

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

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**DEPARTMENT OF CIVIL ENGINEERING  
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY  
DHAKA**

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USING MANGANESE OXIDE COATED SAND.**

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A thesis submitted to the Department of Civil Engineering of  
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## **DECLARATION**

I hereby declare that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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Md. Ehosan Habib

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## ABSTRACT

Manganese (Mn) and arsenic (As) are common natural groundwater contaminants in Bangladesh. WHO (2004) recommended health-based drinking water guideline values of 0.4 mg/l and 0.01 mg/l for Mn and As, respectively. WHO (2011) eliminated the health-based guideline value for Mn citing that this value (i.e. 0.4 mg/l) is well above concentrations of Mn normally found in drinking water. Obviously this logic is not valid for Bangladesh, since well water Mn concentration in many regions of Bangladesh exceeds 0.4 mg/l by a large margin. Bangladesh therefore needs a low cost and efficient water treatment technology to remove Mn (as well as As) from groundwater. Removal of dissolved Mn by filtration through granular media (sand) could be an effective treatment method for Mn removal from drinking water. This research work focused on understanding the mechanism of Mn(II) oxidation/removal from water during filtration through granular media (sand), and evaluation of the effectiveness of different Mn-oxide coated media (synthetic/prepared media, “green sand”) in removing Mn and As from water.

The oxidation/removal of Mn(II) in granular media (sand) was carefully evaluated through controlled laboratory experiments. The removal of Mn(II) during filtration through a granular media (sand) has been found to involve adsorption of Mn(II) onto filter media, followed by oxidation of adsorbed Mn(II) in the presence of bicarbonate, creating/regenerating Mn-oxide coating, thus increasing Mn removal capacity of the media with increasing filter run time. The removal/oxidation of Mn(II) is favored at higher pH values and lower flow rates. Thus, removal of Mn(II) during filtration through granular media (sand) could be achieved without the addition of any oxidizing agent [for oxidation of Mn(II) to Mn(IV)], provided the water contains bicarbonate ion.

Laboratory investigations have been carried out to assess removal of As and Mn in three different types of Mn-oxide coated media: (a) “prepared” Mn-oxide coated filter media (prepared by passing Mn-bearing water through filter columns made up of Sylhet sand), (b) “synthetic” Mn-oxide coated media (prepared by treating Sylhet sand with  $\text{MnNO}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$ ), and (c) commercially available Mn-bearing “green sand”. The average Mn content of the “prepared” filter media was about 7,550 mg/kg; average Mn contents of “synthetic” media and “greensand” were 25,250 mg/l and 14,400 mg/kg, respectively.

The three types of Mn-oxide coated filter media have been found to be very effective in removing dissolved Mn from groundwater over a wide range of initial Mn concentration and pH. Results of both column and batch experiments showed that Mn removal efficiency increases with increasing Mn-content of the filter media. Mn removal efficiency also increases with increasing Mn in the influent water and increasing pH (in column experiments). Synthetic Mn-coated media, with the highest Mn content among the 3 media, performed best in removing Mn at higher flow rates. However, the other media (“prepared” media and green sand) also performed well at slower flow rates. A contact time of about 1.5 minutes was found to be sufficient for almost complete removal of Mn under the experimental conditions employed in this study.

Removal of arsenic [As(III)] in Mn-oxide coated filter media has been found to be strongly dependent on pH. Removal of As decreased with increasing pH, especially at pH beyond 7.5 and virtually no As removal took place at pH 9 and beyond. Removal of As(III) by Mn-oxide solids is governed by oxidation of As(III) to As(V) by  $\text{MnO}_2$ , and subsequent adsorption of As(V) onto  $\text{MnO}_2$  solids; the efficiency of both these processes are significantly reduced at higher pH values. In general, As removal increased with increasing Mn-content of the filter media. At relatively lower pH values (less than 7.5), arsenic appears to compete with bicarbonate ions for adsorption onto Mn-coated media. Presence of phosphate significantly reduced arsenic removal due to competitive adsorption.

The leaching or release of Mn from different Mn-oxide coated media has been found to increase with decreasing pH, though the leaching was not found to be significant; release of Mn was relatively higher for the “prepared” and “synthetic” media, compared to greensand. Under anaerobic condition created by oxidation of organic matter (which also reduces pH of water significantly), Mn is leached/released from Mn-coated media; Mn leaching/release from freshly “prepared” Mn-oxide coated media was significantly higher compared to the “synthetic” media and green sand. This suggests that creation of anaerobic condition in a filter bed could result in release of significant Mn from the media.

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## LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
APHA	American Public Health Association
AWWA	American Water Works Association
BAEC	Bangladesh Atomic Energy Commission
BGS	British Geological Survey
BRTC	Bureau of Research Testing and Consultation
BBS	Bangladesh Bureau of Statistics
BUET	Bangladesh University of Engineering and Technology
CR	Continuous Regeneration
DF	Down Flow
DO	Dissolved Oxygen
DPHE	Department of Public Health Engineering
EBCT	Empty Bed Contact Time
EPA	Environmental Protection Agency
FM	Fineness Modulus
GoB	Government of Bangladesh
GF	Graphite Furnace
HLR	Hydraulic Loading Rate
IRP	Iron Removal Plant
IR	Intermittent Regeneration
ITN	International Training Network
MSF	Multi Stage Filter
NGO	Non Government Organization
NDWQS	National Drinking Water Quality Survey
NMSU	New Mexico State University
NTU	Nephelometric Turbidity Unit
OCM	Oxide Coated Media
SEDA	Social Economic Development Authority
R	Raw
TDI	Total Daily Intake
T	Treated
TOC	Total Organic Carbon
SCM	Surface Complexation Model
UNICEF	United Nations International Child Education Fund
UP	Up Flow
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WHO	World Health Organization
XRD	X-ray Diffraction

## CHAPTER 1: INTRODUCTION

### 1.1 Background

The discovery of widespread arsenic(As) contamination of groundwater in Bangladesh has led to a re-assessment of water quality in general. While bacteriological contamination still represents a major threat to public health, it is now recognized that drinking water may also be contaminated with chemicals, which either have direct health impacts or indirect impacts by making the water unpalatable to the consumer.

Two major national level surveys, the National Hydro-geochemical Survey (BGS and DPHE 2001) and the National Drinking Water Quality Survey (NDWQS) (BBS and UNICEF, 2009), showed that in Bangladesh, large numbers of wells exceed permissible limits for arsenic(As), iron(Fe) and manganese(Mn). This is true for shallow tubewells, and also to some extent for deep tubewells and ring-wells, which are common water supply options in As-affected areas of Bangladesh. The National Hydro-chemical survey found that about 25% of the wells exceeded the national drinking water standard for As (0.05 mg/l). The survey also found that half of the 3,534 wells surveyed in 61 out of 64 districts exceeded the Bangladesh drinking water standard (1 mg/l) for iron (Fe), and three quarters exceeded the permissible limit (0.1 mg/l) for Mn; both of these limits are based on aesthetic concerns; above these levels, people may be unwilling to drink the water. Average Fe concentration in the surveyed wells has been reported to be 3 mg/l (median 1 mg/l) and average Mn concentration 0.5 mg/l (median 0.3 mg/l) (BGS and WaterAid 2001). Manganese also has adverse health impacts, and WHO recommended 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 Mn as well (Hasan and Ali, 2010). The NDWQS found that 61 percent of the samples exceeded the Bangladesh standard for Mn (0.1 mg/l), while 35 percent exceeded the WHO guideline value of 0.4 mg/l. In fact, some samples exceed the WHO guideline value of Mn by a factor of ten (BBS-UNICEF, 2009). The NDWQS also found that although 93 percent of deep tubewells meet the

Bangladesh standard for arsenic, only 60 per cent meet the Bangladesh standards for As, Mn and Fe.

It should be noted that the WHO (2011) eliminated the health-based guideline value for Mn noting “A health-based value of 0.4 mg/l can be derived for manganese based on the upper range value of manganese intake of 11 mg/day, identified using dietary surveys, at which there are no observed adverse effects, using an uncertainty factor of 3 to take into consideration the possible increased bioavailability of manganese from water, allocating 20% of the TDI to drinking-water and assuming the consumption of 2 litres of water per day by a 60 kg adult. However, as this health-based value is well above concentrations of manganese normally found in drinking-water, it is not considered necessary to derive a formal guideline value”. It is obvious that this logic is not valid for the situation in Bangladesh, where a major fraction of wells exceed the 0.4 mg/l limit. Therefore, under the circumstances, it is reasonable to assume that the WHO (2004) health-based guideline value of 0.4 mg/l still applies in the context of Bangladesh.

Unlike As, which has a distinct regional distribution pattern with highest contamination in the south, south-west, and north-eastern regions of Bangladesh, high concentrations of Mn can be 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 As (BGS and WaterAid 2001), and elevated Mn is found in both shallow and deep aquifers. In a recent study, groundwater from a deeper aquifer (190-240m) in Munshiganj district has been found to contain low concentrations of As ( $< 10 \mu\text{g/l}$ ), but very high (2 to 5 mg/l) concentrations of Mn (Hug et al., 2011). This means that groundwater with acceptable concentration of As may not have acceptable concentration of Mn.

The Fe problem has long been recognized in Bangladesh, and a number of technologies were developed for Fe removal at municipal, community and household levels in the 1980s (Ahmed, 1981; Ahmed and Smith, 1987, Azim, 1991). However, these community-level iron removal plants (IRPs) did not enjoy wide public



acceptance and were mostly abandoned shortly after commissioning, primarily because of certain design problems and difficulties in operation and maintenance.

With the discovery of widespread As contamination of groundwater in the 1990s, community and household-level groundwater treatment units generated renewed attention (Ahmed, 2003). When water is treated for Fe removal following conventional methods (involving oxidation of dissolved ferrous iron into ferric iron and its subsequent precipitation as ferric hydroxides), some of the As, if present in water, will also be removed as a result of adsorption onto ferric hydroxide flocs and co-precipitation. Since many As-affected areas also suffer from high Fe concentration, many NGOs are now installing different types of such IRPs for arsenic removal. However, some recent studies (BRTC-UNICEF, 2006; Hoque, 2006; ITN-BUET, 2011) showed variable performance of existing community As and As-Fe removal plants in removing Fe, As and Mn. Since many arsenic affected areas also suffer from high Mn concentrations, it is important to understand the mechanisms Mn and As removal and to develop media/plant for simultaneous removal of Mn and As.

Manganese can be removed using the same processes of oxidation, precipitation and filtration as in Fe removal (Fair et al., 1968). Conventionally, a strong oxidant such as chlorine or potassium permanganate is used for oxidation of Mn(II) rather than oxygen alone (Hartmann, 2002). However, some studies (e.g., ITN-BUET, 2011) reported that naturally present DO and other constituents (e.g., bicarbonate) in water could promote removal of Mn in a filter media (by sorption and oxidation) without the addition of an oxidant. This phenomenon needs to be investigated in more detail, through laboratory experiments. Mn(II) oxidation can lead to precipitation of Mn(III, IV) oxides which are in turn good adsorbents and oxidants (Hem, 1978). Microorganisms can catalyze oxidation of both Fe(II) and Mn(II) (Mouchet, 1992; Vandenabeele et al., 1992; Tyrrel and Howsam, 1997; Tyrrel et al., 1998; Tekerlekopoulou and Vayenas, 2007), though the relative contribution of chemical and biological mechanisms to Mn removal remains unclear (Olańczuk-Neyman and Bray, 2000). A number of studies (Kan et al., 2012; Buamah, 2009; Afsana, 2004) showed that Mn is removed effectively from groundwater by oxidation and adsorption processes. Manganese oxide coatings formed on filter media in filtration beds have

been found to act as good adsorbent for Mn and also plays a role in its oxidation (Eley and Nicholson, 1993; Tasneem, 2010; ITN-BUET, 2011). Media coated with synthetic Mn oxides have also been found to have good Mn removal efficiency (Merkle et al., 1997; NMSU, 1999; Dhiman and Chaudhuri, 2007; Maliyekkal et al., 2009). Manganese oxide coated filter media could therefore be potentially used for Mn removal from groundwater, although no report of its use in Bangladesh could be gathered. Besides, there is no data on the ability of such media in removing As from water. More research works are therefore needed for evaluation of Mn and As removal using Mn oxide coated filter media, and to assess potential of such media for development of effective treatment plants for simultaneous removal of Mn and As.

## 1.2 Objectives of the Present Work

The major objectives of the present work were to characterize the mechanisms of Mn(II) oxidation and removal in filter media and to evaluate the effectiveness of Mn and As removal in Mn-oxide coated filter media. The specific objectives included: (a) Evaluation of Mn(II) oxidation mechanism and formation of Mn-oxide coatings on sand particles in a filter bed through which Mn-bearing water is passing; (b) Evaluation of the effectiveness of different Mn-oxide coated media (synthetic/prepared media, “green sand”) in removing Mn and As from water, including effects of various water quality parameters (i.e. initial concentrations, pH, bicarbonate, phosphate); (c) Evaluation of the effect of process variables (e.g., depth of media, flow rate, contact time) and media characteristics on removal of Mn and As; and (d) Assessment of possible leaching of Mn from Mn-rich media under low pH, and anoxic conditions

## 1.3 Outline of Methodology

The methodologies adopted to achieve the objectives of the research work are summarized below:

### Mn(II) oxidation and formation of Mn-oxide coating on filter media:

For evaluating the chemistry of Mn(II) oxidation and formation of Mn(II) oxide coating on filter media, influent water of varying composition (with respect to Mn and other parameters) were passed through a green sand filter column maintaining a specific flow rate and the effluent water was collected and analyzed for residual Mn

and other parameters. The column experiments were carried out to assess the effects of dissolved oxygen (DO), initial Mn concentration and bicarbonate on the oxidation/removal of Mn in green sand filter column by varying these parameters in the influent water. Based on the results of these experiments, additional column experiments were carried out to evaluate the effect of bicarbonate (and pH) on oxidation/removal of Mn(II) in a filter media prepared with Sylhet sand. In addition, batch experiments were also conducted to estimate isotherm constants for describing adsorption of Mn on Sylhet sand and Mn-oxide coated media.

