaluating the potential of these media for simultaneous removal of Mn and As.

Manganese oxide coated sand bed was prepared by passing Mn-bearing (0.5 to 5.0 mg/L Mn) groundwater through filter bed made of locally available natural coarse sand (Sylhet sand). The experiments were carried out at natural pH of groundwater (7±0.1), without addition of any chemical (e.g., oxidant). Bed volume of water required for achieving filter "maturation" (defined as the time when almost all Mn in influent water was retained by the media) varied from 1000 to 1400 (1 bed volume = 43 cm^3); corresponding filter run time varied from 180 to 220 hours. Estimated quantity of Mn retained by the filter media varied from about 10 mg to 100 mg; the corresponding average Mn content of the prepared sand filter media varied from about 0.17 mg Mn/g sand to 1.76 mg Mn/g sand. For each sand bed column, manganese removal increased exponentially with operating time, possibly suggesting autocatalytic effect of Manganese oxidation and precipitation, whereby Mn oxide coating formed on the sand bed promoted further oxidation and precipitation of Mn.

Results from the study shows that the prepared manganese oxide coated sand filter bed have significant capacity to remove manganese from groundwater and flow rate, within a range of 1 to 5 ml/min, has little impact on Mn removal efficiency under the experimental conditions. Manganese removal was possible for a wide range of initial Mn concentration without using any oxidant at natural pH condition, satisfying the national standard and WHO guideline value for 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. Presence of arsenic did not affect Mn removal significantly in the prepared filter media; presence of Mn on the other hand appears to increase As removal to some extent. Results from this study suggest that Mn oxide coated sand filter media are not effective for removal of As, and hence cannot be used for simultaneous removal of As and Mn. However, use of Mn oxide coated sand media could significantly improve Mn removal efficiency of household and community groundwater treatment plants.

Efficiency of iron coated sand bed in removing manganese was also assessed. Iron coated sand bed did not show satisfactory performance for manganese removal, showing only about 20% removal under the experimental conditions. While iron oxide coated media were found to be effective in removing As from groundwater in a previous study, results from this study suggest that this media cannot be used effectively for simultaneous removal of Mn and As. However, a filter media prepared by combining both Mn-coated and Fe-coated sand media has the potential of removing both Mn and As effectively.

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Kazi Mahmuda Tasneem

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List of Abbreviation

AAS	Atomic Absorption Spectrophotometer
AWWA	American Water Works Association
BGS	British Geological Survey
DPHE	Department of Public Health Engineering
DFID	Department for International Development
MDL	Minimum Detection Limit
MW	Molecular Weight
NHS	National Hydrochemical Survey
SMCL	Secondary Maximum Contaminant Level
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Chapter 1
INTRODUCTION

1.1 Background

Manganese is a common natural contaminant of groundwater 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 Hydrochemical Survey conducted by the British Geological Survey and DPHE (BGS and DPHE, 2001) showed that in Bangladesh, large numbers of wells (both deep and shallow) exceed permissible limits for Iron and Manganese. The National Hydro-geochemical Survey found that half of the 3,534 wells surveyed in 61 out of 64 districts exceeded the Bangladesh drinking water standard (1.0 mg/L) for Iron, and three quarters exceeded the standard (0.1 mg/L) for Manganese. Some of the reported iron and manganese concentrations are very high, over ten times the permissible limit. Average iron concentration in the surveyed wells has been reported to be 3.0 mg/L (median 1.0 mg/L) and average Manganese concentration 0.5 mg/L (median 0.3 mg/L) (BGS and WaterAid, 2001).

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 (Institute of Medicine Food and Nutrition Board, 2002). 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 (Calne et al. 1994; Dobson et al. 2004; Yamada et al. 1986). The WHO recommends a guideline value of 0.4 mg/L (WHO, 2004) to protect against neurological damage. About 40% of wells sampled in the BGS-DPHE survey exceeded this limit for Manganese as well.

Again, 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.

There is widespread awareness about iron in groundwater but relatively little regarding presence of Manganese. Some studies (e.g., BRTC-Unicef, 2006; Hoque, 2006) revealed that Manganese removal is significant in some types of community arsenic-iron removal plants currently being used in some arsenic affected areas, while Manganese removal is insignificant in other removal plants. Unlike iron and arsenic, the manganese issue is not well understood, in part because high-Manganese waters are often found to be high in iron, and both result in a similar metallic taste.

Manganese can be removed using the same 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 (Hartmann, 2002). Mn (II) oxidation can lead to precipitation of Mn (III, IV) oxides which are in turn act as good adsorbents and oxidants (Hem, 1978). Manganese oxide coatings formed on filter media in filtration beds have been found to act as good adsorbent for Manganese and also plays a role in its oxidation (Eley and Nicholson, 1993). Media coated with synthetic Manganese oxides have also been found to have good Mn removal efficiency (Merkle et al., 1997; Tilak, undated). However, there is limited or no data on formation of Mn-oxide coating on natural sand media (which are commonly used in As-Fe removal plants) and ability of such media in removing Mn as well as As.

Although significant research works have been carried out on removal of arsenic and iron from groundwater, relatively little work (e.g., Afsana, 2004; Hoque, 2006) has been done on the removal of manganese from groundwater in Bangladesh. The iron problem has long been recognized in Bangladesh, and many technologies have been developed for iron removal at municipal, community and household levels. Manganese can be removed using the same processes of oxidation, precipitation and filtration as in iron removal. While Arsenic is removed in these plants primarily by adsorptive filtration, the mechanism of Manganese removal is vaguely understood.

Adsorption of Mn on filter media an formation of Mn-oxide coating are thought to be responsible for Mn removal. However, limited information is available on factors affecting formation of such coatings. Since most of the As removal systems/ plants currently being used in different parts of the country are based on adsorptive filtration technique, 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 removal of Manganese form natural groundwater in a treatment process.

1.2 Objectives of the Present Research

The objective of the present study is to assess removal of Manganese by a conventional sand filter media and iron coated sand filter bed. Specific objectives of this study include:

a) Preparation of a filter media by promoting formation of Manganese oxide coating on locally available sand for removal of Manganese.
b) Assessment of the time required for obtaining “maturation” of filter bed for optimum Manganese removal.
c) Evaluation of the effects of various parameter, i.e., initial Mn concentration and pH on the formation of Manganese oxide coating by the filter media.
d) Preparation of iron oxide coated sand and evaluation of performance of Fe-oxide and Mn-oxide coated sand filters in removing Mn from groundwater under different conditions.
e) Assessment of the potential of the developed media (Mn-oxide coated sand) for simultaneous removal of Arsenic and Manganese.

1.3 Organization of the Thesis

Apart from this chapter, the remainder of the thesis has been divided into four chapters. Chapter Two presents a brief and selective review of relevant literature. In this chapter, occurrence of Manganese, problem associated with manganese in groundwater in Bangladesh, chemistry of Manganese oxidation and commonly used manganese removal techniques are discussed.

Chapter Three presents the methodology of laboratory experiments designed for the preparation of Manganese coated sand bed and Iron coated sand bed. Methodology of the experiments for Manganese removal using Mn-coated and Fe-coated sand bed and simultaneous removal of manganese and arsenic using manganese oxide coated sand bed are also discussed in this chapter.

Chapter Four presents the results of the experiments intended to assess the effects of different parameters (initial concentration, pH) on the formation of Manganese coating on the sand bed the performance of Manganese removal on Manganese oxide coated sand bed and Iron oxide coated sand bed. Removal efficiencies under different parametric condition (initial concentration, flow rate) are discussed here. Also, simultaneous removal performances of Arsenic and Manganese in Manganese oxide coated sand bed are also discussed in this chapter.

Finally, Chapter Five presents the major conclusion of the study and also provides recommendations for the further study.

Chapter 2
LITERATURE REVIEW

2.1 Introduction

Manganese is a naturally-occurring element that can be found ubiquitously in the air, soil, and water. Manganese is an essential nutrient for humans and animals. Adverse health effects can be caused by inadequate intake or over exposure. Manganese is the third most abundant transition metal in the earth's crust (9.5×10^2 mg/L). It occurs naturally in soils, rocks and minerals. Manganese occurs naturally in ground water and can be found in many types of rocks. Pure manganese does not occur naturally. The level of manganese in groundwater from natural leaching processes can vary widely depending upon the types of rock and minerals present at the water table. Typically, manganese concentrations from natural processes are low but can range up to 1.5 mg/L or higher. Sources of pollution rich in organic matter (e.g., runoff from landfills, compost, brush or silage piles, or chemicals such as gasoline) can add to the background level by increasing manganese release from soil or bedrock into groundwater. In the aquifer, groundwater comes in contact with these solid materials dissolving them, releasing their constituents, including Manganese, to the water. Manganese in objectionable concentration has been detected in many water supply sources. The redox chemistries of manganese (I/III/IV) have important roles and impacts in the environment. So, chemistry of a natural constituent like manganese plays an important role in the removal mechanism of this element from water. In this chapter relevant literature on occurrence of Manganese and also the chemistry of manganese that influence their oxidation and precipitation have been reviewed. Many different factors, which influence manganese oxidation, have also been reviewed briefly. This chapter also provides an overview of manganese removal techniques.

2.2 Occurrence of Manganese

Manganese is an abundant element in the earth's crust. Upper crustal abundance is around 0.05–0.1% MnO (Taylor and McLennan, 1985). The element is distributed mainly in manganese oxides of which pyrolusite (MnO_2) is the most common. Manganese also occurs as an impurity in iron oxides, some silicates and carbonates. It occurs more rarely as a major constituent of rhodocrosite ($MnCO_3$). The structure and compositions of manganese oxides is complex due to variable oxidation states and to their ion-exchange properties. These properties are important in soils and aquifers as they can play a significant role in trace-metal adsorption. In sediments, manganese oxides also typically occur as fine-grained and poorly-crystalline forms which are easily dissolved under favorable conditions. Manganese occurs in several oxidation states, from –III to VII, but usually in the forms II or IV in the environment.

Concentration ranges of manganese in groundwater span several orders of magnitude, from <0.001 mg/L to values occasionally in excess of mg/l. Manganese commonly coexists with iron in water. However, where this occurs, the concentrations of iron are generally greater because iron has a greater crustal abundance. Problems with manganese in groundwater are widespread, and many countries throughout the world have areas with unacceptably high concentrations (USEPA, 2004).

The principal controls on manganese concentration in groundwater are pH (acidity) and redox (oxidation-reduction) condition. Manganese is mobilized under acidic conditions. Hence concentrations can be relatively high in acidic waters such as some industrial waters and those issuing from mines rich in weathered sulphide minerals (coal, gold or base-metal mines). In this situation, high manganese concentrations are often accompanied by high concentrations of other metals such as iron, copper, zinc and arsenic, as well as sulphate, which are all derived by oxidation of the sulphide minerals. Under such conditions, dispersion of dissolved manganese away from the site of oxidation is greater than that of iron (Hem, 1992).

In pH-neutral conditions, the mobility of manganese is determined by ambient redox conditions. Under aerobic conditions typical of many shallow aquifers and surface waters, manganese is stable in its oxidized form, $Mn(IV)O_2$ which is highly insoluble. Hence, concentrations of manganese in aerobic water are usually low and commonly below analytical detection limits. Under anaerobic conditions, manganese is reduced to the more soluble form, Mn (II), which is released from minerals. Mn2+ is the soluble form in most waters. As a result, much higher manganese concentrations can be found in anaerobic groundwater. As dissolved oxygen concentrations in groundwater tend to decrease with well depth, anaerobic conditions and hence high manganese concentrations tend to occur more commonly in deep wells. Under strongly reducing conditions in the presence of dissolved sulphide, manganese can be immobilized by the formation of insoluble manganese sulphide (MnS), although this is usually only important at high pH (>8). As anaerobic conditions occur commonly in aquifers, problems with iron and manganese in groundwater are relatively widespread, though the concentrations attained vary widely (USEPA, 2004).

As groundwaters infiltrate through soils and aquifers, their compositions typically evolve from aerobic to anaerobic, the rates of change depending on the rates of diffusion of oxygen and other oxidants in the system. Reduction reactions in aquifers and soils follow a sequence as the conditions become progressively more reducing. Typically the first compound to be removed from the system is oxygen, followed by nitrate and thereafter manganese. Progressively more reducing conditions lead to reduction of iron followed by sulphate.

Manganese is dissolved in anoxic and acid water. Homogeneous precipitation of Mn(II) as an oxide phase does not occur below pH 8, but Mn(II) oxidation does occur in the presence of different mineral surface and /or via bacterial process between pH 6 and 8. it is also known that bacterial mediated oxidation of dissolved manganese (Davidson et al, 1989).

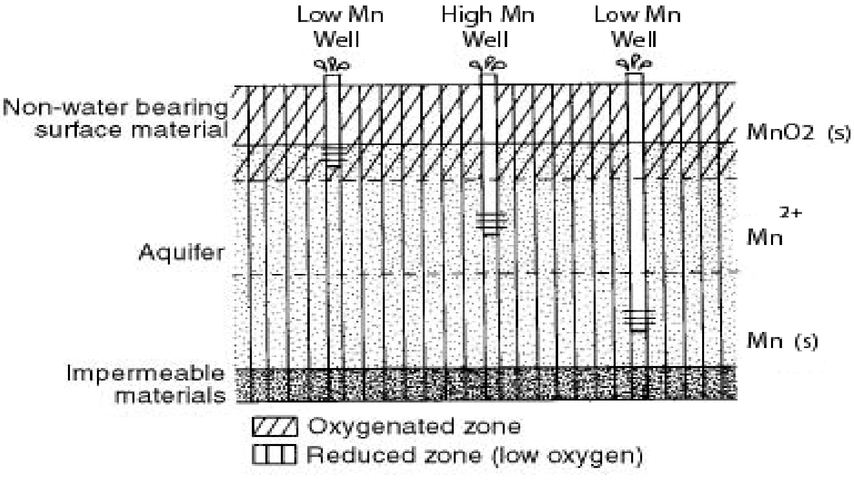


Figure 2.1: Dissolve manganese concentration with variation in depth of well (Seelig et al., 1992).