#### Preparation of sand with Mn oxide coatings:

Two methods have been used for preparation of sand with Mn oxide coatings. In the first method, Mn-oxide coated sand was prepared by passing Mn(II) bearing groundwater through filter columns made of Sylhet sands of known size fractions. Influent water with known Mn concentration was passed through the filter columns and the residual Mn concentration was measured at regular interval in order to estimate retention of Mn in the media. At the same time, the formation of Mn oxide coatings on the filter media was observed visually. The quantity of Mn oxide coatings formed on the media was quantified by extracting the Mn from the media with hydroxylamine hydrochloride (selective leaching method, Eley and Nicholson, 1993) and measuring its concentration. Mn-oxide coated sand prepared by this method has been referred to as “prepared Mn-coated media”.

Manganese oxide coated sand was also prepared following the methods of Merkle et al. (1997), using  $\text{MnNO}_3$ ,  $\text{H}_2\text{O}_2$  and NaOH. This Mn-coated sand has been referred to as “synthetic sand”. In addition, commercially available Mn-rich “green sand” was also procured. The effectiveness of these three different Mn-coated media (i.e., prepared media, synthetic media and green sand) in removing Mn and As from groundwater was evaluated in column experiments (described below).

#### Mn and As removal in Mn-coated filter media:

Removal of Mn and As in three different filter media (i.e., prepared media, synthetic media and green sand) was evaluated by passing groundwater with known concentrations of Mn and As through filter beds set in acrylic glass columns and

measuring the residual concentrations. Effects of water quality parameters such as initial concentrations, pH, bicarbonate and phosphate on removal have been evaluated by changing these parameters in the influent water.

Assessment of the effect of selected process variables (depth of media, flow rate, contact time) on removal of Mn and As in filter columns was carried out by varying these parameters/ processes.

#### Leaching of Mn and As from media:

Possible leaching of Mn from Mn-coated media have been evaluated in batch experiments. Leaching have been evaluated: (i) under low-pH environment, and (ii) under anoxic condition.

### **1.4 Organization of the Thesis**

This thesis has been presented in five chapters. Chapter 1 describes the background of the study and the major objectives of the research work. Chapter 2 presents an overview of Mn and As chemistry in water, water quality problems associated with the presence of Mn and As in water including health effects, and common methods and techniques for removal of Mn and As from water. This chapter presents a detail discussion on previous research works conducted on removal of soluble Mn and As by adsorption onto manganese oxide coated media. The results of previous studies have been analyzed to identify the needs for further experimental works for enhancement of knowledge in this area.

Chapter 3 describes the experimental setup (for both batch and column experiments) and analytical methods used to carry out the laboratory experiments. Chapter 4 presents the results of laboratory experiments carried out to characterize oxidation/removal of Mn in filter media and to evaluate the effectiveness of different Mn-coated media in removing Mn and As from groundwater. Finally chapter 5 presents the major conclusions of the study and recommendations for future studies. Appendix A presents data of experiments carried out for determination of isotherm constants for Mn adsorption on Mn-coated media. As a part of this study, the As, Mn and Fe removal performance of selected As and Fe-As removal plants currently operating in different As affected areas of the country have been assessed by

analyzing the raw and treated water, characteristics of the filter media at these plants and other relevant information. Appendix B presents the results obtained from field investigations and summarizes the major findings drawn from the study. Appendix B also presents, based on laboratory experimental results and the assessment of community groundwater treatment plants, a set of criteria for design of groundwater treatment plant for simultaneous removal of Fe, As and Mn.

## **CHAPTER 2: LITERATURE REVIEW**

### **2.1 Introduction**

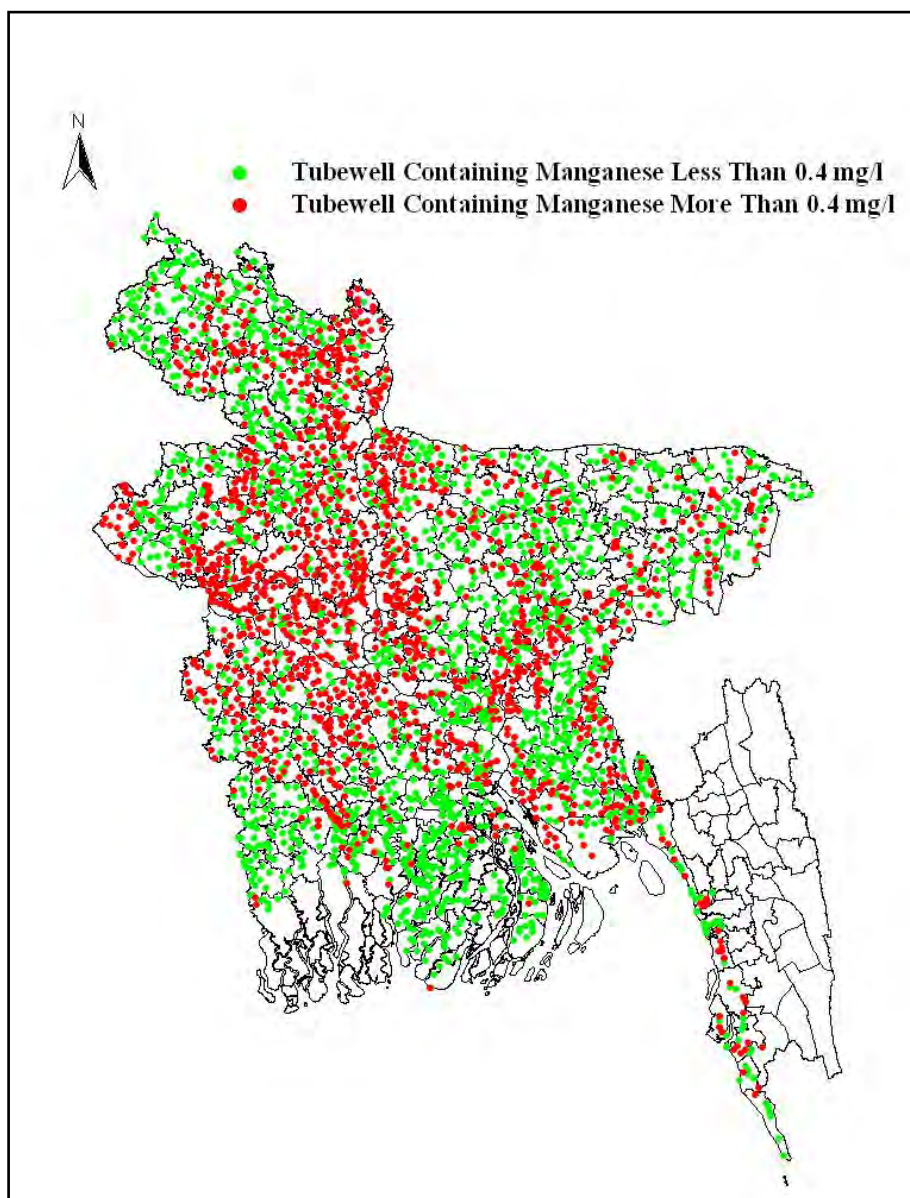
The main objectives of the research work were to characterize the mechanisms of Mn(II) oxidation and removal in filter media and to evaluate the effectiveness of Mn and As removal in Mn-oxide coated filter media. This chapter presents an overview of manganese and arsenic chemistry in water, water quality problems associated with presence of manganese and arsenic in water including health effects, and common methods and techniques for removal of manganese and arsenic from water. This chapter presents a detail discussion on previous research work conducted on removal of soluble manganese by adsorption onto manganese oxide coated media. The factors which influence manganese oxidation/removal have also been reviewed briefly. The results of previous studies have been analyzed to identify the needs for further research for enhancement of knowledge in this area.

### **2.2 Distribution of Mn in Groundwater of Bangladesh**

In Bangladesh, manganese is a common natural contaminant of groundwater. A number of studies (BGS and DPHE, 2001; Hug et al., 2011) showed that apart from arsenic (As), large numbers of drinking water wells exceed permissible limits for iron(Fe) and Mn in Bangladesh. This is true for shallow tube wells, and also to some extent for deep tube wells and ring-wells, which are common water supply options in As-affected areas. The National Hydro-geochemical Survey (BGS and DPHE, 2001) found that half of the 3,534 wells surveyed in 61 out of 64 districts exceeded the Bangladesh drinking water standard (1 mg/l) for Fe, and three quarters exceeded the permissible limit (0.1 mg/l) for Mn. Both of these limits are based on aesthetic concerns; above these levels, people may be unwilling to drink the water, and turn instead to a better-tasting, but microbiologically less safe water sources. Some of the reported Fe and Mn concentrations (BGS and DPHE, 2001) are very high, over ten times the permissible limit. Iron and manganese concentrations as high as 25 mg/l and 10 mg/l, respectively have been reported. Average Fe concentration in the surveyed

wells has been reported to be 3 mg/l (median 1 mg/l) and average Mn concentration 0.5 mg/l (median 0.3 mg/l) (BGS and Water Aid, 2001).

Figure 2.1 shows the distribution of Mn in groundwater of Bangladesh. 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 groundwater with acceptable concentrations of arsenic may not have acceptable concentrations of manganese. It is notable that groundwater from the deep aquifer (>150 m) contain relatively low concentrations of both arsenic and manganese. Medians of the concentrations in the shallow and deep aquifers were 0.34 mg/l and 0.03 mg/l respectively (BGS and DPHE, 2001). This highlights the large difference in concentrations between the shallow and deep aquifers.

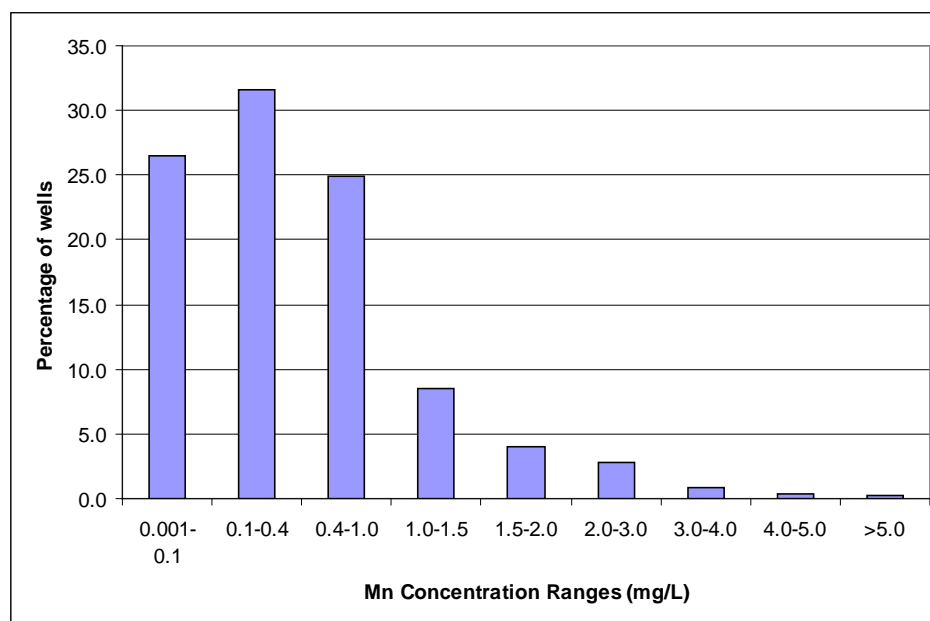


**Figure 2.1:** Distribution of manganese in groundwater of Bangladesh (Source: BGS and DPHE, 2001)

Figure 2.2 shows distribution of Mn in well water of Bangladesh, based water quality data obtained from the National Hydro-geochemical Survey (BGS and DPHE, 2001). It shows that about 27% of the surveyed tube wells 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.



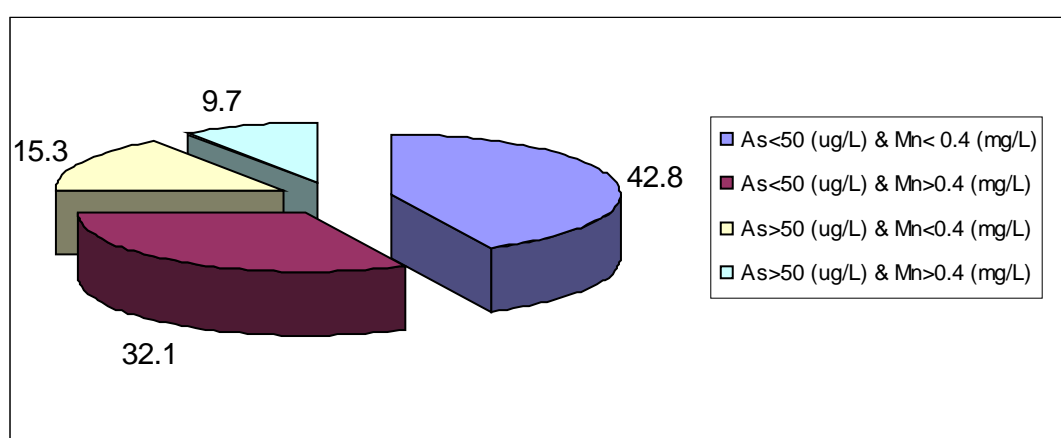
**Figure 2.2:** Wells with different ranges of manganese concentrations (Source: Hasan and Ali, 2010)

WHO (2004) recommends a guideline value of 0.4 mg/l for Mn in drinking water to protect against neurological damage. However, WHO (2011) eliminated the health-based guideline value noting that “this health-based value is well above concentrations of Mn normally found in drinking-water”. However, this logic is not valid for Bangladesh, since, about 40% of wells sampled in the BGS-DPHE survey in Bangladesh exceeded the WHO (2004) recommended health based guideline value of 0.4 mg/l for Mn. As shown in Figure 2.1, the people of central, north and south-east regions of Bangladesh is exposed to great health risk for presence of high concentration of Mn (>0.4 mg/l) in groundwater in this regions.

According to BGS and DPHE (2001), nationwide about 32% of wells, which contain safe level of As (i.e., < 0.05 mg/l) have been found to contain unsafe level of Mn (i.e., >0.4 mg/l). Therefore, this would significantly increase the population exposed to unsafe water, beyond that estimated for arsenic alone. Detection of high concentrations of Mn in groundwater has introduced a new dimension to the already difficult safe water supply scenario in Bangladesh. However, Mn issue has attracted

relatively less attention so far in the water supply sector in Bangladesh. Due to widespread presence of Mn in groundwater in addition to As and Fe, it is important to raise awareness among the stakeholders about the Mn issue and develop Mn removal technologies from water.

As noted earlier, the distribution of Mn generally does not correspond to that of As, which means that groundwater with acceptable concentration of arsenic may not have acceptable concentration of manganese (BGS and DPHE, 2001). Figure 2.3 shows distribution of As and Mn 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 2.3 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 2.3:** Status of wells with respect to arsenic and manganese concentrations (Source: Hasan and Ali, 2010)

## 2.3 Health and Undesirable Effects of Manganese and Arsenic

### 2.3.1 Effects 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.

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. These symptoms are generally the result of very high exposures via inhalation, as might occur in an industrial setting. 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 (Yamada et al. 1986; Calne et al., 1994; Dobson et al., 2004).

Water with a high concentration of manganese may cause the staining of plumbing fixtures or laundry. 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. Manganese solids may form deposits within pipes and break off as black particles that give water an unpleasant appearance

and taste. Manganese causes a metallic or vinyl type taste in the water. 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).

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 of manganese in high concentrations may cause an unpleasant metallic taste to the water (Raveendran et al., 2001).

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. 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.

As noted earlier, WHO (2004) recommended guideline value of 0.4 mg/l (WHO, 2004) for Mn in drinking water 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.

### ***2.3.2 Effects of Arsenic***

Arsenic occurs naturally, being the twentieth most abundant element in the earth's crust. Humans are exposed to arsenic primarily through air, food, and water. Exposure through air is negligible unless the area is heavily polluted by smelters or power plants. Exposure to arsenic through food ingestion is significant. Based on market-basket surveys of the total arsenic content in United States food, the US food and drug administration has estimated that adults ingest an average of about 53 µg/day of arsenic from the diet".

USEPA estimates that only twenty percent of the arsenic in food, or about 10 µg/day, is inorganic arsenic, which is the most toxic form of arsenic (Pontius et al., 1994). Ingestion of inorganic arsenic in drinking water thus possibly becomes the largest source of exposure to the toxic and carcinogenic effects of arsenic, if the arsenic concentration in the water is more than 5 µg/l, assuming an adult drinks two liters of water per day. Three possible types of health effects exist for exposure to arsenic. The first effect is toxic effects due to short term, acute exposure to larger amounts of arsenic. The second effect is toxic effects due to long term, chronic exposure to smaller amounts of arsenic. The third effect is increased risk of cancer due to long term, chronic exposure to smaller doses of arsenic. The carcinogenic effect is probably the controlling factor in determining how low to set the drinking water standard for arsenic. Complicating this is the fact that each species of arsenic has a different toxicity. Studies of organic arsenic excretion suggest that doses of inorganic arsenic up to around 200 µg/day are detoxified, but the validity of the studies was questioned by other scientists (Pontius et al., 1994).

The Bangladesh drinking water standard for Arsenic is 0.05 mg/l, while WHO recommends a guideline value of 0.01 mg/l.

## 2.4 Chemistry of Manganese

Manganese is the 10<sup>th</sup> most abundant element in the earth's crust and a naturally-occurring element that can be found ubiquitously in the air, soil, water and is normal constituent of the human diet. On the average crustal rocks contain about 0.1% Mn (Davison, 1991). Manganese occurs naturally in groundwater 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 chemistry of manganese has important roles and impacts in the environment. It is a transition metal which has numerous oxidation states between 0 and +7. The most commonly encountered states are Mn(II), Mn(III), Mn(IV), and Mn(VII). The reduced Mn(II) is generally found as the soluble  $Mn^{2+}$  cation. The highly oxidized Mn(VII) is widely known as permanganate and found in the form of the soluble  $MnO_4^-$  anion. The insoluble oxides of manganese are formed from Mn(III) and Mn(IV) and are often found as  $MnOOH(s)$  and  $MnO_2(s)$ , respectively. Mixed oxides also exist in the form of  $MnO_x$ , where  $x$  varies from 1.1 to 1.8 (Morgan and Stumm, 1964). Manganese 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.

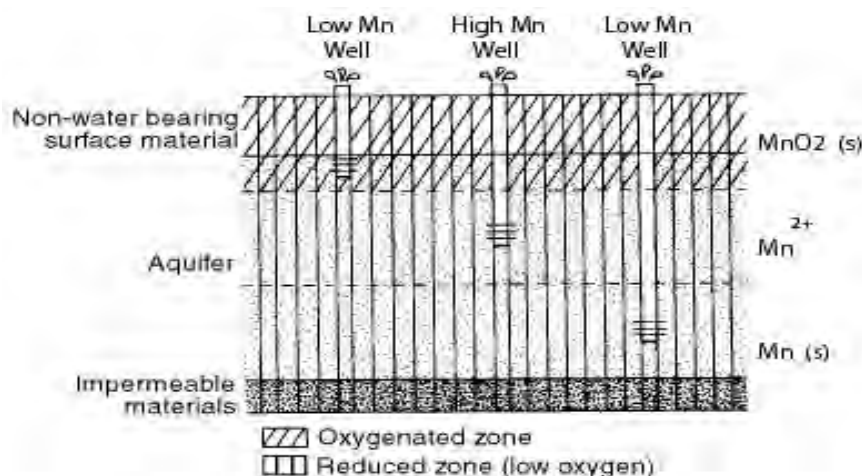
Eh-pH diagram for the Mn-O<sub>2</sub>-H<sub>2</sub>O system indicates that solubility of Mn is lowered in water which is well oxygenated. As the system becomes more oxidizing, the aqueous Mn(II) is converted directly to various solid manganese forms,  $Mn_3O_4$  (Hausmannite),  $Mn_2O_3$  (manganite or Feitknechtite) and  $MnO_2$ . Birnessite and feitknechtite are the most commonly found solid forms (Murray et al., 1985). The direct conversion of Mn(II) to solid oxide forms in water apparently does not occur without the presence of hydroxide (Hem, 1981; Coughlin and Matsui 1976). In fact the rate of oxidation depends on the oxygen concentration and the square of the hydroxide concentration, suggesting that although the oxides are stable, the creation of the oxides proceeds through a manganese hydroxide intermediate form. Manganese removal is catalyzed by solids, including Mn oxides (autocatalysis) (Coughlin and

Matsui, 1976; Kessick and Morgan, 1975); the presence of small amounts of solid through sludge recycling or due to turbidity may increase the rate of Mn oxidation.

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,  $\text{MnO}_2$  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,  $\text{Mn(II)}$ , which is released from minerals.  $\text{Mn}^{2+}$  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 sulfide, manganese can be immobilized by the formation of insoluble manganese sulfide ( $\text{MnS}$ ), 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).

Manganese is dissolved in a noxic and acid water. Homogeneous precipitation of  $\text{Mn(II)}$  as an oxide phase does not occur below pH 8, but  $\text{Mn(II)}$  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 bacteria mediate oxidation of dissolved manganese.

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. As shown in Figure 2.4, 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).



**Figure 2.4:** Dissolve manganese concentration with variation in depth of well (Source: 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 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.

## 2.5 Chemistry of Arsenic

### 2.5.1 Properties of Arsenic

Arsenic is a chemical element in the nitrogen family (group VA of the periodic table), existing in both grey and yellow crystalline forms. Although some forms of arsenic are metal-like, it is best classified as metalloid and non-metal. It can be manufactured in three allotropic forms, the yellow ( $\alpha$ ) form, the black ( $\beta$ ) form and the steel grey ( $\gamma$ ) form. These have different physical properties. The cubic  $\alpha$ -form is made by condensing the vapor at very low temperatures; it is metastable, is soluble in  $\text{CS}_2$  and consists of tetrahedral  $\text{As}_4$  units. The black  $\beta$ -polymorph is iso-structural with black phosphorous (II), and is also metastable. Both of these forms revert to the stable  $\gamma$  form, grey or metallic, rhombohedral arsenic, on heating or exposure to light. Gray or metallic arsenic, which is more stable and more common than the softer yellow form,

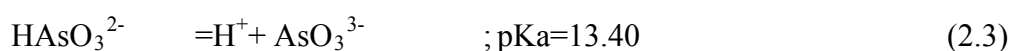
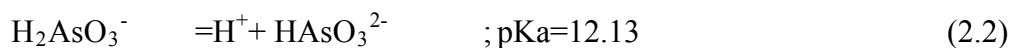
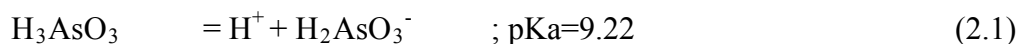


is very brittle, tarnishes in air and sublimes when heated at 610 °C, i.e., it passes directly into vapor form without melting and reverts to the crystalline solid without liquefying upon cooling the vapor.

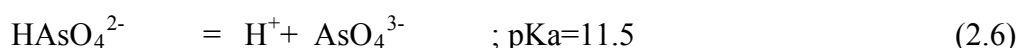
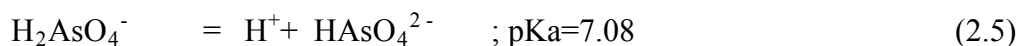
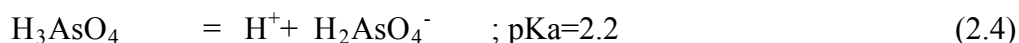
### 2.5.2 Acid-Base Reaction

Apart from the elementary arsenic with oxidation state 0, arsenic is stable in the oxidation states of +5, +3, and -3 (see Table 2.1), but generally found in water only in the trivalent and pentavalent states. The oxides of both As (III) and As(V) are soluble in water. The dissolution implies direct reaction with water, hydration, where the oxides behave like non-metals and exhibit acidic character. Arsenic (III) forms arsenious also called arsenic acid. Arsenic (V) forms the arsenic acid, also called arsinic acid. The two acids dissociate to form respectively arsenite and arsenate ions as shown in the following reactions.

Arsenious Acid Dissociation:



Arsenic Acid Dissociation:

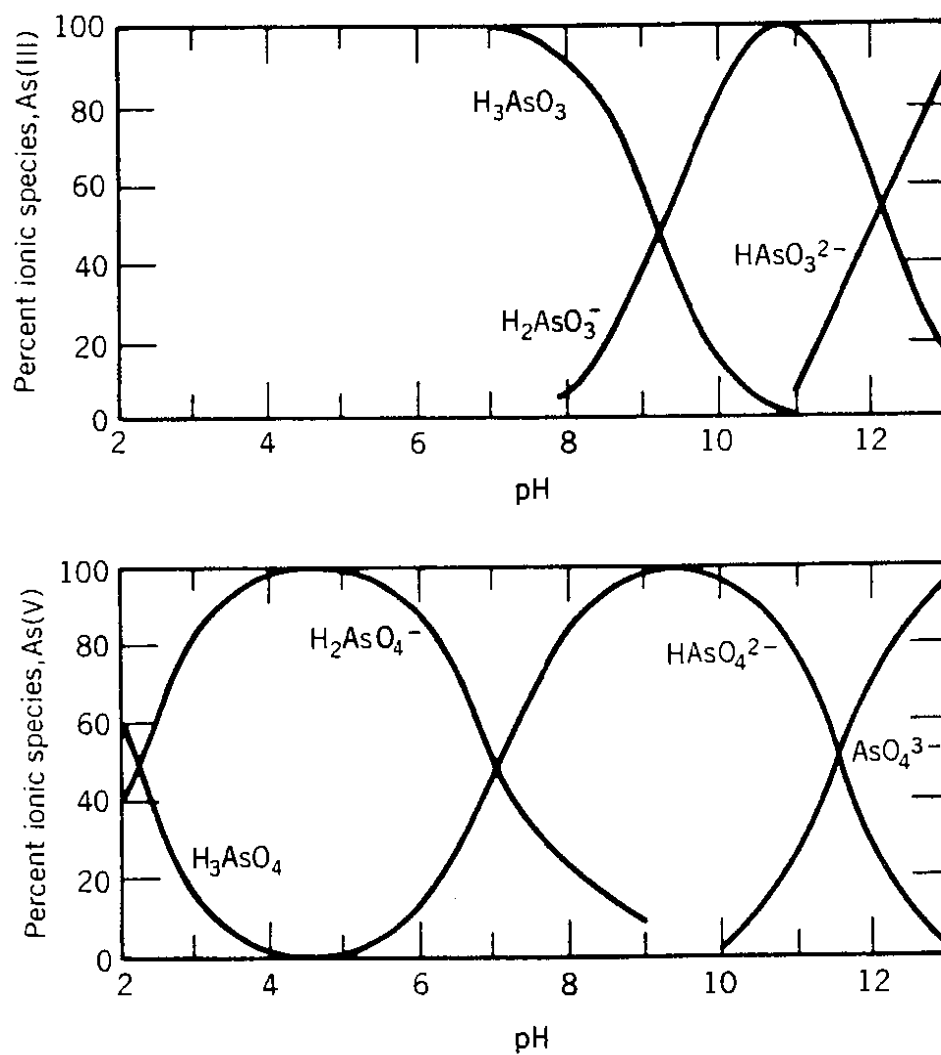


**Table 2.1:** Arsenic species and their environmental significance in water

Compounds	Example	Environmental significance/ Dominant pH region
Arsine Oxidation state: -3	$\text{As}^{3-}$	Minor importance [Most toxic As species]
Elemental Arsenic Oxidation state: 0	As	Minor importance [Least toxic As species]
Trivalent Arsenic Oxidation state: +3	As(III)	Dominant under anaerobic condition [10 times more toxic than As(V)]
Arsenite, Inorganic	$\text{H}_3\text{AsO}_3$	pH = 0 – 9
	$\text{H}_2\text{AsO}_3^{1-}$	pH = 10 – 12
	$\text{HAsO}_3^{2-}$	pH = 13
	$\text{AsO}_3^{3-}$	pH = 14 Important
Methylated As(III) MMAs(III) DMAs(III) TMAs(III) Organo-As(III)	$\text{CH}_3\text{As(III)O}_2^{2-}$ $(\text{CH}_3)_2\text{As(III)O}^{1-}$ $(\text{CH}_3)_3\text{As(III)}$	Minor importance [Less toxic than inorganic As(III)]
Pentavalent Arsenic Oxidation state: +5		Dominant under aerobic condition [10 times less toxic than As(III)]
Arsenate, Inorganic	$\text{H}_3\text{AsO}_4$	pH = 0 – 2
	$\text{H}_2\text{AsO}_4^{1-}$	pH = 3 – 6
	$\text{HAsO}_4^{2-}$	pH = 7 - 11
	$\text{AsO}_4^{3-}$	pH = 12 - 14 Important
Methylated As(V) MMAs(V) DMAs(V) TMAs(V) Organo-As(V)	$\text{CH}_3\text{As(V)O}_3^{2-}$ $(\text{CH}_3)_2\text{As(V)O}_2^{1-}$ $(\text{CH}_3)_3\text{As(V)O}$	Minor importance [Less toxic than inorganic As(V)]

Figure 2.5 shows the predominance diagram of arsenic species as a function of pH. From Fig. 2.5 it is seen that arsenic acid is stronger than arsenious acid. Within the pH range of natural waters (particularly groundwater), where pH is usually between 6 to 9, the trivalent inorganic arsenic is found as non-dissociated arsenious acid ( $\text{H}_3\text{AsO}_3$ ); while the pentavalent arsenic is primarily found as the ionized dihydrogen arsenate ( $\text{H}_2\text{AsO}_4^-$ ) and mono-hydrogen arsenate ( $\text{HAsO}_4^{2-}$ ). The relatively more mobile monomethylated and dimethylated forms are observed in ocean and lake waters, but seldom in groundwater. As most treatment processes are more capable to remove

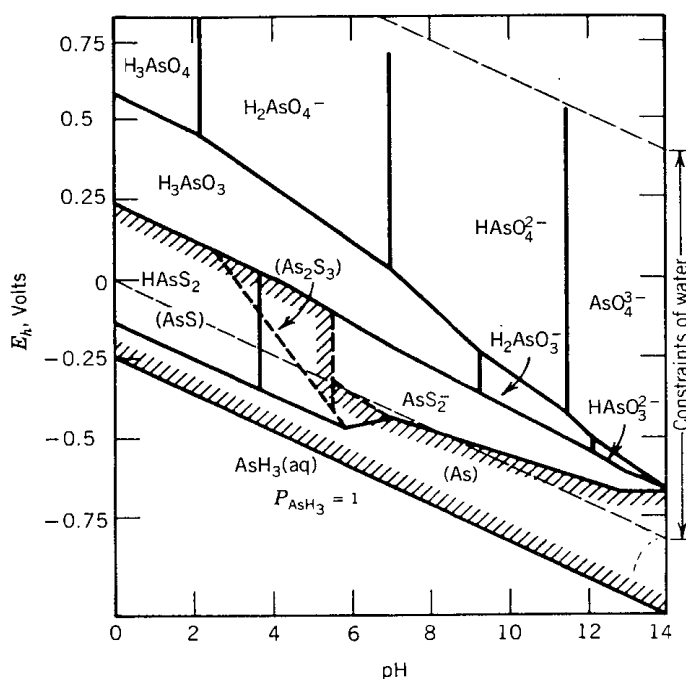
ions, the trivalent arsenic is more difficult to remove from the water than the pentavalent (Kartinen and Martin, 1995).



**Figure 2.5:** Predominance diagram of As(III) and As(V) species as a function of pH (Montgomery, 1985)

### 2.5.3 Redox Reaction

Arsenic is a redox sensitive element. Arsenate [As(V)] and arsenite [As(III)] are common oxidation states of arsenic in water. The mobility of arsenic is controlled, in large part, by the oxidation-reduction (redox) transformations. The valence in which arsenic exists is related to both pH and the redox potentials,  $Eh$ . The hypothetical electron activity at equilibrium,  $pE$ , is used interchangeably with  $Eh$ . These parameters are related by  $pE = (F/2.3 RT) Eh$ , where  $T$  is the absolute temperature and  $F$  &  $R$  are the Faraday and Gas constants, respectively. Thus at  $25^\circ\text{C}$ ,  $2.3 RT/F = 0.059 \text{ V}$  and  $pE = Eh/0.059$ . The equation linking arsenic speciation to pH and  $pE$  are readily available, but  $Eh$  versus pH diagrams (Fig. 2.6), are the most concise way of presenting this information. Figure 2.6 represents equilibrium conditions of arsenic under various redox potentials. Well-aerated surface waters would tend to induce high  $Eh$  values, therefore, any arsenic present should be in the arsenate [As(V)] form. Mildly reducing conditions, such as can be found in groundwater, should produce arsenite [As(III)]. By determining the pH and  $Eh$  of water, it is possible to determine which species of arsenic will be prevalent.



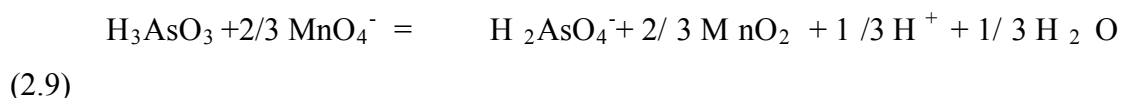
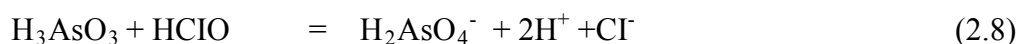
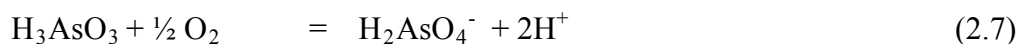
**Figure 2.6:** The  $Eh$ -pH diagram for As at  $25^\circ\text{C}$  and 1 atm with total arsenic  $10^{-5} \text{ M}$  and total sulfur  $10^{-3} \text{ M}$ . Solid species are enclosed in parenthesis in cross-hatched area, which indicates solubility less than  $10^{-5.3} \text{ M}$  (Montgomery, 1985)

As stated earlier, arsenate is dominant in oxygenated water, while arsenite is dominant in non-oxygenated water. Although thermodynamics can provide an accurate prediction of possible changes in a given non-equilibrium conditions, they give no insight to the rate at which those changes will occur. While As(III) and As(V) acid-base reactions can be assumed to occur instantaneously, changes between oxidation states require indeterminate time periods in natural waters. For instance, the conversion of As(III) to As(V) in oxygenated water is thermodynamically favored, yet the transformation takes days, weeks or months depending on the specific conditions. The reduction of As(V) to As(III) is similarly kinetically constrained. This is the reason why arsenic (V) can be found in some anoxic waters (Dahi, 1997). This process is however also known to be facilitated through catalysis and bacterial mediation.

In strongly acidic or alkaline solutions, the presence of copper salts, carbon, certain catalysts and higher temperatures can increase the arsenic oxidation rate (Ferguson and Davis, 1972). Catalytic oxidation of As can be achieved by powered active carbon and dissolved oxygen in stirred reactions. The rate of oxidation can be described by the first-order equation.

The effective removal of arsenic from water often requires the complete oxidation of As(III), especially if the drinking water standard is low. There are various means of oxidation available, but in drinking water treatment there are important considerations such as the limited list of safe chemicals, the residuals of oxidants, oxidation by-products and the oxidation of other inorganic and organic compounds. In the oxidation processes with dosing of chemicals, effective oxidants are free chlorine, hypochlorite, ozone, permanganate, and hydrogen peroxide/ $\text{Fe}^{2+}$  (Fenton's reagent), but not the chloramines (Frank and Cliford, 1986). These oxidants can directly transform As(III) to As(V) in the absence of oxygen. Chlorine is widely used for oxidation purpose, but may lead to chlorinated by-products, namely trihalomethenes (THMs), from reactions with natural organic matter. Ozone, widely used in surface water treatment for oxidation and disinfection, is quite effective but is not feasible for a specific application with As(III) oxidation. The most feasible oxidants are potassium permanganate and Fenton's reagent ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ). Permanganate oxidizes As(III),

ferrous and manganese ions specifically and quickly. Chlorine and permanganate are able to oxidize As(III) to As(V) within a very short time, e.g., half an hour or even few minutes (Dahi, 1997). Arsenious acid oxidations by most common oxidants are shown in the following reactions (Dahi, 1997):



#### 2.5.4 Adsorption-Desorption

Adsorption-desorption reactions are very important in determining the mobility of arsenic in nature as well as its removal in many treatment systems. Attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, arsenic becoming detached from such a surface is an example of desorption. Both arsenate and arsenite adsorb to surfaces of a wide range of solids including iron, aluminum and manganese oxides (e.g., iron oxyhydroxides), and clay minerals.

The strong adsorption characteristics of arsenic has been utilized in its removal from water by coagulation using alum, lime or ferric salts, where arsenic is removed primarily by adsorption onto solid flocs (e.g., aluminum hydroxide or ferric hydroxide) and subsequent precipitation. Arsenate is much more strongly adsorbed and removed than arsenite. Ferric salts have been found to be more effective in removing arsenic than alum on a weight basis and effective over a wider pH range. The strong adsorption of arsenic onto hydrous iron, aluminum and other solids has also been utilized in removing arsenic using a wide range of solid sorption media. These include activated alumina, iron coated sand, granular ferric hydroxide, and a wide range of other materials. Besides arsenic, a number of other ions present in natural water (e.g., phosphate, silicate, sulfate) also have strong affinity for solid surfaces and presence of high concentrations of these ions can reduce removal efficiency of arsenic in adsorption-based treatment systems.

Adsorption-desorption of arsenic onto iron oxide surfaces are important controlling reactions in the subsurface because iron oxides are widespread in the hydro-geologic

environment as coatings on other solids, and because arsenate adsorbs strongly to iron oxide surfaces in acidic and near-neutral pH conditions. Desorption of arsenate is favored at higher (i.e., alkaline) pH values. The pH dependence of arsenate adsorption-desorption appears to be related to the change in net charge on iron-oxide surface with pH. The net charge on iron oxide surface changes from positive to negative as pH increases above the “zero-point-of-charge” (pH at which net surface charge is zero). The “zero-point-of-charge” is about 7.7 for goethite (crystalline iron oxide) and about 8.0 for ferrihydrite (amorphous iron oxide). Thus as pH increases above about 8, the net negative surface charge on iron oxides can repel the negatively charged ions such as arsenate. Compared to arsenate, arsenite is less strongly adsorbed by iron oxides. Arsenate and arsenite adsorption-desorption reactions onto other common surfaces are less well characterized.

In Bangladesh arsenic-rich iron oxyhydroxides present in aquifer materials appear to be the primary source of arsenic in groundwater. In the subsurface environment, adsorption-desorption of arsenic onto iron oxyhydroxides is an important mechanism controlling its mobility. As noted earlier, presence of ligands, which may compete with arsenic for adsorption sites on iron oxyhydroxides, e.g., phosphate, silicate and sulfate can also influence the mobility of arsenic in the subsurface, if present in large enough concentrations. Besides oxyanions of molybdenum, selenium and vanadium can also compete with arsenic for adsorption sites.

As a result of pH dependence of arsenic adsorption, changes in groundwater pH can promote adsorption or desorption of arsenic. Similarly, redox reactions can control aqueous arsenic concentration by their effect on arsenic speciation and hence on adsorption-desorption reactions. For example reduction of arsenate to arsenite can promote arsenic mobility because arsenite is less strongly adsorbed than arsenate. It should be noted that in nature bacteria often mediate oxidation-reduction reactions.