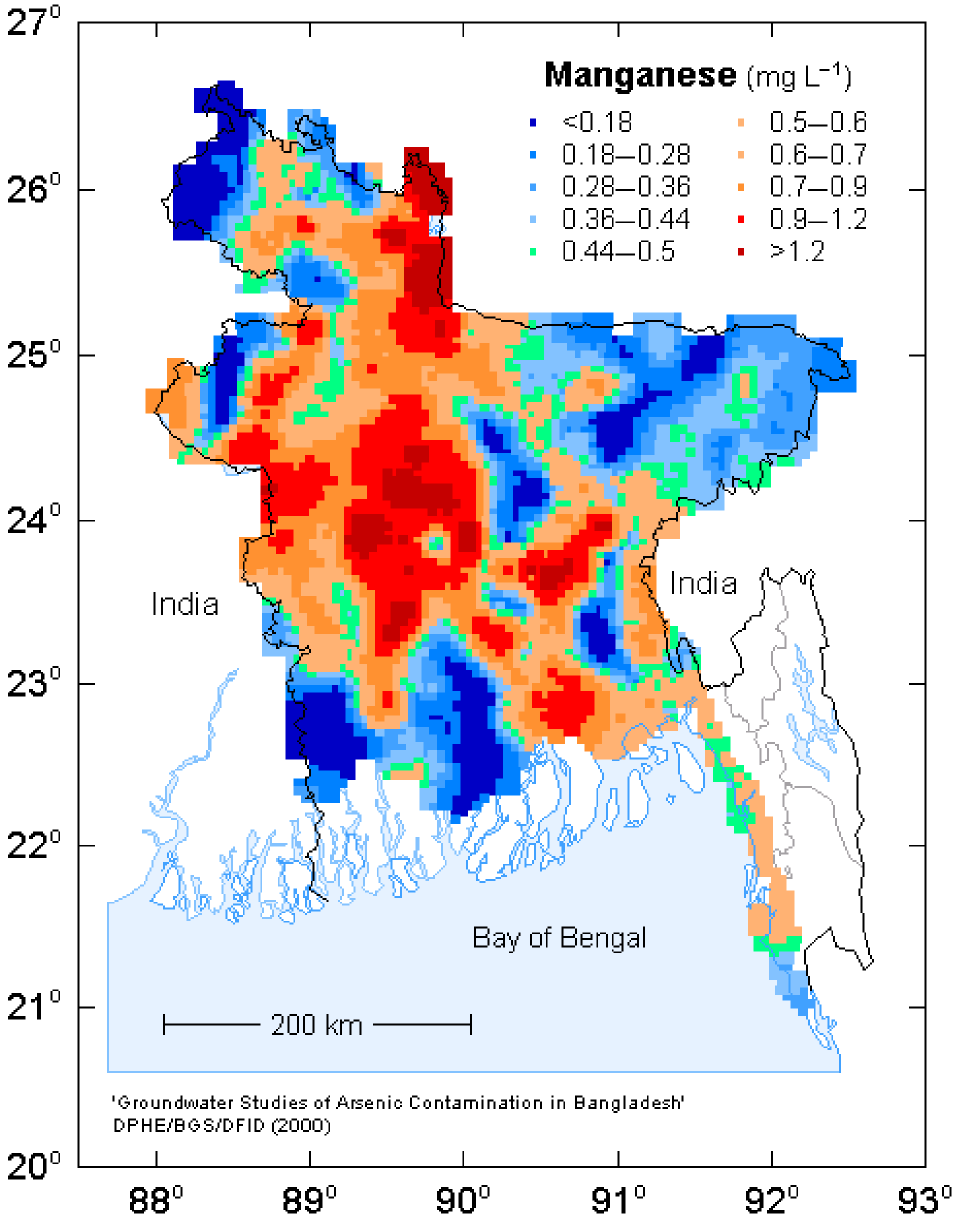
Manganese problems are most likely to develop in water from wells with high carbonate and low oxygen. Problems occur when this type of water is pumped to the surface. The chemical equilibrium is changed upon exposure to the atmosphere. The end result is precipitation of manganese compounds in plumbing, on fixtures, and on clothing, dishes and utensils. The amount of manganese dissolved in water often follows a trend of low to high back to low again as depth of the well increase (Seelig et al., 1992).

The mobilization of manganese is increased in organic-rich waters through complexation with organic acids (humic or fulvic acids). Such conditions occur for example in peaty soil waters and upland lakes associated with them. They also occur in some strongly reducing aquifers. Waters with high concentrations of organic acids typically have a brown coloration (not caused by particulate matter) and may develop a surface froth.

Some forms of bacteria gain energy by oxidation of soluble Mn in water and can produce notable surface slimes where concentrations of manganese are high. Bacteria can accelerate the oxidation process and may also exacerbate staining problems. The occurrence of black staining of laundry, food and domestic water-distribution pipes and occasional development of slimes means that manganese in water can often be detected qualitatively. This may be a first indicator of potential manganese problems.

2.3 Manganese Contamination of Groundwater in Bangladesh

The report provided in the National Hydrochemical Survey (NHS) conducted in 2000 by British Geological Survey (BGS) in collaboration with DPHE and DFID provides the most comprehensive information on manganese in groundwater of Bangladesh. Groundwater survey indicates that iron and manganese are present in high concentrations. According to the national hydrochemical survey, 39% of shallow tubewells and 2% of deep tubewells exceeded the WHO guideline value. Concentration of manganese in groundwater has been found as high as 10 mg/L, with an average value of 0.5 mg/L. The high values are related to the anaerobic conditions dominant in the aquifers (BGS and WaterAid, 2001). High concentrations are found in most areas, but particular high-manganese areas are seen in the current Brahmaputra and Ganges floodplains. The distribution generally does not correspond with that of arsenic. This means that groundwaters with acceptable concentrations of arsenic may not have acceptable concentrations of manganese. It is notable that groundwaters from the deep aquifer contain relatively low concentrations of both arsenic and manganese.



'Groundwater Studies of Arsenic Contamination in Bangladesh'
DPHE/BGS/DFID (2000)

Figure. 2.2: Distribution of manganese in groundwater of Bangladesh (Source: BGS and DPHE, 2001)

Concentrations of manganese in the Bangladesh groundwaters were measured between <0.002 mg/l and 10 mg/l (BGS and DPHE, 2001). Figure 2.2 represents manganese concentration in groundwater of Bangladesh. Medians of the concentrations in the shallow and deep aquifers were 0.34 mg/L and 0.03 mg/L respectively. This highlights the large difference in concentrations between the shallow and deep aquifers. This figure indicates that the central, north and south-east regions of Bangladesh have higher concentrations of manganese.

Figure 2.3 shows distribution of Mn in well water of Bangladesh, based water quality data obtained from the national hydro-chemical survey (BGS and DPHE, 2001). It shows that about 27% of the surveyed tubewells have manganese concentrations within the Bangladesh drinking water standard of 0.1 mg/L. About 32% of groundwater samples have manganese concentration between 0.1 and 0.4 mg/L, and about 25% have concentration between 0.4 and 1.0 mg/L. About 17% of samples have manganese concentration exceeding 1.0 mg/L; only 10 samples have concentration exceeding 5 mg/L.

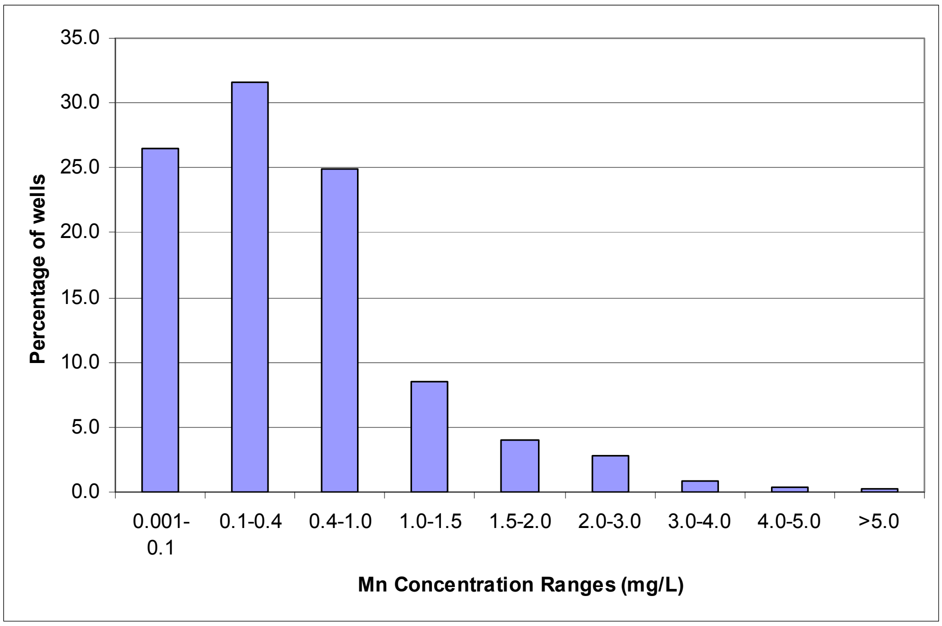


Figure 2.3: Wells with different ranges of manganese concentrations (Source: Hasan and Ali, 2010)

Table 2.1 shows the division-wise status of manganese concentration in groundwater of Bangladesh. It shows that the Rajshahi division, located on the north-western region has the highest average manganese concentration (0.73 mg/L); this division also has the highest percentage of wells exceeding the Bangladesh drinking water standard (82.9%) and WHO guideline value (55.6%). The lowest average manganese concentration (0.11 mg/L) is found for wells of Barisal division, located in the southern region of the country; this division also has the least number of wells exceeding the Bangladesh standard

(19.3%) and WHO guideline value (6.4%). This is followed by the Sylhet division, with an average concentration of 0.29 mg/L, 74.6% wells exceeding the Bangladesh standard and 27.7% exceeding the WHO guideline value.

Table 2.1: Division-wise status of manganese concentration in tube well water (Source: Hasan and Ali, 2010)

Division	No. of wells surveyed	Mean conc. (mg/L)	% exceeding Bangladesh standard (0.1 mg/l)	% exceeding WHO guideline value (0.4 mg/l)
Barisal	295	0.11	19.3	6.4
Chittagong	445	0.46	78.9	38.0
Dhaka	988	0.65	77.4	44.6
Khulna	474	0.46	73.8	38.4
Rajshahi	1072	0.73	82.9	55.6
Sylhet	260	0.29	74.6	27.7
Total	3534	0.55	73.7	41.9

Among the 3534 wells surveyed in the BGS and DPHE (2001) study, 3207 were shallow wells (< 150 m) and the rest 327 were deep wells (> 150 m). From analysis of manganese concentrations of these wells, it appears that the deeper wells contain much less manganese compared to the shallower wells. Among the shallow wells, 79% exceed the Bangladesh drinking water standard and about 46% exceed the WHO guideline value. On the other hand, about 22% of deep wells exceed the Bangladesh standard and only about 3.4% exceed the WHO guideline value. It should be noted that the BGS-DPHE survey found also the deeper wells to be relatively free from arsenic contamination, with only 5% exceeding the WHO guideline value of 0.01 mg/L and 1% exceeding the Bangladesh standard of 0.05 mg/L. However, as noted in BGS and DPHE (2001), it must be kept in mind that most of deep wells surveyed in the study were from southern coastal region where shallow groundwaters are affected by salinity and therefore may not be typical of those from elsewhere in Bangladesh.

Arsenic versus manganese concentrations

As noted earlier, the distribution manganese generally does not correspond to that of arsenic, which means that groundwater with acceptable concentration of arsenic may not have acceptable concentration of manganese (BGS and DPHE, 2001). In this study, available data were analyzed to determine acceptability of well water with respect to both arsenic and manganese. Figure 2.4 shows distribution of arsenic and manganese in well water. It shows that about 32% of surveyed wells which are safe with respect to arsenic (i.e., with arsenic less than 0.05 mg/L) are in fact unsafe with respect with manganese concentration (i.e., with manganese concentration exceeding 0.4 mg/L). Figure 2.4 shows that about 10% of wells have both arsenic and manganese concentrations exceeding the Bangladesh standard and WHO health-based guideline value, respectively. Thus, there are areas which are relatively safe from arsenic contamination, but are at the risk of contamination by manganese. For example, in Rajshahi division, about 50 % of sampled wells are safe with respect to arsenic, but contaminated with manganese about the WHO health-based guideline value.

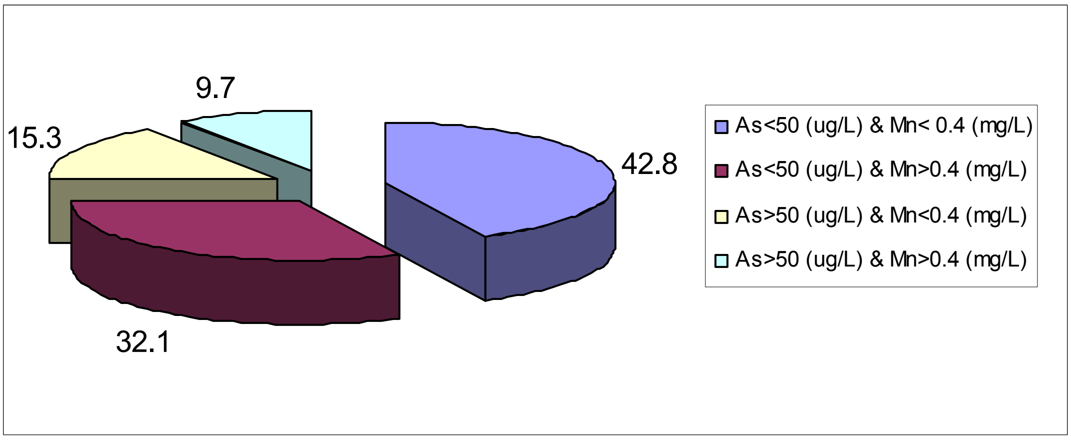


Figure 2.4: Status of wells with respect to arsenic and manganese concentrations (Source: Hasan and Ali, 2010)

Widespread presence of manganese in well water exceeding the WHO health-based guideline value of 0.4 mg/L has added a new dimension to the already complicated safe water supply scenario of the country. According to BGS and DPHE (2001), about 35 million people of Bangladesh are exposed to arsenic concentrations exceeding the Bangladesh standard of 0.05 mg/L and about 57 million people are exposed to arsenic concentration exceeding the WHO guideline value of 0.01 mg/L. Thus, if wells with unsafe manganese concentrations are considered, then population exposed to unsafe water would increase significantly.

2.4 Health and Undesirable Effect of Manganese

Health effect of manganese

Manganese is an essential element for many living organisms, including humans. It is necessary for proper functioning of some enzymes (manganese superoxide dismutase) and for activation of others (kinases, decarboxylases, etc) (USEPA, 2004). The National Academy of Science set an adequate intake for manganese at 2.3 mg/day (for men) to 1.8 mg/day (for women), with an upper limit of 11 mg/day (NRWA, 2004).