Finally, structural changes in solid phases at the atomic level can also affect arsenic adsorption-desorption (USGS, 1999). For example, conversion of amorphous ferrihydrite to crystalline goethite may occur gradually over time (Dzombak and Morel, 1990) and this can be accompanied by a decrease in adsorption site density.

This reduction in site density may result in desorption of adsorbed arsenic. Structural changes in other solid phases may also affect arsenic mobility (USGS, 1999).

### ***2.5.5 Precipitation and Dissolution Reactions***

Precipitation-dissolution reactions are important mechanisms controlling mobility of arsenic in the subsurface. Arsenic contained within solid phases, either as a primary structural component of arsenic bearing minerals (e.g., arsenopyrite) or an impurity in any of a variety of solid phases (e.g., pyrite), is released to groundwater when these solid phases dissolve. Similarly, arsenic is removed from groundwater when solid phases containing arsenic precipitate from aqueous phase. As an example, because arsenic often co-precipitates with iron oxide, iron oxides may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for groundwater (USGS, 1999). Besides, solid phase dissolution will contribute not only arsenic contained within that phase, but also any arsenic adsorbed to the solid-phase surface. In Bangladesh, reductive dissolution iron oxyhydroxides and consequent release of adsorbed arsenic could be an important mechanism of arsenic mobilization in the subsurface.

The interplay of redox reactions and solid phase precipitation and dissolution may be particularly important with regard to aqueous arsenic and solid-phase iron oxides and sulfide minerals (USGS, 1999). High concentrations of arsenic often are associated with iron oxides and sulfide minerals. Iron oxides frequently dissolve under reducing conditions (e.g., in the presence of organic matter), but often precipitate under oxidizing conditions. Sulfide minerals generally are unstable under oxidizing conditions, but may precipitate under reducing conditions (e.g., precipitation of  $As_2S_3$ ). Thus, as a result of redox sensitive nature of iron oxides and sulfide minerals, transfer of large amounts of arsenic between these solid phases and neighboring water may result from redox-facilitated precipitation and dissolution reactions (USGS, 1999).

Precipitation of arsenic has been utilized in the removal of arsenic from water. The insolubility of certain inorganic arsenic(V) compounds is the basis of many hydrometallurgical arsenic removal processes (Robins et al., 2001). The most common methods of removing arsenic from aqueous systems are by precipitation as



arsenic(III) sulfide, calcium arsenate, or ferric arsenate. Other solids of interest include ferrous arsenate [ $\text{Fe}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$ ], calcium-arsenate-phosphate [ $\text{Ca}_{10}(\text{AsO}_4)_6(\text{PO}_4)_6(\text{OH})_2$ ], and ferric sulfide [ $\text{Fe}_2\text{S}_2$ ].

## 2.6 Common Treatment Options for Removal of Mn from Water

There are a number of removal technologies used to remove manganese from water. The most common removal technologies are chemical oxidation, sequestration, and adsorption. Adsorption using oxide coated media is discussed in more detail in the following section. The soluble manganese can be removed by the physical process of aeration. Both groundwater and surface water can be aerated using various techniques during treatment. However, the rate of reaction between manganese and oxygen is slow and a retention tank with several hours of detention time is recommended to allow adequate conversion (Wong, 1984). Alkaline pH ( $> 9.0$ ) is generally required to oxidize the soluble manganese in this way within the duration of water treatment (Morgan and Stumm, 1964). Filtration is then applied for the removal of the solid manganese oxide particles. Aeration is not often used for large plants or for water with high levels of manganese.

Manganese removal has been accomplished by the addition of various types of chemical oxidants, including free chlorine, chlorine dioxide, potassium permanganate and ozone. Knocke et al. (1987) revealed that alkaline conditions ( $\text{pH} > 8$ ) are required for adequate manganese removal by chlorine addition. Low temperatures ( $< 5^\circ\text{C}$ ) were also shown to hinder the process. Since traditional coagulation-flocculation treatment benefits from acidic pH conditions, the only use of chlorine as an oxidant for manganese removal is not recommended. Chlorine is the oxidant preferred to enhance removal via oxide coated media by regenerating the media while oxidizing the soluble Mn.

Knocke et al. (1987) used chlorine dioxide ( $\text{ClO}_2$ ) for removal of Mn from water. The theoretical stoichiometric amount of chlorine dioxide needed for manganese oxidation is  $2.45 \text{ mg/mg Mn}^{2+}$ . Laboratory testing showed that twice the theoretical amount could be required for effective soluble manganese removal (Knocke et al., 1987). The concentration of organic material in the water significantly affects the dosage of

chlorine dioxide required. At low total organic carbon (TOC) concentrations ( $< 2.5$  mg/l), chlorine dioxide dose between 1.0–1.5 mg/l was effective across a large range of pH values. However, water with higher organic demands (8-10 mg/l TOC) required doses of over 3 mg/l of  $\text{ClO}_2$  for similar removal. Due to health concerns of chlorite and chlorate presence in drinking water, most regulatory agencies do not permit dosage of chlorine dioxide outside the range of 0.5-2.0 mg/l. Hence, chlorine dioxide is an effective oxidant for manganese removal but should be used in conjunction with another oxidant when high concentrations of organic material and/or high initial soluble manganese levels are present.

Soluble manganese oxidation has been performed conventionally by potassium permanganate ( $\text{KMnO}_4$ ). Also affected by organic concentrations, the permanganate dosage increases to much higher than the theoretical stoichiometric amount when the TOC levels increase above 3 mg/l (Knocke et al., 1987). The chemical cost per unit of potassium permanganate is higher than the cost per unit required for oxidation by free chlorine (Knocke et al., 1987).

A strong and rapid-acting oxidant Ozone ( $\text{O}_3$ ) has become a widely accepted disinfectant in water treatment since it does not produce disinfection by-products, except when bromide is present in the water. Reckhow et al. (1991) conducted a study to determine the stoichiometry and kinetic rates of the oxidation reaction between ozone and manganese under both low and moderate organic concentration conditions. The study found that the reaction rate increased with increasing pH; further, at a pH of 8.0 the required dose was practically equal to the theoretical stoichiometry. However, with the addition of organics, between 2-5 times the stoichiometric dose was required to oxidize the manganese. Bicarbonate was added to minimize the formation of unproductive radicals and hence, reduce the dose of ozone required. Therefore, Ozone use is more often recommended for oxidizing manganese in water with low organic concentration.

Most of the removal methods discussed above chemically or physically oxidize manganese to its solid form. These oxide particles are then required to be physically removed. This is often accomplished by traditional treatment methods consisting of

coagulation, flocculation, clarification, and filtration to remove the oxides along with other water impurities. However, oxidized manganese often forms particles in the colloidal range which are not efficiently removed when applied directly to filtration media (Knocke et al., 1988). Therefore, research on membrane filtration as a viable method for removing oxidized manganese particulate has also been conducted (Suzuki et al., 1998; Rahman et al., 2000).

Sequestration of manganese is another limited used method of controlling manganese oxidation. The addition of polyphosphates or a combination of sodium silicate and chlorine has been shown to sequester the inorganic with various degrees of success. However, limited research has been found in developing this treatment method.

## 2.7 Adsorption and Oxidation of Mn onto Filter Media

The focus of this research is the adsorption of soluble manganese onto manganese oxide coated sand. The coating of manganese oxide adsorbs soluble manganese from water and, in the presence of an oxidant, these adsorbed Mn(II) are oxidized to solid Mn(IV) to create more available sites (Merkle et al., 1997). Various oxidizing agents can be used to change the oxidation state of Mn so that it can be removed from water. Table 2.2 shows the Mn oxidation reactions for oxidants typically used in drinking water treatment, listing ideal or theoretical stoichiometric ratio of oxidant to Mn for each reaction.

**Table 2.2:** Theoretical reaction stoichiometry for Mn(II)

Oxidant	Reaction	Stoichiometric ratio, mg oxidant : mg Mn metal
O <sub>2</sub>	$\text{Mn}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{MnO}_2(\text{s}) + 2\text{H}^+$	0.29 : 1
HOCl	$\text{Mn}^{2+} + \text{HOCl} + \text{H}_2\text{O} \Rightarrow \text{MnO}_2(\text{s}) + \text{Cl}^- + 3\text{H}^+$	1.30 : 1
MnO <sub>4</sub>	$3\text{Mn}^{2+} + 2 \text{KMnO}_4 + 2\text{H}_2\text{O} \Rightarrow 5 \text{MnO}_2(\text{s}) + 2\text{K}^+ + 4\text{H}^+$	1.92 : 1
O <sub>3</sub> (aq.)	$\text{Mn}^{2+} + \text{O}_3 + \text{H}_2\text{O} \Rightarrow \text{MnO}_2(\text{s}) + \text{O}_2 + 2\text{H}^+$	0.88 : 1
ClO <sub>2</sub>	$\text{Mn}^{2+} + 2\text{ClO}_2 + 2\text{H}_2\text{O} \Rightarrow \text{MnO}_2(\text{s}) + 2\text{ClO}_2^- + 4\text{H}^+$	2.45 : 1

*Source:* Adapted from Sommerfeld (1999)

The technology of manganese removal through sorption and oxidation on manganese greensand has been applied for decades, primarily in treating groundwater with elevated soluble manganese levels. Manganese oxide coatings formed on media acts

as good adsorbents for Mn and also play a role in its oxidation by autocatalysis (Kessick and Morgan, 1975; Eley et. al., 1993; AWWA, 1994; Merkle, et. al., 1997b; Zuravnsky, 2006; Subramaniam, 2010; Tasneem, 2010). Oxide-coated media (OCM) perform a dual function in the Mn removal process, permitting two modes of operation for soluble  $Mn^{2+}$  removal (Merkle et al., 1997b). In the intermittent regeneration (IR) mode, the filter media bed absorbs  $Mn^{2+}$  in the absence of a strong oxidant. Sorption capacity is periodically regenerated by application of oxidant (e.g., chlorine, potassium permanganate). In the continuous regeneration (CR) mode, oxidant is continuously supplied to oxidize the sorbed  $Mn^{2+}$  to insoluble  $MnOx(s)$  on the coated media surface, continuously regenerating sorption capacity and catalytic function. There are a number of parameters that affect the manganese removal performance of oxide coated media (OCM). Researchers have noted the significance of the type of oxidant applied, the pH of water applied to the bed, and the capacity of the media as related to the available surface sites on the oxide coating.

Knocke et al. (1988) analyzed the use of four different oxidants to promote manganese removal across the OCM filter bed. Oxidants were applied to the water prior to passage through the filter bed. Strong oxidants such as permanganate, chlorine dioxide, and ozone oxidized the soluble manganese almost immediately in the bulk solution. On the other hand, the addition of free chlorine prior to the filtration through OCM filter bed did not oxidize the manganese in the bulk solution. Instead, the majority of the manganese reaching the filter bed was in the soluble form. In this case, the removal mechanism was determined to be direct sorption of soluble manganese onto the media surface. The chlorine residual provided the necessary oxidant to regenerate the active adsorbent sites on the media. The capacity of the media in combination with the regenerative properties of the free chlorine caused the necessary manganese removal at both low and high loading rate conditions. The results indicated that the presence of free chlorine at a concentration of  $>1-2$  mg/l was sufficient for rapid soluble manganese removal (Knocke et al., 1988). The study revealed that continuous removal of manganese can occur with the application of free chlorine, while without free chlorine, the capacity of the media is eventually exhausted. Zuravnsky (2006) found a free chlorine concentration of greater than 1.0

mg/l was required for effective soluble Mn removal; furthermore, increased free chlorine concentrations generally improved the soluble Mn removal profile.

Knocke et al. (1991) used shallow bed depths (5-6 in) and high influent manganese concentrations (1.0 mg/l) to promote rapid exhaustion of the available sorption sites to evaluate the effects of the absence of chlorine on manganese removal. There was no evidence of auto oxidation found and no active sites were being regenerated without the presence of an oxidant. The media was found to start being exhausted (breakthrough point) after passing of 25 liter water without the presence of HOCl at pH = 7.8.

A number of studies have shown significant effects related to the pH of the applied water on oxide-coated filter media performance (Knocke et al., 1988; Knocke et al., 1990; Zuravnsky, 2006). In the absence of free chlorine, the effect of pH on the media capacity was observed and, the detrimental effects of an acidic pH on the media manganese adsorption capacity and the benefits of alkaline conditions for effective removal have been found. A slightly alkaline bulk solution pH (7.0-8.0) provided a greater percentage of soluble Mn removal across the contactor depth than a mildly acidic pH (6.3-6.7) (Zuravnsky, 2006). Research has been conducted to find the relationship between removal efficiency and the amount of extractable manganese oxide present on the media (Bouchard, 2005). The capacity of the media to remove manganese was found to increase as the extractable manganese oxide amount increased. In research, the correlation between extractable coating and manganese adsorption capacity has been evaluated more directly by Bouchard (2005).

Since the process of adsorption and oxidation adds layers of manganese oxide to the filter media grains, research was conducted to determine the effect of oxide coatings on the physical properties of the media. No significant changes in the physical size or density of the media (Knocke et al., 1990) were found, and therefore, no significant changes in the hydraulic properties in the media bed should be expected.

Zuravnsky (2006) investigated the effect of initial soluble Mn concentrations on the removal efficiency of OCM. Increasing the initial soluble Mn concentration was found to have a slightly positive effect on the soluble Mn removal profile. This is

because an increased soluble Mn concentration in solution provides a slightly larger driving force between bulk solution concentration and concentration at the surface of the media. The accumulation of Mn oxide coating is often found to be concentrated in the upper portions of the filter bed. This phenomenon has been observed in both operating utilities (Bouchard, 2005; ITN-BUET, 2011) and pilot-scale experiments (Hargette and Knocke, 2001).

### ***Factors affecting Manganese oxidation***

The oxidation and control of Mn 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 Fe and Mn is 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<sub>2</sub> is at least 10<sup>6</sup> times slower than that occurs for Fe(II) oxidation at circum-neutral pH (Martin, 2003). Only for pH > 8 does 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<sup>+</sup>. However, strong oxidizing agents 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 affects 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°C and a contact time of 10 mins at 1°C.

### ***Effect of alkalinity***

Stumm and Morgan (1981) stated that sorption capacities of Mn(II) increase at slightly alkaline solutions as low alkaline waters tend to dissolve minerals and metals. As indicated by Gaveland and Heertjes (1975) in his manganese oxidation rate equation, 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 oxidizable 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 be 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 dissolved oxygen, there is no significant dependence on concentration of dissolved 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 Fe(II), metal ions like copper 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 the 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).

## **2.8 Common Treatment Options for Removal of As from Water**

Several methods have been investigated for removal of arsenic, including reverse osmosis, ultrafiltration, electro-dialysis, ion exchange, adsorption, and chemical precipitation or adsorption by metal hydroxides (Huang and Vane, 1989). Because conventional treatment steps are already in place at many utilities, capital expenses can be minimized if arsenic can be removed using existing processes. The optimization of these conventional treatments has been studied by many sources. The most common treatment options include: (a) Iron coagulation; (b) Alum coagulation; (c) Softening; (d) Activated alumina filtration; and (e) Adsorptive filtration through a range of adsorbents.



## 2.9 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 the iron and manganese concentrations reported in the national hydro-chemical survey (BGS and DPHE, 2001) are very high, over ten times the permissible limits. Iron and manganese concentrations 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 on filter media and ability of these coatings in removing Mn and As from groundwater.

Among several Mn removal technologies, adsorption and oxidation of Mn on filter media has been found to be very effective. Several studies have been performed to investigate the simultaneous adsorptive removal of Mn and regeneration of the Mn oxide coating onto filter media by using strong oxidizing agent. However, some recent studies suggest that naturally present DO and other constituents (e.g., bicarbonate) in water could promote removal of Mn in a filter media (by sorption and oxidation) without the addition of an oxidant. This phenomenon needs to be investigated in more detail, through laboratory experiments.

## CHAPTER 3: METHODOLOGY

### 3.1 Introduction

In this study, oxidation of Mn(II) and formation of Mn oxide coatings on filter media was evaluated in an effort to better understand the processes of oxidation and removal of dissolved Mn(II) in filter media. The effectiveness of different Mn-oxide coated media (synthetic/prepared media, “green sand”) in removing Mn and As from water was also evaluated under different conditions. The Mn-oxide coated media used in this study included “prepared” and “synthetic media”, prepared in the laboratory and commercially available “green sand”. Bench-scale experiments were carried out to evaluate the process of Mn(II) oxidation and removal of Mn in filter media, and assess the efficiency of different Mn-coated media in removing Mn from groundwater under different conditions. This chapter describes the methodology followed for carrying out the laboratory studies.

### 3.2 Mn(II) Oxidation and Formation of Mn-oxide Coating on Filter Media

#### 3.2.1 *Effect of Dissolved Oxygen (DO) and Bicarbonate*

Column experiments were carried out to assess the effects of dissolved oxygen (DO), bicarbonate and initial Mn concentration on the oxidation/removal of Mn in “green sand” filter column at a pH of around 7. The objective of the experiment was to assess whether dissolved oxygen present in water could promote oxidation/removal of Mn (in the absence of any added oxidizing agent) in a filter media.

For evaluating the mechanism of Mn oxidation/removal in Mn coated filter media, influent water of varying composition (with respect to Mn and other parameters) were passed through a “green sand” filter column maintaining a specific flow rate and the effluent water was collected and analyzed for residual Mn. Filter beds were prepared with green sand using glass burette (50 ml) with a cross sectional area of  $1 \text{ cm}^2$ . The Fineness Modulus (FM) and unit weight of the green sand used as filter media were determined as 4.6 and  $2.33 \text{ g/cm}^3$  (measured from apparent specific gravity), respectively. Fractional pore volume (porosity) of green sand was measured as 0.44.

The initial average Mn-content of the “green sand” was determined after selectively leaching Mn from the sand media using hydroxylamine hydrochloride, following the method reported in Eley and Nicholson (1993), and was found to be about 14,400 mg Mn/kg green sand. Total depth of filter media in the filter column was 50 cm, consisting of top 48 cm green sand and bottom 2 cm gravel (to avoid clogging of burette outlet by finer particle).

The experimental setup consisted of a bucket and an acrylic glass column (cross-sectional area of  $26.4 \text{ cm}^2$  and depth 45 cm) for holding raw water, green sand filter beds in glass burette, a pump, collector buckets and flow control (manual valve) arrangements (see Figure 3.1). Raw influent water was first stored in a bucket and thereafter, it was pumped from the bucket to the acrylic glass column. A constant head of the influent water had to be maintained in the acrylic glass column (to maintain a fixed effluent flow rate of  $6 \text{ ml/min.cm}^2$ ), which was accomplished by providing an outlet point near the top (8 cm from top) of the acrylic glass column to flow out the excess influent water back to the raw water bucket. Influent water in acrylic glass column was allowed to flow by a pipe through the green sand column in glass burette with a constant flow rate. Effluent water was then collected in a collector bucket. It should be noted that the surface of the influent water stored in the bucket and acrylic glass column was in contact with atmosphere during experiment.

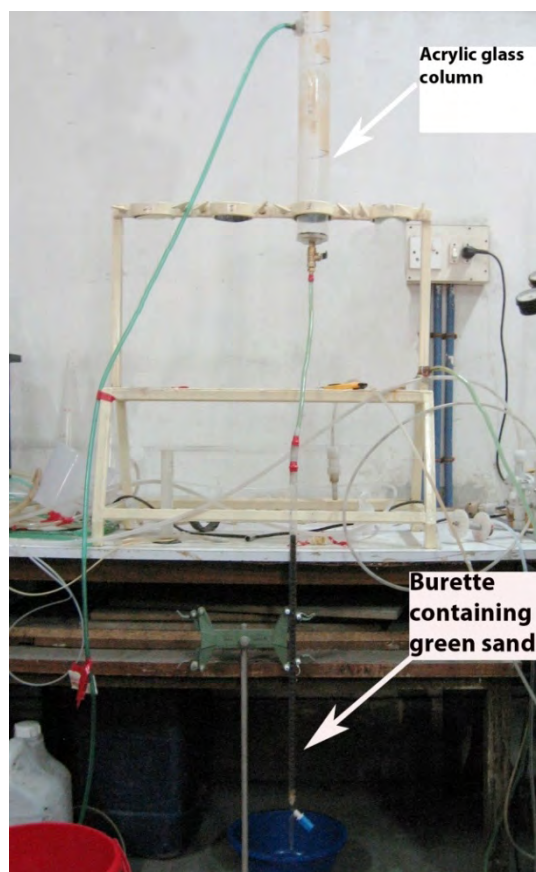
Column experiments were carried out to assess the effects of dissolved oxygen (DO) and bicarbonate on the removal of Mn in “green sand” filter column. Three types of influent water containing Mn(II) were passed through the filter column:

- (1) Influent water containing 0.01 M KCl (electrolyte), varying Mn concentration, and varying DO (dissolved oxygen);
- (2) Influent water containing 0.01 M KCl (electrolyte), varying Mn concentration; and
- (3) Influent water containing 0.01 M KCl (electrolyte), varying Mn concentration, and varying bicarbonate concentration.

For column experiments, deionized water containing 0.01 M KCl was prepared, which was spiked with Mn(II) and bicarbonate stock solutions to attain desired concentrations of Mn and bicarbonate concentration. Mn(II) stock solution was prepared by dissolving manganese salt  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in distilled water; while bicarbonate stock solution was being prepared using sodium bicarbonate ( $\text{NaHCO}_3$ ). Addition of bicarbonate increased pH of influent water above 8.0 which was adjusted to about 7.0 by adding dilute nitric acid. Influent Mn(II) concentration was varied from 7.21 mg/l to 10.24 mg/l; while bicarbonate concentration was varied from about 200 mg/l to 443 mg/l, which was estimated from measured alkalinity and pH.

To assess the effect of DO, experiments were carried out using influent water prepared from deionized water containing 0.01 M KCl and desired concentration of Mn. Argon gas was passed through this solution to drive off DO, and with continuous passage of argon, a DO level of about 2.0 mg/l could be maintained throughout the column experiment; the DO level could not be reduced below this value under the experimental conditions used in this study.

Influent water was passed through the prepared “green sand” column and surface overflow rate or flow rate (ml/min divided by x-area) was kept fixed at approximately 6 ml/min.cm<sup>2</sup>. pH was found to increase with filter run time for the influent water containing bicarbonate. Hence, pH was adjusted (nearly 7) by applying dilute nitric acid to the raw influent water (when required during the experiment); however, it did not decrease the applied bicarbonate concentration significantly (up to 5%). Effluent water sample was collected to determine Mn concentration; DO and pH of influent water were measured at different filter run times (up to 350 minutes). New “green sand” media was used for each individual column experiment.



**Figure 3.1:** Experimental set up for assessment of Mn oxidation and removal in a “green sand” column.

### 3.2.2 *Effect of Bicarbonate: Verifying the hypothesis for Mn(II) oxidation*

Experiments carried out in “green sand” columns (described in Section 3.2.1) in this study provided evidence for significant role of bicarbonate in oxidation/removal of Mn in Mn coated filter media. In order to verify the “hypothesis” [regarding role of bicarbonate on oxidation of Mn(II)], additional experiments were therefore carried out to evaluate the effect of bicarbonate (and also pH) on oxidation/removal of Mn. For evaluating the effects of bicarbonate ( $\text{HCO}_3^-$ ) and pH on oxidation/removal of Mn in filter media, experiments were carried out in filter columns prepared with Sylhet sand in acrylic glass columns with a cross sectional area of  $28.2 \text{ cm}^2$ ; depth of filter media was  $40 \text{ cm}$  (see Fig. 3. 2). The Sylhet sand used as media consisted of two size fractions; size fraction passing #20 sieve and retaining on #30 sieve, and fraction passing #30 sieve and retaining on #40 sieve in the ratio of 1:2. The fineness modulus (FM) and unit weight of the Sylhet sand size fractions used as filter media have been found to be 2.33 and  $1.31 \text{ g/cm}^3$ , respectively. It may be mentioned that FM and unit

weight of un-sieved Sylhet sand have been found to be 2.66 and 1.33 g/cm<sup>3</sup>, respectively. Initial Mn-content of the selected size fractions of Sylhet sand, determined after selective leaching with hydroxylamine hydrochloride (Eley and Nicholson, 1993), was found to be 5 mg Mn/kg; Mn-content of un-sieved Sylhet sand was found to be about 7 mg Mn/kg.



**Figure 3.2:** Experimental set up for assessment of effect of bicarbonate and pH on Mn oxidation and removal in a “Sylhet sand” column.

The experimental set ups consisted of Sylhet sand filter beds in acrylic glass column, a pump, buckets with tap for holding raw water, collector buckets and flow control (constant hydraulic head) arrangements (see Figure 3.2). Four types of influent water containing 2.5 mg/l Mn(II) and 0.01 M KCl were passed through the filter column:

- (1) Influent water containing no bicarbonate and pH 7.0± 0.2.
- (2) Influent water containing about 208.6 mg/l bicarbonate and pH 7.0± 0.2
- (3) Influent water containing no bicarbonate and pH 8.0± 0.2 and
- (4) Influent water containing about 245.2 mg/l bicarbonate and pH 8.0± 0.2

Influent water was passed through the filter columns maintaining a flow rate of 1.0 ml/min/cm<sup>2</sup>, and residual manganese concentration was measured at different time intervals; corresponding filter run time was also recorded. At the same time, manganese coating formed on the media was observed visually; Mn coating could be identified by the formation of dark colored coatings on the sand grains.

For these experiment deionized water containing 0.01 M KCl was prepared, which was spiked with Mn(II) and bicarbonate or only Mn(II). Mn(II) stock solution was prepared by dissolving manganese salt MnCl<sub>2</sub>·4H<sub>2</sub>O in deionized water with HNO<sub>3</sub> (5ml HNO<sub>3</sub> per liter); while bicarbonate stock solution was prepared using sodium bicarbonate (NaHCO<sub>3</sub>) and deionized water. The pH of influent water was adjusted to about 7.0 or 8.0 by adding dilute nitric acid (HNO<sub>3</sub>) or NaOH.

Efforts were made to characterize the manganese precipitates/ oxide phases on the filter media by X-ray Diffraction (XRD) and structural identification. The XRD analysis was out at the Bangladesh Atomic Energy Commission (BAEC).

### **3.3 Removal of Mn and As from Groundwater using Mn-oxide Coated Filter Media**

#### **3.3.1 Preparation of Manganese Oxide Coated Sand**

##### ***3.3.1.1 “Synthetic” Mn-oxide Coated media***

Synthetic Mn-oxide coated sand was prepared following the methods of Merkle et al. (1997), using Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and NaOH. The Sylhet sand used for preparation of Mn-oxide coated media consisted of two size fractions; size fraction passing #20 sieve and retaining on #30 sieve, and fraction passing #30 sieve and retaining on #40 sieve, mixed in the ratio of 1:2. The Fineness Modulus (FM) and unit weight of these mixed size fractions have been found to be 2.33 and 1.31 g/cm<sup>3</sup>, respectively.