Adverse health effects can be caused by inadequate intake or over exposure. Manganese deficiency in humans appears to be rare because manganese is present in many common foods. Animals experimentally maintained on manganese-deficient diets exhibit impaired growth, skeletal abnormalities, reproductive deficits, ataxia of the newborn, and defects in lipid and carbohydrate metabolism (Keen et al., 1999; Hurley et al., 1987; USEPA, 1984). The health effects from over-exposure of manganese are dependent on the route of exposure, the chemical form, the age at exposure, and an individual's nutritional status. Irrespective of the exposure route, the nervous system has been determined to be the primary target with neurological effects generally observed (USEPA, 2004). Exposure to toxic levels of manganese affects the nervous system, and may cause neurological and behavioral symptoms, including dementia, anxiety, and a “mask-like” face (NRWA, 2004). These symptoms are generally the result of very high exposures via inhalation, as might occur in an industrial setting.

The Environmental Protection Agency (EPA) standards for drinking water fall into two categories: Primary Standards and Secondary Standards. Primary Standards are based on health considerations and are designed to protect people from three classes of pollutants: pathogens, radioactive elements and toxic chemicals.

Secondary Standards are based on taste, odor, color, corrosivity, foaming and staining properties of water. Iron and manganese are both classified under the Secondary Maximum Contaminant Level (SMCL) standards. The SMCL for manganese in drinking water is 0.05 mg/L (Lemley et al., 1999).

Undesirable effect of manganese

Manganese is one of the most difficult elements to remove from surface waters. Although dissolved manganese is not known to be toxic, and even blocks the toxic effect of H^+ (Gage et al., 2001) it has undesirable effects on water use. In higher concentrations manganese causes the following problems (Seelig et al., 1992):

Staining: At levels exceeding 0.1 mg/L, manganese in water supplies stains sanitary ware and laundry. Where the concentration of manganese is high, the color of the staining tends toward more black or gray.

Taste: Manganese causes a metallic or vinyl type taste in the water.

Appearance: Manganese will often give an oily appearing, "crusty" sheen to the water surface. (Oil does not appear "crusty" when disturbed, but "feathers out" like a rainbow).

Sulfur Taste: Hydrogen Sulfide, which causes a characteristic "rotten egg" odor, can also be liberated by the same conditions (i.e. low dissolved oxygen and low pH) that cause manganese to dissolve in water. Hydrogen sulfide is frequently encountered in water with excessive manganese. Some of the treatment methods used to remove iron and manganese will also "remove" hydrogen sulfide gas. Presence in high concentrations, manganese may cause an unpleasant metallic taste to the water (Raveendran et al, 2001).

Deposits accumulation: The presence of manganese in drinking water may lead to accumulation of deposits in the distribution system. Even at a concentration of 0.02 mg/L, manganese may form coating on distribution pipes, which may slough off as a black precipitate.

Clogging: Manganese supports the growth of manganese bacteria. This non-health related bacteria can clog strainers, pumps, and valves. Periodic or continuous chlorination is the best means to control manganese bacteria. Once present, manganese bacteria is difficult to purge from a well.

For high intake Manganese having adverse neurotoxic health effect, WHO recommends guideline value of 0.4 mg/L (WHO, 2004) to protect against neurological damage; drinking water standard from aesthetic considerations is even more stringent, 0.1 mg/L. Bangladesh Standard for manganese in drinking water is also 0.1 mg/L.

2.5 Chemistry of Manganese Oxidation

2.5.1 Factors affecting manganese oxidation

The oxidation and control of manganese reaction is complicated by factors that range from misunderstanding of reaction chemistry to the relatively slow kinetics and the numerous oxidation states (Montgomery, 1985). In general, the removal of iron and manganese greatly influenced by some environmental parameters, such as pH, temperature, alkalinity etc.

Effect of pH

Reaction rate of Mn (II) has second order relationship with hydroxyl ion concentration. Reaction of Mn (II) with O_2 is at least 10^6 times slower than that occurs for iron (II) oxidation at circum-neutral pH (Martin, 2003). Only for pH>8 dose the reaction rate become appreciable.

According to Marble et al. (1999), overall mass transfer of Mn (II) from solution to active sites at the surface decreases as pH decreases because of competition with H^+. As reported by Benschoten and Lin (1992), sorption of Mn (II) in excess of 0.5 mol of Mn (II) adsorbed per mole of $MnO_2(s)$. However, strong oxidizing agent like permanganate or chlorine dioxide can effectively oxidize manganese at a pH range from 5 to 10 (Samblebe, 2003). But for slow oxidizing agents like chlorine, it is necessary to raise the pH above 8.5 for effective oxidation reaction of manganese (Samblebe, 2003).

Effect of temperature

Temperature change can affect the oxidation reaction rate of manganese. As ionization constant of water is dependent on temperature variation, which in turn effects hydroxyl ion concentration of water. From oxidation kinetics it can be found that at a given pH value, the rate increases about 10 fold for a 15° C increase in temperature (Stumm et al., 1961). A number of research review indicates that oxidation rate gets slower with decrease in temperature (Benschoten and Lin, 1992). As reported by Montgomery (1985), oxidation of manganese by permanganate solution needs a contact time of 5 mins at 20^0 C and a contact time of 10 mins at 1^0 C.

Effect of alkalinity

Stumm and Morgan (1981) stated, sorption capacities of Mn (II) increase at slightly alkaline solutions as low alkaline waters tend to dissolve minerals and metals. As indicated by Graveland and Heertjes (1975) in his manganese oxidation rate equation that manganese oxidation rate is directly dependent on bicarbonate alkalinity. There is lack of clear information about the mechanism of direct effect of alkalinity on manganese removal.

Effect of organic matter

Mn (II) is capable of forming complexes with organic matter and as such, is resistant to oxidation. The relative strength of such complexes has a stability constant of approximately 10^4 (Theis and Singer, 1974). Again, presence of oxidize able organics or inorganics in the water reduces the oxidation effectiveness of the oxidizing agent (e.g., chlorine, permanganate etc.) used to remove manganese from water because some of the applied dose will consumed in the oxidation of organics and inorganic.

Presence of dissolved oxygen

The rate of manganese oxidation is of the first order with respect to the partial pressure of oxygen, Po_2 (Stumm and Morgan, 1981). It is also observed that above about 30% of saturation value of dissolve oxygen, there exhibits no significant dependence on concentration of dissolve oxygen. Below this value the net rate of Mn (II) removal was approximately first-order with respect to DO concentration and an approximate linear dependence at lower DO values (Marble et al., 1999).

Mn (II) concentration in solution

As described in Marble et al. (1999), the net rate of Mn (II) removal is directly proportional to Mn (II) and that a simple first-order dependence on Mn (II) is a reasonable assumption. And it was more difficult to remove Mn when the initial concentration was low, regardless of the oxidant used.

Effect of presence of metal ions

Unlike iron (II) metal ions like Cu^+ and complex formers do not appear to have any marked effect upon reaction rate of manganese (Stumm and Morgan, 1981).

Presence of oxide surfaces

The rate of Mn (II) oxidation by O_2 is catalyzed by metal oxide surfaces (>S). These surfaces are terminated by hydroxyl groups (>SOH), which bind Mn(II) as $(>SO)_2Mn$. The inner-sphere surface complexes promote rapid oxidation. The catalysis occurs both on foreign surfaces, e.g., Mn (II) on FeOOH and also for the special case of autocatalysis, e.g., Mn (II) on MnOOH producing additional MnOOH (Martin, 2003).

Again in autocatalytic reaction, heterogeneous oxidation occurs when the product of the oxidation further accelerates the reaction rate. The rate laws of autocatalysis are less precise than those of heterogeneous reactions on foreign mineral surfaces. Detailed descriptions for the autocatalysis pathways are hindered both by the complexities of separating homogeneous from heterogeneous pathways and by limitations in characterizing the increasing mineral surface area and the altering mineral phases during reaction (Martin, 2003).

2.5.2 Process kinetics of manganese oxidation

Although iron and manganese are chemically similar, the rate of manganese oxidation does not follow the same rate law as for Fe (II) oxygenation (Stumm and Morgan, 1981). The chemistry of manganese is substantially more complex than that of iron and only a limited understanding of manganese oxidation exists (Montgomery, 1985). The oxidation and control of manganese is completed by factors that range from misunderstanding of the reaction chemistry to the relatively slow kinetics and the numerous oxidation states that result from this oxidation (Stumm and Morgan, 1981). The oxidation of manganese (II) with molecular with oxygen is an autocatalytic process, that is, the spontaneous oxidation by free oxygen at room temperature. According to Stumm and Morgan (1981), the reaction might be visualized as proceeding to the following pattern:

$$Mn^{2+} + O_2(g) \xrightarrow{\text{Slow}} MnO_2(s) \ldots\ldots\ldots\ \ldots\ldots\ldots\ \ldots\ldots\ldots\ .(2.1)$$

$$Mn^{2+} + MnO_2(s) \xrightarrow{\text{Fast}} Mn^{2+} \cdot MnO_2(s) \ldots\ldots\ldots\ \ldots\ldots\ldots(2.2)$$

$$Mn^{2+} \cdot MnO_2(s) + O_2(g) \xrightarrow{\text{Slow}} 2MnO_2(s) \ldots\ldots\ldots\ .(2.3)$$

The higher valent manganese oxide suspensions show large sorption capacities for Mn^{2+} in slightly alkaline solutions. The removal mechanism indicates that presence of manganese dioxide generally increases the apparent rate of oxidation of Mn (II).

The integrated form of autocatalytic reaction rate of Mn (II) can be expressed as follows:

$$\frac{-d\left[Mn\,(II)\right]}{dt} = ko\left[Mn\,(II)\right] + k\left[Mn\,(II)\right]\left[\mathrm{MnO}_2\right] \text{ - (2.4)}$$

where

$\frac{-d\left[Mn\,(II)\right]}{dt}$ = Rate of manganese(II) oxidation $\left[\mathrm{mole/L/min}\right]$

k_0 = Reaction rate constant $\left[\mathrm{l^2/mol^2.atm.min}\right]$

k = Reaction rate constant $\left[\mathrm{l^3/mol^3.atm.min}\right]$

$\left[Mn\,(II)\right], \left[MnO_2\right]$ = Ionic concentrat ion $\left[\mathrm{mol/L}\right]$

Both manganese (II) oxidation and removal rates follow the rates law of equation (1). The rate dependence on the oxygen concentration can expressed as:

$$\frac{-d\left[Mn(II)\right]}{dt} \Rightarrow \mathrm{k}\left[\mathrm{Mn(II)}\right]\left[\mathrm{OH^-}\right]^2 \mathrm{Po}_2 \text{ -(2.5)}$$

Therefore, k in equation (1) can be formulted as

$$\mathrm{k} = \mathrm{k'}\left[\mathrm{OH^-}\right]^2 Po_2$$

Where,

$\mathrm{OH^-}$ = Hydroxide ion concentration $\left[\mathrm{mol/L}\right]$

Po_2 = Partial pressure of oxygen $\left[\mathrm{atm}\right]$

Graveland and Heertjes (1975) suggested another reaction rate equation for manganese. According to Graveland overall manganese removal is also dependent on temperature, alkalinity as well as rate of filtration and media diameter. His equation is expressed as,

$$\frac{-d[Mn(II)]}{dt} = \mathrm{k.[Mn(II)].}\left[O_2\right].\left\{\left[OH^-\right] - 10^{-7.0}\right\}.\left\{\left[4.32x10^{-3} + \left[HCO_3^-\right]\right]\right\}.\exp(-7000/T).V_0^{0.35}.d_m^{-1.11}$$

Where, ...(2.6)

$\left[\mathrm{Mn(II)}\right]$ = concentration of Mn(II)(mg/l)

t = time(sec)

k = reaction rate constant(sec)

$\left[\mathrm{O_2}\right]$ = oxygen concentration (mg/l)

$\left[\mathrm{OH^-}\right]$ = concentration of hydroxyl ion (mg/l)

$\left[\mathrm{HCO_3^-}\right]$ = bicarbonate concentration (mg/l)

T = teperature (0 Kelvin)

$\mathrm{V_0}$ = Filtration rate (cm/sec)

$\mathrm{d_m}$ = mean particle diameter (cm)

Aqueous Mn (II) is oxidized by reaction with dissolved oxygen. The reaction proceeds through the aqueous $Mn(OH)_2$ species, although the bimolecular rate constant of $Mn(OH)_2$ with O_2 is $10^{5.2}$ lower than that of $Fe(OH)_2$. The reaction product (Mn (III)), in the absence of strongly complexing ligands, rapidly polymerizes to form Mn oxide solids, which catalyze further Mn (II) oxidation. Hence separating homogeneous from heterogeneous pathway in Mn (II) oxidation is difficult because they occur simultaneously under most experimental conditions (Martin, 2003).

2.6 Manganese Removal Techniques

Generally speaking, there are two basic methods for treating water containing manganese either by exchanging manganese with any other cation or by oxidizing soluble manganese to precipitate as insoluble form(s). Oxidation processes, both physical-chemical and biological basically involves oxidation-reduction and surface adsorption followed by suitable filtration option. Surface adsorption is influenced by autocatalytic behavior of manganese. It is also dependent on the type of oxidation procedure used to remove manganese. A separate explanation for each type of manganese removal processes is summarized below.

Removal of Manganese is primarily achieved by: (i) physical-chemical processes involving oxidation followed by filtration, (ii) physical-chemical processes involving oxidation filters (e.g., manganese green sand filter, zeolite filter), (iii) biological processes (using biological filters), and (iv) ion exchange (e.g., using water softeners).

Aeration followed by filtration

Aeration can be used to oxidize manganese ions to manganic dioxide. However, the kinetics of oxidation by oxygen is slow in typical water treatment conditions and so a long detention time is required especially at pH less than 8.5 (AWWA, 1990). Aeration is useful as an option to oxidize manganese in reservoirs. The reaction between manganese and molecular oxygen is: $2Mn^{2+} + O_2\,(g) + 2H_2O = 2MnO_2\,(s) + 4H^+$……… (2.7)

Operation of the aeration process requires careful control of the flow through the process. If the flow becomes too great, not enough air is applied to oxidize the iron and manganese. If the flow is too small and the aeration is not cut back, the water can become saturated with dissolved oxygen and, consequently, become corrosive to the distribution system. During aeration, slime growths may be created on the aeration equipment. If these growths are not controlled, they could produce taste and odor problems in the water. The growth of slime can be controlled by the addition of chlorine at the head of the treatment plant. The process should be inspected regularly to catch the problems in their early development (Seelig et al., 1992).