For preparation of Mn-Oxide coated media, 100 gm of the selected sand was taken in a glass tray. Then 100 ml of Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Loba, India) solution, with Mn concentration of 10.5 g/l, was added to the tray and mixed thoroughly with the sand. Then 0.1N NaOH solution and 1:1 30% H<sub>2</sub>O<sub>2</sub> solution were added to the tray until the pH of the mixture was increased to about 9.0. During this process, the contents of

the tray were thoroughly mixed with glass rod. As the pH of the solution gradually decreased, 0.1N NaOH solution was added to the mixture two to three times, once every two hours, to raise the pH to about 9.0. The tray with its contents was then kept open to air. During the next two days 0.1N NaOH was added to the tray once every day to raise the pH to about 9.0. The above process (starting from the addition of 100 ml  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution to the tray to pH adjustment by addition of 0.1N NaOH once a day) was then repeated twice.



**Figure 3.3:** Synthetic Mn-oxide coated media in a glass tray

The sand in the tray was then kept open to the air for drying for about a month; the contents of the tray were stirred with a glass rod occasionally. The sand was then washed, first two to three times with groundwater adjusted to pH 9.0, then a few times with groundwater, and finally a few times with deionized water. The Mn-oxide coated sand was then air dried. The Mn content of the prepared sand was then determined after selective leaching with hydroxylamine hydrochloride (Eley and Nicholson, 1993), and was found to be about 25,250 mg Mn/kg. Figure 3.3 shows the “synthetic” Mn-coated sand media in a glass tray.

### 3.3.1.2 “Prepared” Mn-oxide Coated media

Assessment of selected community Fe-As removal plants (carried out as a part of this study; see Appendix B for details) revealed that Mn-oxide coating could form on filter (sand) media during passage of groundwater containing Mn. Efforts were therefore



made to prepare Mn-oxide coated sand in the laboratory by allowing Mn(II) bearing groundwater to flow through filter columns made of Sylhet sand. Filter beds were prepared with locally available “Sylhet sand” in glass burettes (column height 43 cm) with a cross sectional area of  $1 \text{ cm}^2$ . The specifications of Sylhet sand used as media are the same as those used for column experiments described in Section 3.2.2.

The experimental set ups consisted of sand filter beds in burettes, buckets with tap for holding raw water, collector buckets and flow control (manual) arrangements (see Figure 3.4). Concentrated HCl (37%) was first diluted with deionized water (at the ratio of 1:5 by volume) and then used for washing one set of sand bed column in order to assess the effect of pre-washing on formation of manganese oxide coating.



**Figure 3.4:** Experimental set up for preparation of Mn-oxide coated sand (referred to here as “prepared” Mn-oxide coated media)

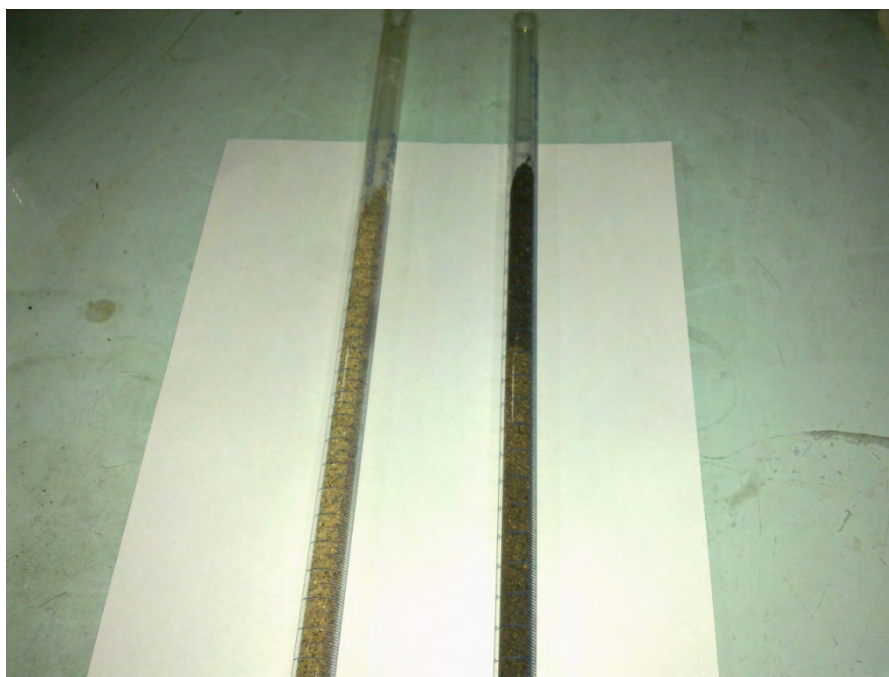
Influent water with known concentrations of manganese was passed through the filter columns and residual manganese concentration was measured at different time intervals. Manganese concentration in the influent water was varied from 0.5 mg/l to 5.0 mg/l, and flow rate was fixed at  $1 \text{ ml/min/cm}^2$ . Groundwater, collected from a

deep tubewell pump station at BUET with manganese concentration of around 0.022 mg/l, was spiked with Mn(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 was close to the pH of natural groundwater,  $7 \pm 0.1$ . Table 3.1 provides a detailed characterization of groundwater used in the experiments.

**Table 3.1:** Characteristics of groundwater used in laboratory experiments

Parameter	Unit	Concentration
pH	--	$7 \pm 0.1$
Alkalinity as $\text{CaCO}_3$	mg/l	216
Carbon dioxide	mg/l	71
DO	mg/l	3.32 at $28^\circ\text{C}$
Hardness as $\text{CaCO}_3$	mg/l	256
Chloride ( $\text{Cl}^-$ )	mg/l	55
Iron (Fe)	mg/l	0.01
Manganese (Mn)	mg/l	0.022
Arsenic (As)	mg/l	$< 0.001$

The column experiments were continued for up to 220 hours, until the Mn concentration in the effluent water became negligible. At the same time, manganese oxide coating formed on the media was observed visually; as noted earlier Mn-oxide coating could be identified by the formation of dark colored coatings on the sand grains (see Fig. 3.5). After the completion of experiment, Mn contents of the media were determined by selectively leaching Mn from the media using hydroxylamine hydrochloride. The average Mn content of the media (i.e., sand) expressed as mg Mn/kg sand varied from about 149 mg Mn/kg sand (for the column with initial Mn = 0.5 mg/l) to 1384 mg Mn/kg sand (for the column with initial Mn = 5.0 mg/l). This Mn-oxide coated sand obtained by passing Mn bearing influent water through Sylhet sand filter column has been referred to as “prepared Mn-coated media”.



**Figure 3.5:** Manganese oxide coating formed on sand and particles turning them dark (right column); left column showing initial condition of column

### 3.3.2 Removal of Mn and As in Mn-oxide Coated Media

#### 3.3.2.1 Mn Removal in Filter Columns

Removal of both Mn and As in three different Mn-oxide coated media (i.e., “prepared” media, synthetic media, and “green sand”) was evaluated by passing groundwater with known concentrations of Mn and/or As through a filter bed made of these media (in acrylic glass columns) and measuring the residual concentrations (after 90, 120 and 150 minutes of filter run time). The filter beds were set in transparent acrylic glass filter column with cross-sectional area of  $28.2 \text{ cm}^2$  (for “prepared” media and “synthetic” media) or  $26.5 \text{ cm}^2$  (for “green sand”), fitted with flow control arrangements. Figure 3.6 shows the experimental set up for assessment of the performance of different Mn-oxide coated media in removing Mn and As from groundwater.

For the “prepared Mn-oxide coated media”, the total depth of filter media in the column was 40 cm; the “prepared media” consisted of the top 5 to 6 cm (approximately) of the column, while Sylhet sand consisted of the rest of the column. The Sylhet sand used as media consisted of two size fractions; size fraction passing

#20 sieve and retaining on #30 sieve, and fraction passing #30 sieve and retaining on #40 sieve in the ratio of 1:2. The initial average Mn-content of the “prepared Mn-oxide coated media” was estimated to be about 1480 mg Mn/kg of media. However, Mn-content of the top portion (about top 1 cm) of the media was much higher, about 7550 mg Mn/kg of media. As noted earlier, average Mn-content of the selected Sylhet sand fractions was 5 mg Mn/kg sand.



**Figure 3.6:** Experimental set up for assessing performance of different Mn-coated media in removing Mn and As from groundwater; from left to right: (a) “prepared” Mn-oxide coated media; (b) Green Sand (20 cm; Column 2); (c) Synthetic Mn-coated sand media

For the “synthetic Mn-oxide coated media”, total depth of media in the filter column was 40 cm; top 6 cm (approximately) consisting of the “synthetic media” and bottom 30 cm consisting of Sylhet sand (of same specification as noted above). As noted above, the Mn-content of the “synthetic media” was 25,250 mg Mn/kg of media.

For “green sand”, the total depth of filter media in the filter columns was 40 cm, consisting of “green sand” and Sylhet sand (of same specification noted above). The F.M. of “green sand” and Sylhet sand used as filter media have been found to be 4.60 and 2.33, respectively. The depths of “green sand” and Sylhet sand media were varied as follows: (i) Column 1: top 10 cm “green sand”, bottom 30 cm Sylhet sand; (ii) Column 2: top 20 cm “green sand”, bottom 20 cm Sylhet sand; (iii) Column 3: top 30 cm “green sand”, bottom 10 cm Sylhet sand. The initial average Mn-content of the “green sand” was found to be about 14,400 mg Mn/kg Green Sand.

For assessment of removal efficiency, manganese concentration in the influent water (prepared as described earlier in Section 3.3.1.2) was varied from 0.5 to 10.0 mg/l; while arsenic concentration was varied from 100 to 1,000 µg/l. No effort was made to adjust the pH of the influent water; pH of influent water was close to the pH of natural groundwater,  $7 \pm 0.1$ . However, during the experiment the pH of the influent water gradually increased to about 7.55 due to gradual release/escape of  $\text{CO}_2$  from groundwater (used for preparing the influent water). Apart from initial Mn and As concentrations, effects of a number of water quality parameters and process variables on removal was evaluated. The surface overflow rate through the filter media was varied from 0.5 to 8.0 ml/min/cm<sup>2</sup> (i.e., flow rate through the filter column was varied from 14.1 ml/min to 225.6 ml/min) to assess its impact on removal of Mn.

Removal of As (by adsorption) is known to be influenced by pH and presence of competing anions (e.g., phosphate). In this study, effect of pH, phosphate and bicarbonate (alkalinity) on removal of As was therefore evaluated by varying these parameters in the influent water. In these experiments, flow rate was maintained at 1 ml/cm<sup>2</sup>/min, alkalinity of influent water was varied from 50 to 410 mg/l (as  $\text{CaCO}_3$ ), and phosphate concentration was varied from 1 to 10 mg/l. For varying alkalinity in the influent water, natural groundwater with an alkalinity of 216 mg/l (as  $\text{CaCO}_3$ ) was either diluted with deionized water, or amended with  $\text{NaHCO}_3$  solution to increase or decrease alkalinity of influent water. Both pH and alkalinity of influent water was measured. However, addition of  $\text{NaHCO}_3$  caused an increase in the pH of influent water.

### 3.3.2.2 Batch Experiments

Batch experiments were conducted to estimate the isotherm constants for describing adsorption of Mn on Mn-oxide coated media (“prepared media”, “synthetic media” and green sand) and Sylhet sand. Freundlich isotherm constants ( $K$ ,  $n$ ) were calculated using data from batch experiments in which Mn uptake of different adsorbent at pH of  $7.2 \pm 0.1$  and temperature of  $26.6 - 27.4^\circ\text{C}$  was measured. Several airtight containers (50 ml) containing groundwater with different initial Mn concentrations (3.40-12.9 mg/l) were prepared; to each container a different mass (0.2-6.0 gm) of adsorbent (i.e., Mn-oxide coated media or Sylhet sand) was added. The suspensions were then continuously rotated (for up to 52 hours) using a tilted rotator (shown in Figure 3.7), allowed to equilibrate and filtered with filter paper (0.20  $\mu\text{m}$ ). For each set of experiment, three tests were conducted with equilibration time of 48, 50 and 52 hours. At the end of specific equilibration time, concentration of Mn in the filtrate was measured. The Mn uptake capacity ( $q$ ) was calculated as shown in Equation 3.1. The results (data tabulated in Appendix A) were used to determine Freundlich isotherm constants for the different adsorbents. The equation for a linear trend line fitted to this plot is analogous to the linearized form of the Freundlich isotherm equation (Equation 3.2), which allows the values of  $K$  and  $n$  to be determined. Freundlich Isotherm constants were verified by plotting the isotherm relationship along with the experimental data.

$$q = \frac{V(C_i - C_f)}{M} \quad (3.1)$$

$$\ln(q) = \ln(K) + (1/n) \ln(C_f) \quad (3.2)$$

where:

$C_i$  = Initial soluble Mn concentration (mg/l)

$C_f$  = Final soluble Mn concentration (mg/l)

$M$  = Mass of media (green sand) in column (gm)

$q$  = Mn uptake capacity of media (mg Mn/gm media)

$V$  = Volume of solution in reservoir (l)



**Figure 3.7:** Tilted rotator used for batch experiment to determine Mn uptake capacity of green sand media

### **3.4 Batch Experiments to Estimate Leaching of Mn from Mn-oxide coated Media**

#### **3.4.1 Effects of pH**

A 50 ml airtight polypropylene tube (headspace-free) was filled with groundwater, collected from a deep tubewell pump station at BUET with manganese concentration of around 0.022 mg/l. Characteristics of groundwater used in the experiments is presented in Table 3.1. Initial DO, pH and temperature of the water were 5.06, 6.88 and 27.2°C, respectively. 0.5 g of greensand (with 14,400 mg/kg of Mn), or 0.2 g of “prepared” Mn coated sand (with 11,200 mg/kg of Mn), or 0.2 g of “synthetic” Mn coated sand (with 25,250 mg/kg of Mn) were added to the tubes, and the solutions were mixed several times by manual shaking. In these experiments, pH was varied from about 4.0 to 10.0 by addition of acid or base, in order to assess leaching/release of Mn from Mn-oxide coated sand at different pH conditions. After 24 hours pH was measured, and the suspension was filtered through a 0.2 µm disk filter and analyzed for Mn content.