Manganese removal by simple aeration requires longer contact time depending on manganese concentration present in water. Basically for lower manganese concentration higher reaction time is required, even as high as contact time of 1 to several hours may be needed (Montgomery, 1985). This may due to the autocatalytic behavior of manganese and presence of higher concentration accelerates removal. Aeration is ineffective in oxidizing organically bound manganese. Due to involvement of high cost, complexity in pH adjustment and being time consuming, aeration can only be used as a preliminary treatment to oxidize manganese. Where further oxidation is necessary an oxidizing agent must be introduced to reduce the manganese levels (Raveendran et al, 2001).

After reaction and precipitation of insoluble manganese, the water is allowed to flow through a filter where various filter media are used to screen out oxidized particles of manganese and some elements co precipitated with manganese. The selection of media is important. The media should have a large effective size (>1.5 mm) to reduce head loss and should not have a low uniformity coefficient (Montgomery, 1985). The most important maintenance step involved in operation is periodic backwashing of the filter. As manganese oxidation is slower than for iron, it requires greater quantities of oxygen (Seelig et al., 1992).

Oxidizing filter

An oxidizing filter treatment system is an option for moderate levels of dissolved iron and manganese at combined concentrations up to 15 mg/l. The filter material is usually natural manganese greensand or manufactured zeolite coated with manganese oxide, which adsorbs dissolved iron and manganese. In this adsorption process Mn_3O_4 acts as a catalyst on which Mn^{2+} is adsorbed Mn^{2+}gets oxidized to Mn_3O_4 while older Mn_3O_4 gets oxidized to MnO_2 (Sharma et al., 2001).

As water is passed through the filter, soluble iron and manganese are pulled from solution and later react to form insoluble iron and manganese. Insoluble iron and manganese will build up in the greensand filter and must be removed by backwashing. Backwashing should be done regularly twice a week or as recommended by the designer (Seelig et al., 1992)

Synthetic zeolite requires less backwash water and softens the water as it removes iron and manganese. The system must be selected and operated based on the amount of dissolved oxygen. Dissolved oxygen content can be determined by field test kits, some water treatment companies or in a laboratory (Kassim, 1994).

Manganese greensand is a specially processed medium for iron, manganese, and hydrogen sulphide removal. Manganese greensand is a premium non-proprietary filter medium which is processed from glauconitic greensand on which a shiny, hard finite thickness manganese oxide coating is formed and is firmly attached on every grain by a controlled process. This process utilizes the ion exchange properties of greensand to form a manganese base material which is converted to manganese oxides by oxidation with potassium permanganate. Manganese greensand contains 0.30% manganese or 0.45% manganese dioxide.

This material has a high buffering or oxidation- reduction capacity due to the well defined manganese oxide coating. Actually, the manganese greensand can oxidize over 300 grains of manganese per cubic foot or reduce over 1 oz. of potassium permanganate per cubic foot, by far the most of any iron and manganese removal filter media. The grains of manganese greensand are of both the size and shape to capture the fine precipitates of iron and manganese which pass through the upper coarse anthracite layer during normal service conditions. No expensive polymer or other filter aid is needed to prevent leakage of these oxidation products (Gregory and Carlson, 1996).

The acidity or pH of the water will influence the ability of the filter to remove both iron and manganese. If the pH of the water is lower than 6.8, the greensand will probably not adequately filter out the iron and manganese. The pH can be raised above 7.0 by running the water through a calcite filter (Seelig et al., 1992).

Chemical oxidation followed by filtration

High levels of dissolved or oxidized manganese can be treated by chemical oxidation, using an oxidizing chemical such as chlorine, permanganate, or sodium hypochlorite, chlorine dioxide or ozone, followed by a sand trap filter to remove the precipitated material. This treatment is particularly valuable when manganese is combined with organic matter or when manganese bacteria are present (Varner et al., 1994).

Chlorine

Chlorine is a stronger oxidizing agent than oxygen. Chlorine forms hypochlorous acid when dissolved in water. For manganese oxidation chlorine needs to be added at the head works or just before filtration. After a retention time of at least 20 minutes to allow for oxidation of soluble manganese into the insoluble manganic form, the solid particles are filtered out (Seelig et al., 1992).

As chlorine is a weak oxidant, manganese removal by chlorination would not be very effective until pH is raised above 8.5 and for high level of manganese it is often needed to raise pH above 9.5 (Benschoten et al, 1990). Soda ash injected with the chlorine will increase the pH to optimum levels. Adjusting the pH to alkaline levels also reduces the corrosivity of the water to pipes and plumbing (Seelig et al., 1992)

Sodium hypochlorite

Sodium hypochlorite also forms hypochlorous acid when dissolved in water. The sodium hypochlorite reaction slightly increases the pH whereas the reaction of chlorine gas slightly reduces the pH. Commercially available sodium hypochlorite has a concentration of 12.5 %. Large quantities of sodium hypochlorite required to achieve adequate Mn removal. Even though sodium hypochlorite is about twice the cost as equivalent chlorine gas, sodium hypochlorite is used only in small systems due its ease of handling and safety (Singer, 1988).

Potassium permanganate

Potassium permanganate is a stronger oxidant than chlorine and sodium hypochlorite. Unlike chlorine, the reaction of potassium permanganate with organic compounds will not produce trihalomethanes but will actually reduce them (Singer, 1991).

Permanganate being highly reactive oxidant, adsorption of Mn (II) to the oxide surface is the rate-limiting step that is rapid surface oxidation reaction is less effective for low manganese concentration (Benschoten and Lin, 1992). As permanganate is very strong oxidizing agent, it is capable to remove manganese over a wide pH range of 5-10 (Samblebe, 2003). But for rapid oxidation it is preferable to raise pH above 7.0 (Benschoten and Lin, 1992). Slight overdosing of permanganate (up to 0.1 mg/L) has been found not to cause any adverse effects (Raveendran et al., 2001), but presence of excess permanganate produce pink color to the water.

In order to remove manganese, potassium permanganate is usually added to solution ahead of a filter. After reaction, oxidized water is delivered to this filter media to remove oxidized substances and as well as color (if produced). Usually manganese green sand, or silica or even anthracite can be used as filter media (Montgomery, 1985). Greensand media requires periodic regeneration with potassium permanganate solution.

Filtration

The filtration step involves the final removal of manganese from the water. It therefore is a critical link in the process. There are two basic types of filters that are used; gravity high rate filters and pressure filters. Basically, they include a means of introducing the water, the filter media and a collection system for the filtered water. The collection system also serves as a distribution system for the backwash water used to clean the filters. The selection of filtration media and operational cycle of a gravity filter is somewhat similar to that of a pressure filter.

The media for the filters can include anthracite filter material, sands and manganese greensand together with the support sands and gravels. If manganese removal is not required, then the filter can be anthracite and sand, sand only or anthracite only. On the other hand, if manganese removal is required, then normally manganese greensand is used. If there are any significant iron levels present, it is beneficial to have an anthracite cap on top of the manganese greensand to protect it from a lot of iron sediment.

Sequestration process: phosphate treatment

Sequestrating of soluble manganese is the opposite of oxidation. Chemical used for sequestrating is sodium hexametaphosphate, commonly known as polyphosphate. Low levels of up to 2 mg/L can be remedied using phosphate compound treatment (Singer, 1988). Phosphate compounds are a family of elements that can surround minerals and keep them in solution. Phosphate compounds injected into the water system can stabilize and disperse dissolved manganese at this level. As a result, manganese compounds are not available to react with oxygen and separate from solution.

Phosphate compound treatment is a relatively inexpensive way to treat water for low levels of manganese. Phosphate treatment is effective in the pH range of 5.0 to 8.0 (NRWA, 2004). Since phosphate compounds do not actually remove manganese, water treated with these chemicals will retain a metallic taste. In addition, too great a concentration of phosphate compounds will make water feel slippery (Varner et al., 1994).

Phosphate compounds are not stable at high temperatures. If phosphate compound treated water is heated (for example, in a water heater or boiled water), the phosphate will break down and release manganese. The released manganese will then react with oxygen and precipitate. Adding phosphate compounds is not recommended where the use of phosphate in most cleaning product is banned. Phosphate, from any source, contributes to excess nutrient content in surface water (Seelig et al., 1992).

2.7 Summary

Analysis of Mn concentration in well water suggests that significant numbers of wells all over Bangladesh exceed permissible limit for Mn. There are areas that are suffering from both As and Mn problems; while at the same time there are areas where one of these two contaminants is the major groundwater quality problem. 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 3.0 mg/L (median 1.0 mg/L) and average manganese concentration 0.5 mg/L (median 0.3 mg/L) (BGS and WaterAid, 2001).

In the household and community As and Fe-As removal systems, that are currently being used in different areas of Bangladesh, no specific measures are taken for removal of Mn and available data suggest that Mn removal in these removal systems are not satisfactory. While Mn adsorption and formation of Mn oxide coatings on filter media are thought to be responsible for removal of Mn, there is limited data on factors affecting formation of such coatings and ability of these coatings in removing Mn from groundwater.

Chapter 3
METHODOLOGY

3.1 Introduction

As noted earlier, Manganese is characterized as a neurotoxin and the WHO recommends a guideline value of 0.4 mg/L (WHO 2004) to protect against neurological damage. Drinking water standard from aesthetic considerations is even more stringent, 0.1 mg/L. But, available data show that large numbers of drinking water wells in Bangladesh exceed these permissible limits for Manganese. So, it is important to develop efficient technologies for removal of Manganese from groundwater in the context of Bangladesh.

In this study, Manganese removal in filter media made of locally available sand and Iron coated sand bed was evaluated. For this purpose, the overall time required for obtaining "maturation" of Manganese oxide coated filter bed for optimum Manganese removal was determined and amount of Manganese retained by sand up to the "maturation" (defined as the condition when all Mn in the influent water would be removed or retained by the filter media) period was assessed. Furthermore, effect of pH on the formation of Manganese coating was also evaluated. In this study, efficiency of manganese removal in filter made of Mn-oxide coated Sylhet sand and iron coated sand has been evaluated in an effort to assess the suitability of these media for simultaneous removal of As and Mn. This Chapter describes the methodology followed in this study for achieving these objectives.

3.2 Preparation of Manganese Oxide Coated Sand Bed

For assessment of formation on Mn-oxide coatings, filter bed was prepared with sand using glass burettes (column height 43 cm) with a cross sectional area of 1sq cm. In this study, locally available Sylhet sand was used as filter media. The experimental set ups consisted of sand filter bed in burettes, buckets with tap for holding raw water, collector buckets and flow control (manual) arrangements. (See Figure 3.1). 20%

commercial grade hydrochloric acid was used for prewashing particularly one set of sand bed column in order to assess its effect of formation of Manganese oxide coating.

Figure 3.1 Experimental Setup for preparation of filter media with Manganese oxide coatings

Influent water with known concentrations of Manganese was passed through the filter columns and residual Manganese concentration was measured at different time intervals. Total filter-run time was 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; Mn-oxide coating could be identified by the formation of dark colored coatings on the sand grains.

Groundwater, collected from a deep tubewell pump station at BUET with Manganese concentration of around 0.2 mg/L, was spiked with Manganese (II) stock solution to prepare influent water with different concentrations of Mn. Manganese concentration in the influent water was fixed at 0.5, 1.0, 2.5 and 5.0 mg/L. 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. Table 3.1 provides a detailed characterization of groundwater used in the experiments.

Table 3.1 Detailed Characterization of Groundwater used in Laboratory Experiments

Parameter	Unit	Concentration
pH	--	7±0.1
Alkalinity as $CaCO_3$	mg/L	216
Carbon dioxide	mg/L	71
DO	mg/L	3.32 at 28^0 C
Hardness as $CaCO_3$	mg/L	256
Chloride	mg/L	55
Iron	mg/L	0.01
Manganese	mg/L	0.205
Arsenic	µg/L	<1

All chemicals to be used in this research work are of reagent grade. Manganese (II) stock solution was prepared by dissolving anhydrous manganese sulfate salt ($MnSO_4.4H_2O$; 98% Pure; Molecular Weight= 197.92) in deionized water (Barnstead Fistreem III). In this study, manganese concentration was measured using AAS-Flame (Shimadzu, AA-6800). The pH of the influent water was varied as necessary using dilute solutions of NaOH or HCl, in order to evaluate its effect on Mn removal. The pH of water samples was measured using pH meter (HAC 11d). Flow rate from 2 to 5 ml/min was maintained manually.

3.3 Manganese Removal using Manganese Oxide Coated Sand Bed

Laboratory batch experiments were carried out to assess Mn removal efficiency of the Manganese oxide coated sand prepared in this study (as described in Article 3.2). Removal of Mn was assessed under different parametric conditions (e.g., initial concentration, flow rate/contact time).

Filter columns were prepared in 1 cm^2 diameter glass burettes using the Mn-coated sand prepared earlier. The depth of the filter columns were 43 cm. Estimated Mn content of the filter media at the beginning of these experiments was about 0.706

mg/g sand. Influent water with known concentrations of Manganese was passed through the filter columns and residual Manganese concentration was measured at different time intervals. As described in previous section, groundwater collected from a deep tubewell water pump station at BUET was spiked with Mn stock solution to prepare influent water of known Mn concentrations. 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. Manganese stock solution was prepared according to the procedure described in Article 3.2. 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.

It should be mentioned that the same column (with initial Mn content of 0.706 mg/gm sand) was used for assessment of Mn removal for different initial Mn concentrations. Multiple columns could not be prepared because of the limited quantity of Mn-oxide coated sand. For each initial Mn concentration (starting from the lowest concentration), experiments were carried out till the achievement of 100% removal of Mn. This procedure has a drawback as far as assessment of filter efficiency is concerned. With passage of Mn bearing water, more Mn-oxide coatings form on the media, which should improve the Mn removal efficiency of the media. However, this is not expected to be a major issue because the prepared sand filter media already had a very high Mn-content, and the additional amount of Mn-oxide coating formed on the media during these experiments are likely to be insignificant compared to the initial Mn-content of the media (0.706 mg Mn/gm sand).

As described in Article 3.2, all chemicals used in this research work were of reagent grade. All measurements (pH, Manganese concentration) were carried out following the procedures described in Article 3.2.

3.4 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 following the procedure similar to that used by Joshi and Chaudhuri (1996) and Ali et al. (2001). The procedure basically consisted of pre-washing sand by immersing in an acid (20% commercial grade hydrochloric acid) solution for 24 hours. After drying, the sand was mixed with 2M ferric nitrate and 10N sodium hydroxide solution (80mL of ferric nitrate solution and 4mL of sodium hydroxide solution is required for each 200 cm^3 of sand). The mixture was then heated in an oven at 110° C for 14 hours. It was then washed with distilled water a number of times and then dried. In this study, locally available sand passing #30 sieve and retaining on #40 sieve (as suggested by Joshi and Chaudhuri, 1996) was used. 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 Section 4.2.1. 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.

3.5 Simultaneous Manganese and Arsenic Removal on Manganese Oxide Coated Sand Bed

In order to assess simultaneous removal performance of manganese and arsenic on previously prepared manganese oxide coated filter bed, natural groundwater was spiked with Arsenic (III) and Mn (II) solutions. As (III) concentration in the influent water was fixed at 100, 200 and 300 µg/L, while Mn concentration was varied from 0.25 to 3.0 mg/L. Required concentration of arsenic in groundwater was achieved by spiking groundwater with arsenic stock solution having As (III) concentration of 1000 mg/L (prepared from As_2O_3; May & Baker Ltd., Dagenham, England).

Laboratory batch experiments similar to those described in the previous Sections were carried out for assessment of simultaneous removal of Mn and As. For assessing effect of As on Mn removal in the prepared Mn-oxide coated sand media, Mn concentration in the influent water was varied from 0.25 to 3.0 mg/L, while As concentration was fixed at 200 μg/L. The experiments were carried out using the same filter column, which was used to carry out the other batch experiments. For each initial concentration of Mn in the influent water, the filter was run for about 240 to 300 minutes; the effluent water was collected at regular interval and tested for Mn (and also As) concentration, to assess Mn removal efficiency in presence of As. For assessment of the effect of Mn on As removal in the Mn-coated sand filter media, influent water with different combinations of initial As and Mn concentrations was passed through the column and As removal efficiency was assessed.

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Introduction

Laboratory experimental set ups, described in the previous Chapter, were designed to observe formation of manganese oxide coating on sand bed and to assess the efficiency of the prepared manganese oxide coated media in removing Mn and As from groundwater. This Chapter presents the results of batch experiments carried out for the preparation of Mn-oxide coated sand bed and the evaluation of Mn and As removal efficiency of Mn-oxide and Fe-oxide coated sand filter media.

4.2 Preparation of Manganese Oxide Coated Sand Bed

Experiments were conducted primarily to assess (i) the effect of acid wash of sand on the formation of manganese oxide coating, (ii) the effect of pH on the formation of manganese oxide coating on the sand filter, and (iii) the time required for obtaining "maturation" of filter bed for optimum Manganese removal. The filter bed was considered to have reached "maturation" when Mn removal through the filter bed approached 100%.

4.2.1 Effect of pre-washing on the formation of manganese coating on sand bed

In order to assess the effect of prewashing on the formation of Manganese coating, hydrochloric acid (20%) was allowed to pass through one sand bed column prepared with Sylhet sand. Another set of column was prepared without any pre-washing. For assessment of Mn-oxide formation, influent water with initial Manganese concentration of 1.0 mg/L was passed through both columns and formation of Mn oxide coating was assessed in both columns. Sylhet sand contains some natural iron oxide coating on its surface (most of which could be washed out by acid washing), and these experiments were carried out to see if these iron coatings have any effect on formation of Mn oxide coating on the sand grains.

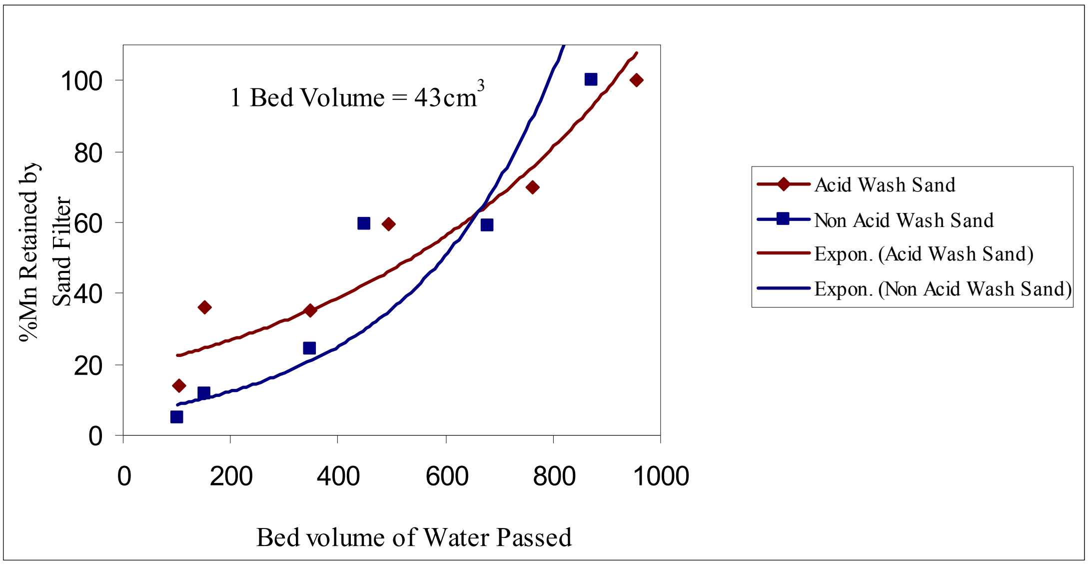


Figure 4.1: Formation of Manganese oxide coatings on acid wash and non-acid wash sand particles

Figure 4.1 shows retention of Mn by the sand filter as a function of bed volume of water passed through the filter column. Bed volume is expressed as volume of water passed per volume of sand bed. It shows that Mn retention characteristics (that is formation of Mn-oxide coating) of both natural and acid-washed Sylhet sand are similar. In both types of column, Mn retention approach 100%, that is filter bed reach "maturation" after passage of about 1000 bed volumes of water containing 1.0 mg/L of Mn. Thus, there appears to be no significant effect of acid-wash of sand on the formation of manganese oxide coatings on Sylhet sand. Therefore, acid wash of sand was not considered necessary for preparation of Mn-oxide coated sand.

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

Since pH plays an important role on the oxidation of Manganese, effect of pH on the formation of manganese coating was evaluated. For this purpose, 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 1.0 mg/L.

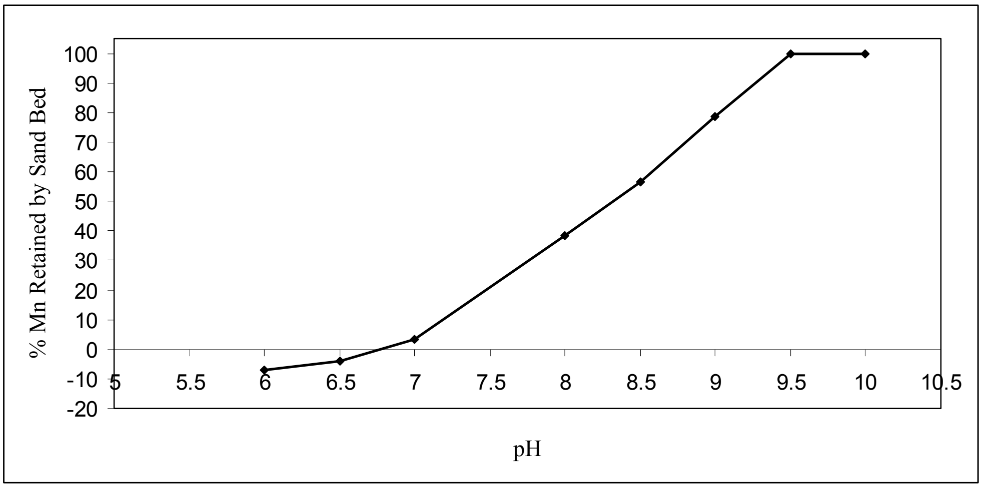


Figure 4.2: Effect of pH on Manganese coating formation on a sand filter bed

Figure 4.2 shows effect of Mn retention by the sand filter media as a function of pH of influent water. It shows that, as expected, Mn removal (or retention) by filter media increases as pH of influent water increases. In fact, 100% of Mn was removed when pH of influent water was above 9.5. This happens because oxidation of Mn is favored as pH increases. At higher pH values, Mn forms Mn-oxide precipitates and these precipitates are removed in the sand filter media. This figure also indicates that below pH 7, Mn leaches out of the filter media resulting in more Mn content in effluent than that in influent Mn-bearing water.

Figure 4.2 shows that if pH of influent water could be raised at or above 9.5, Mn could be easily removed in a sand filter. In this case, the water coming out of the filter would have to be adjusted back to neutral levels for potable use. 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 (e.g., acid/base) and to develop treatment systems that operate at natural pH of water (i.e., in the neutral pH range). Figure 4.2 shows that in the neutral pH range, Mn removal is insignificant in freshly prepared sand filter media. Therefore, it is important to develop/prepare media that would remove significant Mn in the neutral pH range.

4.2.3 Effect of initial Mn concentration and time on formation of Mn oxide coating on sand

As explained earlier, if Mn-bearing water is passed though a filter media (e.g., sand), Mn-oxide coatings form naturally on the media. These coatings in turn promote further oxidation and retention of Mn by the media, thereby significantly improving Mn removal efficiency of the media. In this study, efforts were made to assess the effect of initial Mn concentration in water and filter run time on the formation of Mn oxide coating on natural Sylhet sand at natural pH (neutral range) of groundwater. 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.

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 pH groundwater pH (7±0.1) and residual Manganese concentrations were measured.

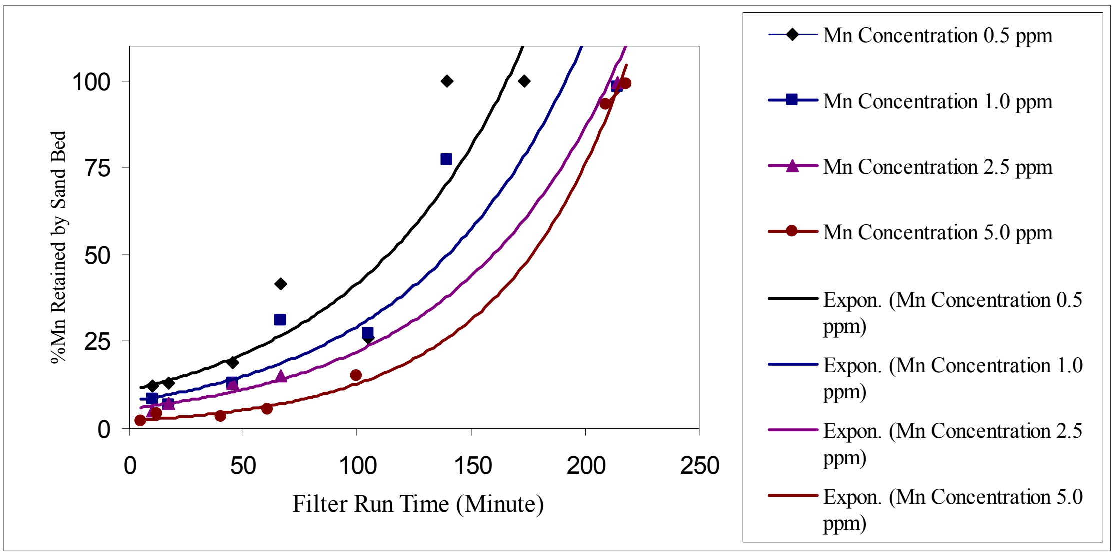


Figure 4.3 (a): Manganese removal on sand bed with different concentration of Manganese at pH (7±0.1) as a function of filter run time

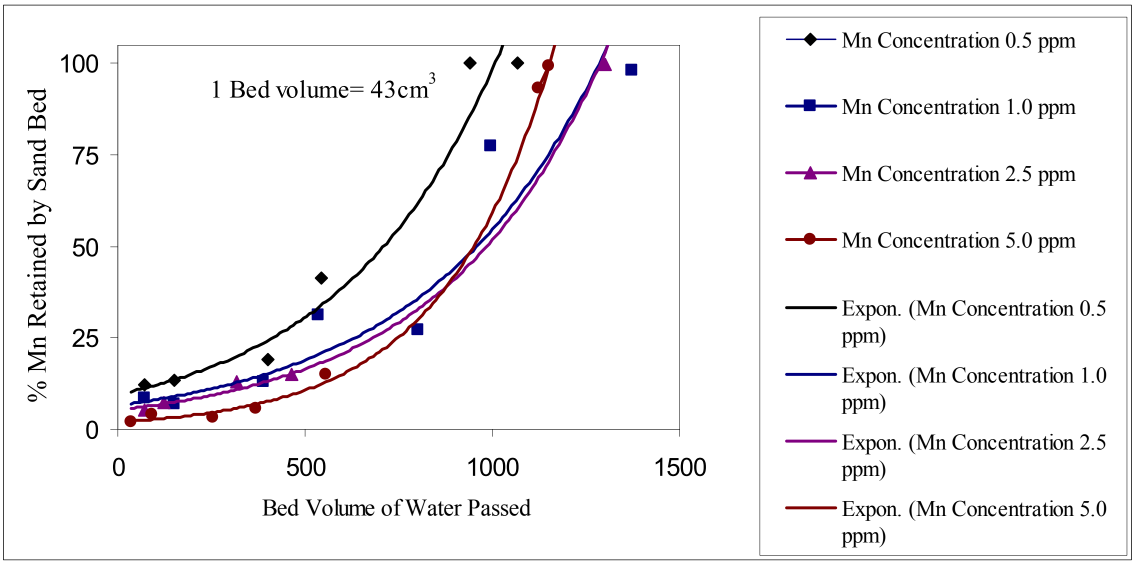


Figure 4.3 (b): Manganese removal on sand bed with different concentration of Manganese at pH (7±0.1) as a function of bed volume of water passed

Figure 4.3 (a) and 4.3 (b) shows Mn retention by the sand filter media as a function of "filter run time" and "bed volume of water passed through the column", respectively. The Figures show that Mn accumulation on filter media increases with passage of Mn-bearing water through the column. The figures show 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. Figure 4.4 shows a photograph of a sand filter column after maturation period; the sand grains turned dark due to formation of Mn oxide coatings.

As noted earlier, a filter column has been considered to have reached "maturation" when it retained (i.e., removed) almost 100% of Mn flowing with the influent water. The Figures shows that the "bed volume" of water required for "maturation" varied from 1000 to 1400 (1 bed volume= 43 cm^3), depending on the Mn concentration in influent water. Corresponding filter run time varied from about 180 to 220 hours. In general, the media achieved maturation faster, when Mn concentration in the influent water was lower. Amount of Mn retained by sand grains varied depending on Mn concentration in raw water. When Mn concentration in the influent water was higher, it took more time to achieve maturation, but more Mn accumulated on the media (discussed in the next Section).

4.2.4 Quantity of Mn coating by the filter media

The quantity of Manganese retained by the sand bed up to the bed maturation was estimated for all filter beds through which water with different initial concentrations of Mn was passed.

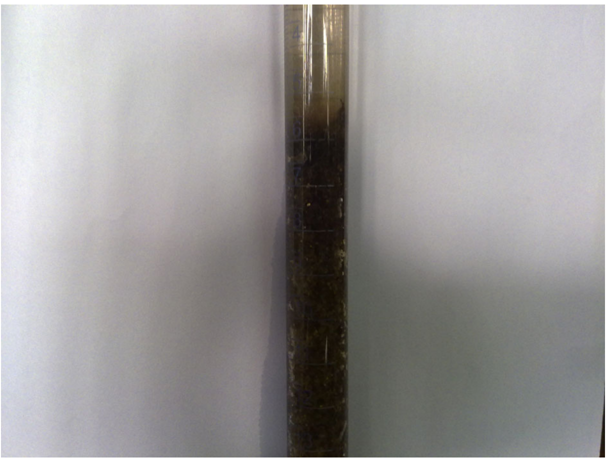


Figure 4.4: Manganese oxide coating formed on sand particles turning them dark (photograph taken after maturation period).

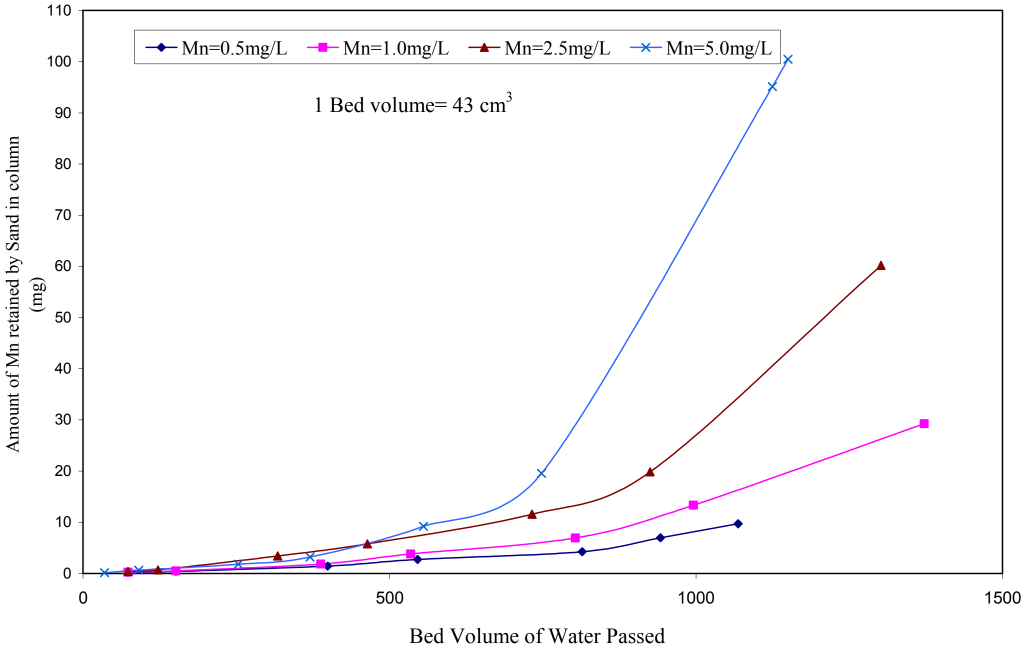


Figure 4.5: Amount of Manganese retained by sand in each column upto maturation at pH (7±0.1).

The quantity of Mn oxide coating was assumed to be equal to the the quantity of Mn retained by the media; in other words it was assumed that all Mn retained by the media formed Mn oxide coating on the media. Amount of Manganese accumulated on the Sand bed was assessed for different initial concentration (0.5, 1.0, 2.5, 5.0 mg/L) of Manganese in the influent water.

Figure 4.5 shows retention of total Mn by the sand filter media as a function of bed volume of water passed through the media for different initial Mn concentrations. It shows that in most cases, especially for higher initial Mn concentration, the rate of accumulation of Mn on the filter media increased with time. This phenomenon is most pronounced for the highest initial Mn concentration used in this study (i.e., 5.0 mg/L). Figure 4.5 shows that about 100 mg of Manganese was retained on the Sand bed at maturation for the column with initial Manganese concentration of 5.0 mg/L; while about 10 mg Mn was retained when initial concentration was 0.5 mg/L.

At maturation, the sand grains in different columns contained different quantity of Mn. The average quantity of Mn retained by sand expressed as mg Mn/g sand varies from about 0.17 mg Mn/g sand (for the column with initial Mn = 0.5 mg/L) to 1.76 mg Mn/g sand (for the column with initial Mn = 5.0 mg/L). However, it was obvious from physical observation (dark color formed on the sand grains) that sand grains at the top of the filter column accumulated higher amount of Mn compared to those at the bottom of the column. In subsequent laboratory experiments, the ability of these Mn coated sand filter media, prepared as describe above, in removing both Mn and As from groundwater have been evaluated (results presented and discussed in Article 4.3, 4.4 and 4.5).

4.3 Manganese Removal using Manganese Oxide Coated Sand Bed

This section presents the results of laboratory experiments carried out to assess the removal of Mn in Mn-oxide coated filter media. Results of laboratory experiments were used to assess (i) the effect of initial Mn concentration on Manganese removal, (ii) variation of Mn removal efficiency with filter run time, and (iii) the effect of flow rate (contact time) on manganese removal.

4.3.1 Effect of initial Mn concentration on manganese removal

In order to assess the effect of initial manganese concentration 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.

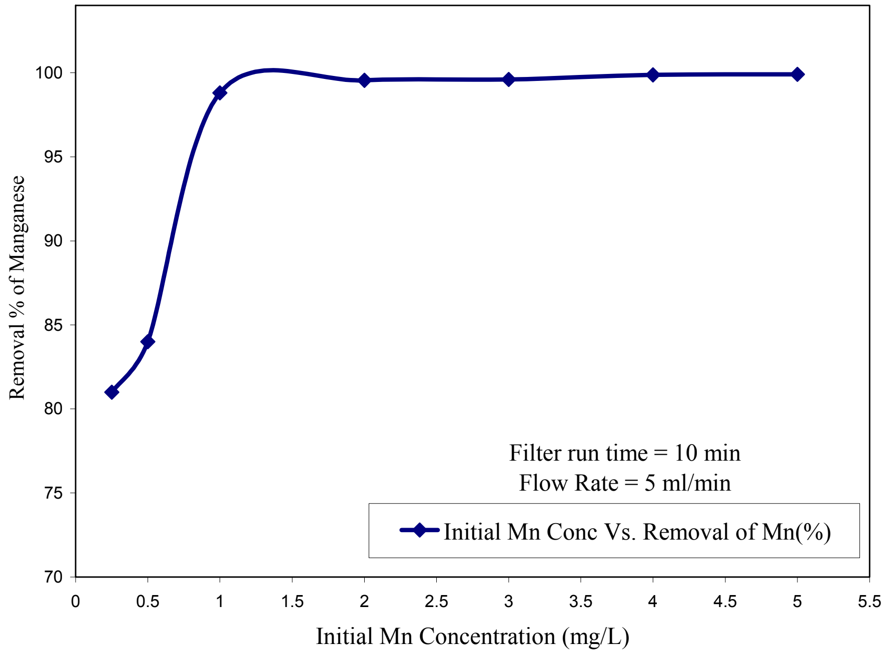


Figure 4.6: Manganese removal on Manganese oxide coated sand bed with different initial concentration of Manganese after 10 min filter run time at pH (7±0.1) and constant flow rate of 5 ml/min.

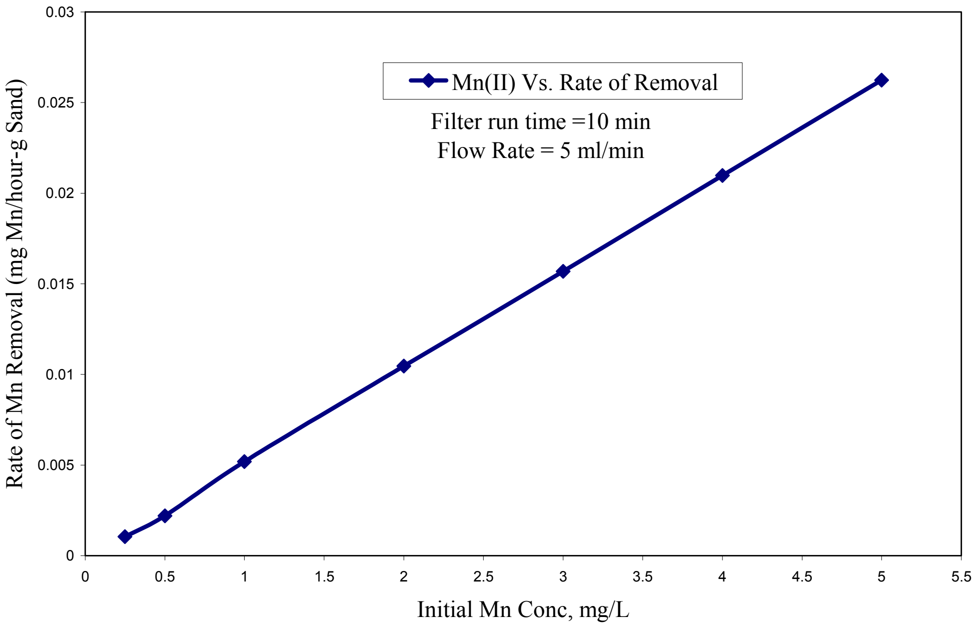


Figure 4.7: Rate of manganese removal with different initial concentration of Manganese after 10 minute filter run time (at pH (7±0.1) and flow rate of 5 ml/ min.

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. Figure 4.6 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 1.0 mg/L, Mn removal after 10 min of filter run approached about 100%. This observation appears to be consistent with that of Hoque (2006), who found that among the community As-Fe removal units assessed; Mn removal was higher when raw water Mn concentration was higher. 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 Table 4.1).

Figure 4.7 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 in Section 4.2.3, this is possibly due to autocatalytic effect of Mn oxidation, whereby previously formed Mn coating promotes further oxidation and precipitation of Mn.

4.3.2 Changes in manganese removal efficiency with the filter run time

Table 4.1 shows residual Mn concentration of water after passing through the Mn-oxide coated filter media as a function of time for different initial Mn concentration.

Table 4.1: Manganese removal in Mn-oxide coated sand filter for different initial Mn concentrations at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 0.25 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	0.250	--
10	0.046	81.0
20	0.040	84.0
30	0.022	91.2
60	0.020	92.0
90	0.020	92.0
120	0.064	83.0
150	0.018	95.3
180	0.031	91.8
210	0.016	95.9

Raw Mn Conc.= 0.5 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	0.500	--
10	0.080	84.0
20	0.045	91.0
30	0.017	96.6
60	0.009	98.2
90	0.007	98.4
120	0.003	99.4
150	0.011	97.7
180	0.009	98.0
240	0.009	98.0

Raw Mn Conc.= 1.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	1.000	--
10	0.016	98.8
30	0.019	98.1
60	0.010	99.0
90	0.010	99.0
120	0.004	99.6
180	0.005	99.5
210	0.024	97.6
270	0.012	98.8

Raw Mn Conc.= 2.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	2.000	--
10	0.009	99.6
20	0.003	99.8
30	0.003	99.8
60	0.008	99.5
80	0.012	99.3
100	0.013	99.4
120	0.012	99.3
180	0.010	99.5
240	0.012	99.4
270	0.012	99.4
300	0.016	99.1
330	0.007	99.6

Raw Mn Conc.= 3.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	3.000	--
10	0.010	99.6
20	0.011	99.6
40	0.006	99.8
60	0.012	99.6
180	0.005	99.8
240	0.010	99.6
300	0.011	99.7

Raw Mn Conc.= 4.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	4.000	--
10	0.005	99.9
30	0.011	99.7
60	< MDL	100
120	< MDL	100
180	< MDL	100
210	< MDL	100
270	< MDL	98.9

Raw Mn Conc.= 5.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	5.000	--
10	0.005	99.9
30	< MDL	100
90	< MDL	100
180	< MDL	100
210	< MDL	100
270	< MDL	100
300	< MDL	100

Table 4.1 shows that residual manganese concentration reaches almost zero even at filter run time of 10 minutes for higher initial Mn concentration. Even for lower initial Mn concentration, almost complete removal is achieved very quickly. The results suggest that the freshly prepared Mn coated media will be able to remove Mn with a wide range of initial concentration from groundwater to levels satisfying the national standard and WHO guideline value; and the efficiency of these media in removing Mn will improve further with time. Natural sand media could also achieve high Mn removal, but only after prolonged exposure to Mn bearing water as shown in Article 4.2. But if the prepared media are used, then very good Mn removal could be achieved from almost the very beginning of filter run.

4.3.3 Effect of flow rate on manganese removal

Figure 4.4 shows removal of Mn in Mn-oxide coated sand filter bed for different flow rates. The pH and Mn concentration of the influent water were fixed at 7±0.1 and 1.0 mg/L, respectively; while the flow rate was varied from 1 to 5 ml/min.

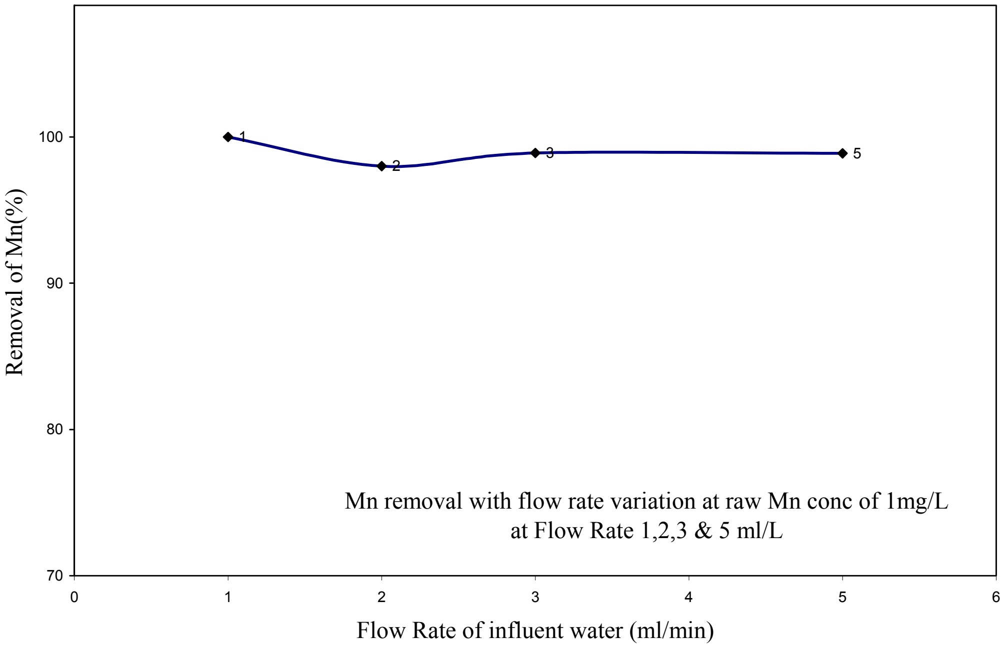


Figure 4.8: Manganese removal on Manganese oxide coated sand bed at different flow rates at pH (7±0.1) and constant initial Mn concentration of 1.0 mg/L.

Figure 4.8 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 2.6 minutes) will not produce any adverse effect on Mn removal in the prepared media.

4.4 Manganese Removal on Iron Oxide Coated Sand Bed

Removal performance of arsenic through Iron coated sand bed was assessed previously (Ali et al, 2001). In this study, manganese removal using iron coated sand bed was assessed. Figure 4.9(a) 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.

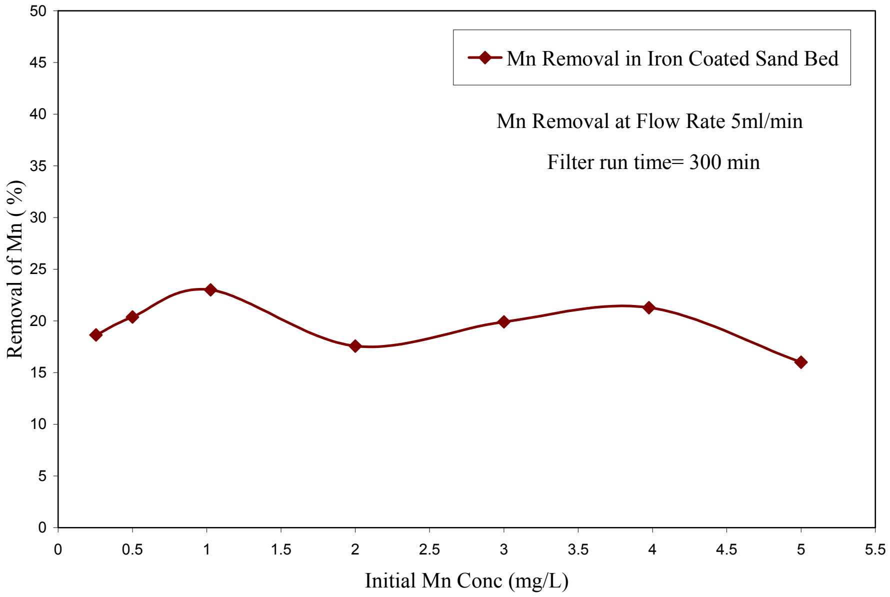


Figure 4.9 (a): Manganese removal on Iron oxide coated sand bed with different initial concentrations of Manganese at pH (7±0.1) and constant flow rate of 5 ml/min.

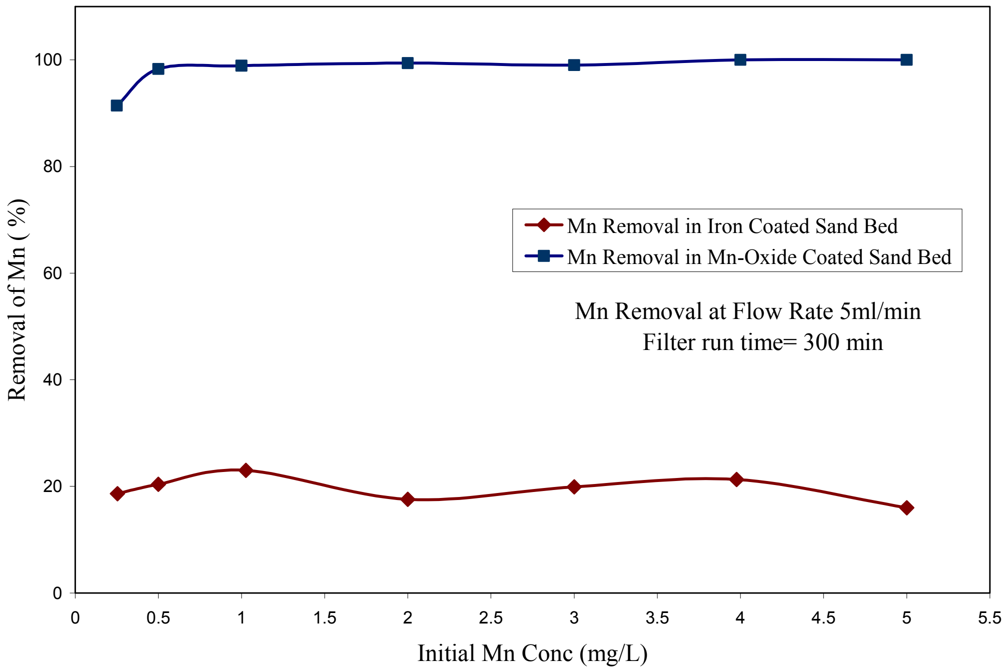


Figure 4.9 (b): Manganese removal on Manganese oxide coated sand bed and Iron oxide coated sand bed with different initial concentrations of Manganese at pH (7±0.1) and constant flow rate of 5 ml/min.

Figure 4.9 (b) 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 As from water (Ali et al., 2001), it has very limited capacity to remove Mn from groundwater.

4.5 Simultaneous Manganese and Arsenic Removal on Manganese Oxide Coated Sand Bed

Laboratory experiments were carried out to assess (i) effect of arsenic on manganese removal, and (ii) arsenic removal and effect of manganese on arsenic removal using manganese oxide coated sand bed.

4.5.1 Effect of arsenic on manganese removal

To assess the effect of arsenic on the removal of Manganese, simultaneous removal of manganese and arsenic was evaluated on previously prepared manganese oxide coated filter bed. For this purpose, Mn concentration in the influent water was fixed at 0.25, 0.5, 1.0, 2.0 and 3.0 mg/L and arsenic (III) concentration was fixed at 200 µg/L. Data from these experiments were compared with those carried out without As in influent water (discussed in Section 4.3.1).

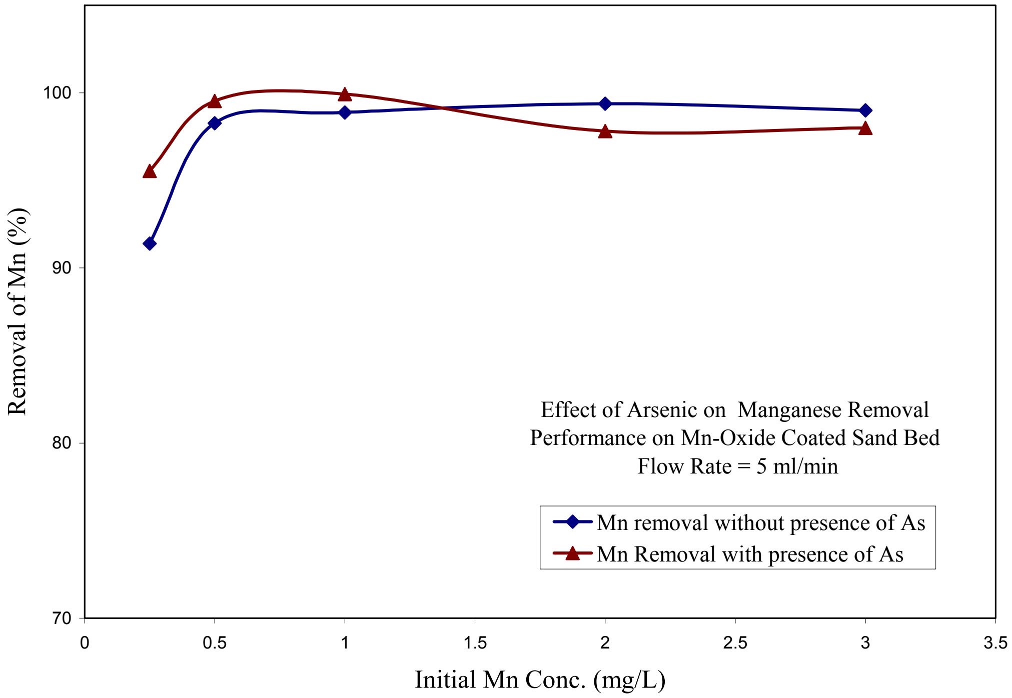


Figure 4.10: Effect of Arsenic on the performance of Manganese removal in Manganese oxide coated sand bed at pH (7±0.1).

Figure 4.10 shows Mn removal in the Mn-oxide coated sand filter column in the present of 200 µg/L of As for different initial Mn concentration, after a filter run-time of 300 minutes. This figure also shows Mn removal under similar conditions in the absence of arsenic. Figure 4.10 shows no significant effect of arsenic on manganese removal under the experimental conditions.

4.5.2 Arsenic removal and effect of manganese on arsenic removal in Mn-coated sand

In order to assess effect of manganese on arsenic removal on Mn-oxide coating filter bed, groundwater spiked with Arsenic (III) at concentration of 100, 200 and 300 µg/L was passed through the filter bed without addition of Mn. Arsenic removal was evaluated with and without presence of Manganese. Manganese concentration varied from 0.25 to 3.0 mg/L with different concentration of As (III) concentration at natural groundwater pH and flow rate was controlled at 5 ml/min.

Table 4.2 shows removal of As in the prepared Mn-coated sand filter bed. It shows that As removal is not significant in the media and that As removal appear to decrease with time.

Table 4.2: Arsenic removal in Mn-oxide coated Sand filter for different initial As concentrations at constant flow rate (5 ml/min) and pH (7±0.1)

Raw As Conc.= 100 µg/L			
Time Interval (minute)	Residual Conc. of As (µg/L)	Removal % of As	Average Removal %
0	100	--	18.2
60	64	36.4	
120	74	25.7	
180	88	12.5	
240	91	8.5	
330	98	8.0	

Raw As Conc.= 200 µg/L			
Time Interval (minute)	Residual Conc. of As (µg/L)	Removal % of As	Average Removal %
0	200	--	29.1
60	123	38.3	
120	129	35.5	
240	149	25.5	
330	166	17.0	

Raw As Conc.= 300 µg/L			
Time Interval (minute)	Residual Conc. of As (µg/L)	Removal % of As	Average Removal %
0	200	--	29.4
60	162	47.1	
120	236	22.6	
180	220	27.9	
300	230	24.6	
330	230	24.8	

Table 4.3 shows removal of both As and Mn in Mn-coated sand filter bed. From Table 4.3 it appears that Mn removal is largely unaffected in the presence of As. On the other hand, removal of As appears to increase to some extent in the presence of Mn. However, as before (see Table 4.2), removal of As appears to decrease with increasing filter run time.

Thus, while the prepared Mn-oxide coated sand filter media has a very high capacity to remove Mn, it appears to have limited capacity to remove As.

Table 4.3: Simultaneous removal of As and Mn in Mn-oxide coated Sand filter for different combinations of initial As and Mn concentrations at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 0.25mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	0.250	--	200	--
30	0.005	98.3	84	58.1
60	< MDL	100	101	55.7
120	0.000	100	152	33.7
180	0.048	83.9	166	27.5
300	0.013	95.6	189	17.7

Raw Mn Conc.= 0.5mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	0.500	--	200	--
60	< MDL	100	102	49.2
180	0.002	99.7	113	34.1
330	0.007	98.9	125	27.5

Raw Mn Conc.= 1.0mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	1.000	--	200	--
60	0.002	99.8	124	38.5
180	0.00	100	167	17.0
240	< MDL	100	152	11.6

Raw Mn Conc.= 2.0mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	2.000	--	200	--
60	0.012	99.4	100	50.5
180	0.040	97.7	111	36.8
240	0.035	98.0	150	14.7
300	0.066	96.6	117	33.2

Raw Mn Conc.= 3.0mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	3.000	--	200	--
60	0.059	98.0	108	46.1
120	0.011	99.6	121	33.1
180	0.066	97.5	115	36.6
300	0.078	97.1	119	34.5

4.6 Summary

Manganese oxide coated filter media was prepared by passing Mn-bearing (0.5 to 5.0 mg/L Mn) groundwater through filter bed made of locally available natural Sylhet sand. The experiments were carried out at natural pH of groundwater (7±0.1), without addition of any chemical (e.g., oxidant). Bed volume of water required for achieving filter "maturation" (defined as the time when almost all Mn in the influent water was retained by the media) varied from 1000 to 1400 (1 bed volume= 43 cm^3); corresponding filter run time varied from 180 to 220 hours.

For each sand bed column, manganese removal increased exponentially with operating time, possibly suggesting autocatalytic effect of Manganese oxidation and precipitation. That means, coating formed by manganese oxidation on the sand bed further promote Manganese oxidation and precipitation.

Amount of manganese retained by the sand particle for each column was also estimated. Estimated quantity of Mn retained by the filter media varied from about 10 mg to 100 mg; the corresponding average Mn content of the prepared sand filter media varied from about 0.17 mg Mn/g sand to 1.76 mg Mn/g sand. These prepared media have significant capacity to remove Mn from natural groundwater containing high Mn.

Laboratory experiments have subsequently been carried out to evaluate the Mn and As removal capacity of these prepared filter media. Results from the study show that prepared manganese oxide coated sand filter bed have significant capacity to remove manganese from groundwater and flow rate has little impact on Mn removal efficiency of the prepared filter bed under the experimental conditions. During initial stage of filter run (first 10 to 20 minutes) filter run, Mn removal was higher for influent water with higher initial Mn concentration; however, Mn removal approached 100% quickly for all initial Mn concentrations. Thus, significant manganese removal (approaching 100%) is possible in the media for a wide range of initial concentration of Manganese without using any oxidant at natural pH condition, satisfying the national standard and WHO guideline for manganese. Good Mn removal was recorded even after few minutes of filter operation, and the removal efficiency improved with filer run time.

Efficiency of Iron coated sand bed for manganese removal was also assessed. Iron coated sand bed did not show satisfactory performance for manganese removal (only about 20% removal under the experimental conditions).

Effectiveness of Manganese oxide coated sand bed was evaluated for simultaneous removal of manganese and arsenic. Presence of As was found to have little effect on Mn removal. However, the Mn-coated sand. Filter bed did not remove As significantly and removal of As decreased with increasing filter run time. Presence of Mn in influent water slightly improved As removal. Results from this study suggest that Mn oxide coated sand filters are not effective in removing As and cannot be used for simultaneous removal of As and Mn.

Chapter 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

The present research work started with the aim to achieve a number of objectives, including preparation of manganese oxide coated sand bed and assessment of factors affecting formation of Mn oxide coating on sand, assessment of manganese removal performance using Mn and Fe oxide coated sand bed, and assessment of the potential of the developed media (Mn-oxide coated sand) for simultaneous removal of Arsenic and Manganese. This Chapter summarizes the major finding and conclusions of the study. It also presents recommendation for future work.

5.2 Conclusions

From the experimental results obtained in this study, the following conclusions can be drawn:

1. Manganese oxide coated filter media could be prepared by passing Mn-bearing groundwater through filter bed made of locally available natural sand, such as Sylhet sand. Manganese oxide coatings form at natural pH of groundwater (7±0.1), without addition of any chemical (e.g., oxidant). Bed volume of water required for achieving filter "maturation" (defined as the time when almost all Mn in the influent water was retained by the media) varied from 1000 to 1400 (1 bed volume= 43 cm^3); corresponding filter run time varied from 180 to 220 hours.

2. The quantity of Mn oxide coating formed on the media depends on filter run time and Mn concentration in the influent water. Under the experimental conditions of this study, the estimated quantity of Mn retained by the filter media varied from about 10 mg to 100 mg; the corresponding average Mn content of the sand filter media varied from about 0.17 mg Mn/g sand to 1.76 mg Mn/g sand.

3. The prepared manganese oxide coated sand filter bed have significant capacity to remove manganese from groundwater and flow rate (in this study, maximum flow rate was fixed at 5 ml/min) has little impact on Mn removal efficiency of the prepared filter bed under the experimental conditions. The prepared bed was effective in removing Mn, satisfying national standard (0.1 mg/L) and WHO guideline value (0.4 mg/L), for a wide range of initial Mn concentrations.

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

5. Effectiveness of Manganese oxide coated sand bed was evaluated for simultaneous removal of manganese and arsenic. Presence of arsenic did not affect Mn removal; presence of Mn on the other hand appears to increase As removal to some extent. Results from this study suggest that Mn oxide coated sand filter media are not effective for removal of As, and hence cannot be used for simultaneous removal of As and Mn. However, use of Mn oxide coated sand media would significantly improve Mn removal efficiency of household and community groundwater treatment plants. And, filter media prepared by combining both Mn- and Fe-coated sand media has the potential of removing both Mn and As effectively.

5.3 Recommendations for Further Studies

The following are recommended for future studies:

1. Manganese removal efficiency should be evaluated under different parametric conditions, i.e., presence of bicarbonate, calcium, magnesium, chloride, phosphate, etc.

2. In this study, maximum flow rate was fixed at 5 ml/min. Experiments should be carried out with higher flow rates to assess the effect of flow rate on the removal.

3. Manganese removal using manganese oxide coated sand bed should be continued for prolonged time periods to assess the saturation of the filter media and to assess possible leaching of Mn from the filter media.

4. The characteristics of precipitated Mn solid formed on the sand media (e.g., exact mineral phase of Manganese oxide) and factors leading to the formation of solids on filter media and their role in manganese removal should be studied in greater details.

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APPENDIX

Table 1: Manganese removal on sand bed for different concentration of Manganese at pH (7±0.1) for preparation of Mn oxide coated sand bed.

Mn concentration 0.5 mg/L				Mn concentration 1.0 mg/L				Mn concentration 2.5 mg/L				Mn concentration 5.0 mg/L			
Flow rate, ml/ min	Cum. Time, Hours	Cum. Vol. of water, L	% Removal	Flow rate, ml/ min	Cum. Time, Hours	Cum. Vol. of water, L	% Removal	Flow rate, ml /min	Cum. Time, Hours	Cum. Vol. of water, L	% Removal	Flow rate, ml /min	Cum. Time, Hours	Cum Vol. of water, L	% Removal
5	10.5	3.2	12.0	5	10.5	3.2	8.5	5	10.5	3.2	5.2	5	5.0	1.5	2.0
7	17.5	6.5	13.2	7	17.5	6.5	6.7	5	17.5	5.3	5.2	5	12.0	3.9	4.2
5	45.5	17.2	19.1	5	45.5	16.7	13.1	5	45.5	13.7	12.9	5	40.0	10.9	3.3
5	66.5	23.5	41.5	5	66.5	23.0	31.2	5	66.5	20.0	15.2	4	61.0	15.9	5.6
5	105.0	35.0	26.1	5	105.0	34.5	27.3	5	105.0	31.5	20.0	3	99.5	23.9	15.2
5	139.5	40.5	100	5	139.5	42.8	77.3	5	139.5	39.8	39.0	5	134.0	32.2	25.0
1.6	**173.5**	46.0	100	2.4	**214.5**	59.0	98.1	4	**214.5**	55.9	99.6	2.2	209.0	48.4	93.3
--	--	--	--	--	--	--	--	--	--	--	--	2.0	**218.0**	49.4	99.2

Table 2: Mn removal using acid wash and non acid wash sand bed at pH (7±0.1).

Acid wash sand bed				Non acid wash sand bed			
Flow rate ml/min	Cum Time, Hour	Cum Vol of water, L	% Removal	Flow rate ml/min	Cum Time, Hour	Cum Vol of water, L	% Removal
5	16.5	4.4	14.0	5	16.5	4.4	5.0
5	23.5	6.5	35.9	5	23.5	6.5	11.6
5	51.5	15	34.9	5	51.5	14.9	24.3
4	72.5	21.2	59.5	4	72.5	19.4	59.6
5	111	32.8	70	4	111	29.2	59.2
5	146	41.1	100	5	146	37.5	100
2	221	57.3	100	2	221	53.7	100

Table 3: Mn removal by sand bed particles at different pH (Mn conc. = 2.5 mg/L)

pH	Sample collection time	% Removal	Avg. % Removal
6.5	After 120 min	4.0	3.9
	After 150 min	4.4	
	After 180 min	3.2	
7.0	After 120 min	4.4	4.1
	After 150 min	3.8	
	After 180 min	4.0	
8.0	After 120 min	41.2	38.2
	After 150 min	37.5	
	After 180 min	32.9	
8.5	After 120 min	56.5	56.6
	After 150 min	57.2	
	After 180 min	56.4	
9.0	After 135 min	78.9	78.7
	After 165 min	79.1	
	After 195 min	78.1	
9.5	After 120 min	100	99.8
	After 150 min	99.5	
	After 180 min	100	
10.0	After 90 min	100	100
	After 150 min	100	
	After 190 min	100	

Table 4: Mn Removal in Mn-oxide coated sand bed for different initial concentration of Mn at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 0.25 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	0.250	--
10	0.046	81.0
20	0.040	84.0
30	0.022	91.2
60	0.020	92.0
90	0.020	92.0
120	0.064	83.0
150	0.018	95.3
180	0.031	91.8
210	0.016	95.9

Raw Mn Conc.= 0.5 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	0.500	--
10	0.080	84.0
20	0.045	91.0
30	0.017	96.6
60	0.009	98.2
90	0.007	98.4
120	0.003	99.4
150	0.011	97.7
180	0.009	98.0
240	0.009	98.0

Raw Mn Conc.= 1.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	1.000	--
10	0.016	98.8
30	0.019	98.1
60	0.010	99.0
90	0.010	99.0
120	0.004	99.6
180	0.005	99.5
210	0.024	97.6
270	0.012	98.8

Table 4 (continued): Mn Removal in Mn-oxide coated sand bed for different initial concentration of Mn at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 2.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	2.000	--
10	0.009	99.6
20	0.003	99.8
30	0.003	99.8
60	0.008	99.5
80	0.012	99.3
100	0.013	99.4
120	0.012	99.3
180	0.010	99.5
240	0.012	99.4
270	0.012	99.4
300	0.016	99.1
330	0.007	99.6

Raw Mn Conc.= 3.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	3.000	--
10	0.010	99.6
20	0.011	99.6
40	0.006	99.8
60	0.012	99.6
180	0.005	99.8
240	0.010	99.6
300	0.011	99.7

Raw Mn Conc.= 4.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	4.000	--
10	0.005	99.9
30	0.011	99.7
60	< MDL	100
120	< MDL	100
180	< MDL	100
210	< MDL	100
270	< MDL	98.9

Table 4 (continued): Mn Removal in Mn-oxide coated sand bed for different initial concentration of Mn at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 5.0 mg/L		
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn
0	5.000	--
10	0.005	99.9
30	< MDL	100
90	< MDL	100
180	< MDL	100
210	< MDL	100
270	< MDL	100
300	< MDL	100

Table 5: Mn Removal in Mn-oxide coated sand bed for different flow rates with initial Mn concentration of 1.0 mg/L and pH (7±0.1)

Flow Rate= 1 ml/min		
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn
0	1.402	--
30	< MDL	100
60	0.002	99.9
120	< MDL	100
180	< MDL	100
270	< MDL	100
330	< MDL	100

Flow Rate= 2 ml/min		
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn
0	1.213	--
60	0.054	95.6
120	0.078	93.6
210	0.147	87.9
240	0.167	86.2

Flow Rate= 3 ml/min		
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn
0	1.280	--
30	0.014	98.9
60	0.003	99.8
120	< MDL	100
180	0.022	98.3
240	0.032	97.5

Flow Rate= 5 ml/min		
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn
0	1.008	--
120	0.004	99.6
180	0.005	99.5
210	0.024	97.6
270	0.012	98.8

Table 6: Mn Removal in Fe-oxide coated sand bed for different initial concentration of Mn at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 0.25 mg/L			
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn	Average Removal %
0	0.250	--	18.6*
30	0.246	31.5	
60	0.212	16.5	
120	0.221	12.9	
180	0.200	21.3	
240	0.209	17.7	
300	0.211	16.9	
360	0.154	39.4	

Raw Mn Conc.= 0.5 mg/L			
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn	Average Removal %
0	0.500	--	20.4*
60	0.350	30.0	
120	0.440	12.0	
180	0.579	1.70	
240	0.417	29.2	
300	0.411	30.2	

Raw Mn Conc.= 1.0 mg/L			
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn	Average Removal %
0	1.000	--	23.0*
60	0.430	58.1	
120	0.705	31.3	
180	0.827	19.4	
240	0.817	20.4	
300	0.726	29.2	

Raw Mn Conc.= 2.0 mg/L			
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn	Average Removal %
0	2.000	--	17.6*
60	1.255	32.56	
180	1.546	16.93	
240	1.584	14.88	
300	1.545	16.98	
330	1.461	21.49	

Table 6 (continued): Mn Removal in Fe-oxide coated sand bed for different initial concentration of Mn at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 3.0 mg/L			
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn	Average Removal %
0	3.000	--	19.9*
60	2.525	10.3	
120	2.543	9.7	
180	2.367	15.9	
300	2.160	23.3	

Raw Mn Conc.= 4.0 mg/L			
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn	Average Removal %
0	4.000	--	21.3*
60	3.610	9.2	
120	3.753	5.6	
180	3.319	16.6	
300	2.943	26.0	

Raw Mn Conc.= 5.0 mg/L			
Time Interval (minute)	Residual Conc. of Mn (ppm)	Removal % of Mn	Average Removal %
0	5.000	--	16.0*
120	5.387	8.1	
210	5.476	6.6	
270	4.955	15.4	
300	4.890	16.6	

*Averages of removal performance are taken between time intervals of 180 minute to 300 minutes.

Table 7: Arsenic removal in Mn-oxide coated Sand filter for different initial As concentrations at constant flow rate (5 ml/min) and pH (7±0.1)

Raw As Conc.= 100 µg/L			
Time Interval (minute)	Residual Conc. of As (µg/L)	Removal % of As	Average Removal %
0	100	--	18.2
60	64	36.4	
120	74	25.7	
180	88	12.5	
240	91	8.5	
330	98	8.0	

Raw As Conc.= 200 µg/L			
Time Interval (minute)	Residual Conc. of As (µg/L)	Removal % of As	Average Removal %
0	200	--	29.1
60	123	38.3	
120	129	35.5	
240	149	25.5	
330	166	17.0	

Raw As Conc.= 300 µg/L			
Time Interval (minute)	Residual Conc. of As (µg/L)	Removal % of As	Average Removal %
0	200	--	29.4
60	162	47.1	
120	236	22.6	
180	220	27.9	
300	230	24.6	
330	230	24.8	

Table 8: Simultaneous removal of As and Mn in Mn-oxide coated Sand filter for different combinations of initial As and Mn concentrations at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 0.25mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	0.250	--	200	--
30	0.005	98.3	84	58.1
60	< MDL	100	101	55.7
120	0.000	100	152	33.7
180	0.048	83.9	166	27.5
300	0.013	95.6	189	17.7

Raw Mn Conc.= 0.5mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	0.500	--	200	--
60	< MDL	100	102	49.2
180	0.002	99.7	113	34.1
330	0.007	98.9	125	27.5

Raw Mn Conc.= 1.0mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	1.000	--	200	--
60	0.002	99.8	124	38.5
180	0.000	100	167	17.0
240	< MDL	100	152	11.6

Raw Mn Conc.= 2.0mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	2.000	--	200	--
60	0.012	99.4	100	50.5
180	0.040	97.7	111	36.8
240	0.035	98.0	150	14.7
300	0.066	96.6	117	33.2

Table 8 (continued): Simultaneous removal of As and Mn in Mn-oxide coated Sand filter for different combinations of initial As and Mn concentrations at constant flow rate (5 ml/min) and pH (7±0.1)

Raw Mn Conc.= 3.0mg/L, As Conc.=200 µg/L				
Time Interval (minute)	Residual Conc. of Mn (mg/L)	Removal % of Mn	Residual Conc. of As (µg/L)	Removal % of As
0	3.000	--	200	--
60	0.059	98.0	108	46.1
120	0.011	99.6	121	33.1
180	0.066	97.5	115	36.6
300	0.078	97.1	119	34.5