#### **3.4.2 Effects of Anoxic Condition**

A 50 ml airtight polypropylene tube was filled with groundwater collected from a deep tubewell pump station at BUET. The groundwater was spiked with 1 g/l of

glucose ( $C_6H_{12}O_6$ ) and seeded with aerated domestic sewage. The mixture was aerated by air diffuser and TC count of the solution was found to be  $4 \times 10^6$  cfu/100 ml of water. Initial DO, pH and temperature of the solution are 6.65, 7.53 and  $26.5^\circ C$ , respectively. Fixed amounts of different types of Mn-oxide coated sand were added to these tubes; 1.0 g of greensand (14,400 mg/kg of Mn), or 0.5 g of prepared Mn coated sand (11,200 mg/kg of Mn), or 0.5 g of synthetic Mn coated sand (25,250 mg/kg of Mn) were added and the solutions were mixed several times by manual shaking. One set of experiment was performed without addition of Mn coated sand. After 120 hours of equilibration time, pH and DO were measured. The suspension was filtered through a  $0.2\mu m$  disk filter and analyzed for Mn content.

### 3.5 Reagents and Analytical Methods

All chemicals used in this work were of reagent grade. Mn(II) stock solution was prepared by dissolving its manganese salt  $MnCl_2 \cdot 4H_2O$  in distilled water. Fe(II) stock solution was prepared by dissolving ferrous sulphate ( $FeSO_4 \cdot 7H_2O$ ) in distilled water. As(III) stock solution was prepared by dissolving arsenic trioxide ( $As_2O_3$ ) in distilled water containing sodium hydroxide (NaOH). Bicarbonate and phosphate stock solutions were prepared using sodium bicarbonate ( $NaHCO_3$ ) and di-sodium hydrogen phosphate ( $Na_2HPO_4$ ), respectively.

Groundwater used in all batch experiments was collected from a deep tubewell pump at B UET. The groundwater samples were analyzed periodically for detailed characterization during the course of the study. The pH of water samples was measured using a pH meter (WTW, Model: 82362, Germany). DO was measured using a DO meter (WTW, Model: 82318). Samples collected for soluble Mn concentration determination were acidified with the addition of 32.5% concentrated nitric acid for sample preservation. Manganese and iron concentrations were measured using Flame-AAS (Shimadzu, Model: AA-6800), while As concentration was measured using GF-AAS (Shimadzu, Model: AA-7000). All other water quality parameters were measured following the Standard Method (AWWA, APHA).



## CHAPTER 4: RESULTS AND DISCUSSION

### 4.1 Introduction

The overall objectives of this work were to characterize the mechanisms of Mn(II) oxidation and removal in filter media and to evaluate the effectiveness of Mn and As removal in Mn-oxide coated filter media. The specific objectives included: (a) Evaluation of Mn(II) oxidation and formation of Mn-oxide coatings on sand particles in a filter bed through which Mn-bearing water is passing; (b) Evaluation of the effectiveness of different Mn-oxide coated media (synthetic/prepared media, “green sand”) in removing Mn and As from water, including effects of various water quality parameters (i.e. initial concentrations, pH, bicarbonate, phosphate); (c) Evaluation of the effect of process variables (e.g., depth of media, flow rate, contact time) and media characteristics on removal of Mn and As; (d) Assessment of possible leaching of Mn from Mn-rich media under low pH, and anoxic conditions.

This chapter presents the results of laboratory investigations carried out in the present study. It presents an assessment of the process of Mn(II) oxidation and formation of Mn-oxide coating on filter media. This chapter also presents an assessment of the efficiency of different Mn-oxide coated filter media in removing Mn and As from groundwater. Possible leaching of Mn from Mn-oxide coated media is also discussed.

### 4.2 Mn(II) Oxidation and Formation of Mn-oxide Coating on Filter Media

#### 4.2.1 *Effect of Dissolved Oxygen (DO) and Bicarbonate*

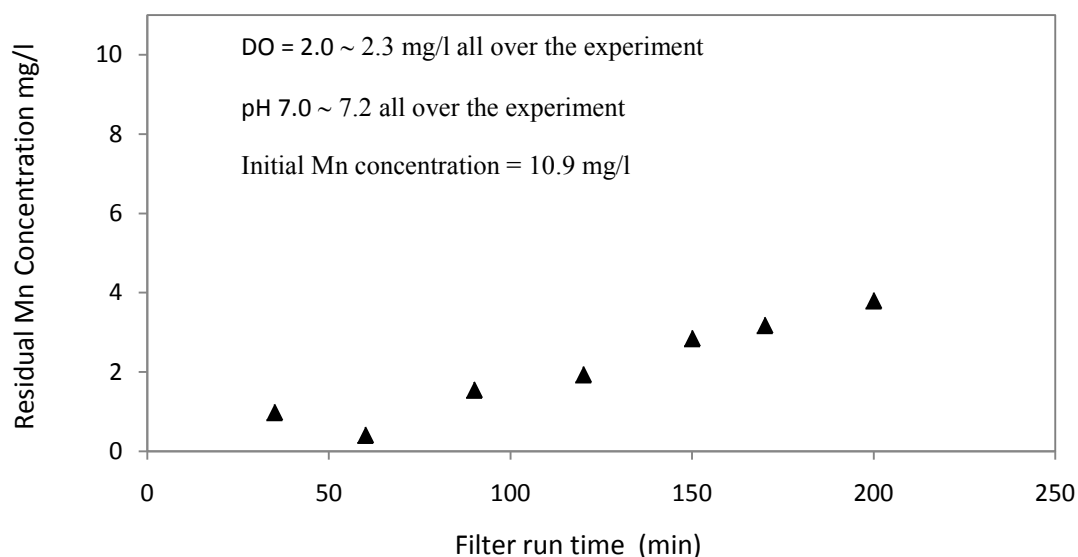
Several studies (Merkle et al., 1997; Zuravnsky, 2006; Subramaniam, 2010; Bierlein, 2012) have been performed on Mn removal by filtration through Mn-oxide coated media where strong oxidizing agents (e.g.,  $\text{KMnO}_4$ ,  $\text{H}_2\text{OCl}_2$ ) have been used to regenerate the Mn-oxide coating by oxidizing the adsorbed Mn. However, results obtained in this study (presented below) show that formations of Mn-oxide coating (indicating the oxidation of adsorbed Mn) on filter media are possible without addition of any oxidizing agent. For evaluating the mechanism of Mn oxidation and removal in Mn-oxide coated filter media, column experiments have been carried out

in this study, specifically focusing on the effects of DO and bicarbonate ( $\text{HCO}_3^-$ ) on Mn removal. The DO could potentially serve as an oxidizing agent for Mn oxidation; from stoichiometric consideration, 0.29 mg/l of  $\text{O}_2$  is required to oxidize 1 mg/l of Mn. Bicarbonate has been reported to catalyze Mn oxidation (Kozlov et al., 2004; Tang et al., 2009). Filter columns prepared with greens and were used for these column experiments.

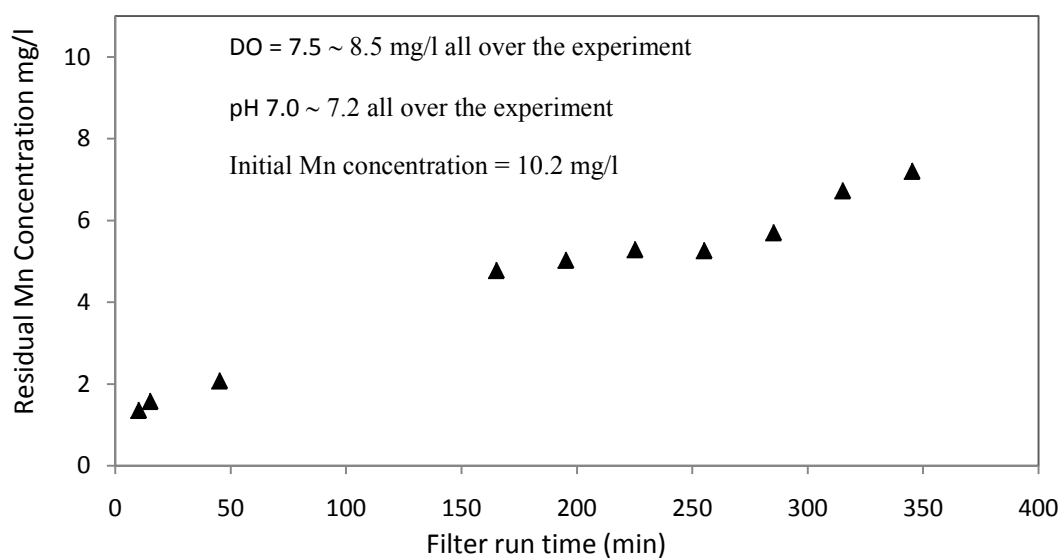
#### ***Effect of Dissolved Oxygen (DO):***

Figure 4.1 and Figure 4.2 show the removal of Mn in green sand filter column under similar conditions, with the exception of DO concentration in influent water. These two sets of experiments were carried out to assess the effect of DO on removal of Mn in the filter media. The figures also show concentrations of Mn, DO and pH of influent water as a function of filter run time. Figure 4.1 shows that effluent Mn concentration increased gradually from nearly 4% (i.e., about 0.44 mg/l at 60 minutes of filter run time) to nearly 35% of influent Mn concentration (i.e., about 3.82 mg/l at 200 minutes of filter run time), indicating significant decrease in removal efficiency and possibly indicating an approach toward the breakthrough point (i.e., where influent and effluent Mn concentration would be the same). The influent pH, DO and Mn concentration remained more or less unchanged throughout the experiment.

Figure 4.2 shows results of column experiments under similar conditions, except at a higher DO concentration of the influent water. Fig. 4.2 shows effluent Mn concentration increased gradually from nearly 13% (i.e., about 1.33 mg/l at 10 minutes of filter run time) to nearly 71% of influent Mn concentration (i.e., about 7.24 mg/l at 350 minutes of filter run time). Figure 4.2 shows a trend of Mn removal similar to those observed in Fig. 4.1; Mn removal efficiency decreases with increasing filter run time, and the system appears to approach a breakthrough point. The influent pH, DO and Mn concentration did not change significantly during the course of the experiment. Thus, DO does not appear to have a significant influence on removal of Mn in the filter media.



**Figure 4.1:** Effluent Mn concentration as a function of filter run time in column experiment carried out with reduced DO ( $\sim 2\text{mg/l}$ ) [influent water prepared with deionized water containing 0.01 M KCl and 10.9 mg/l Mn(II); hydraulic loading rate,  $\text{HLR} = 6 \text{ ml/min.cm}^2$ , Temp= $28^\circ\text{C}$ ]

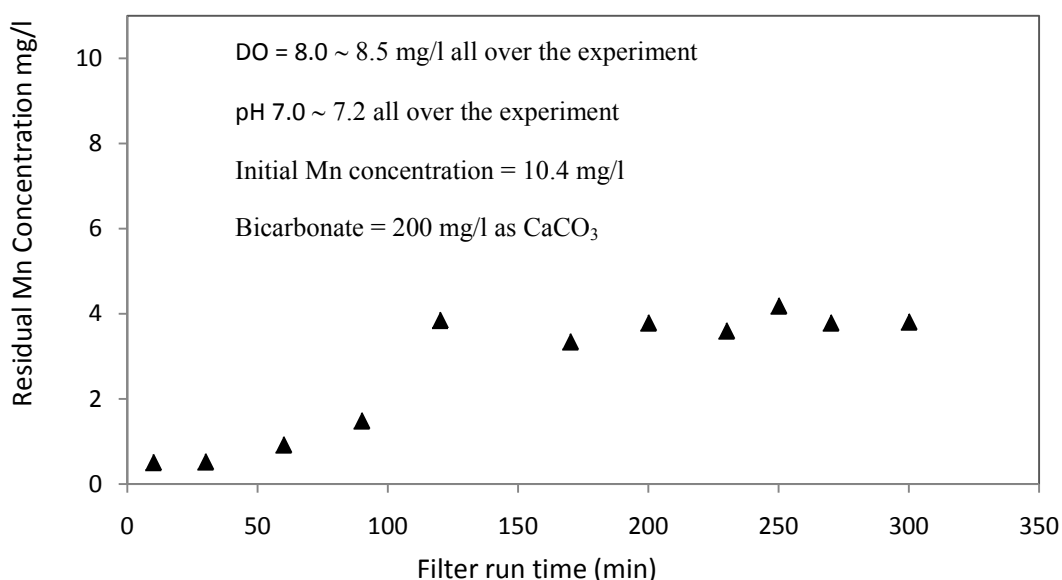


**Figure 4.2:** Effluent Mn concentration as a function of filter run time in column experiment carried out with higher DO ( $\sim 8 \text{ mg/l}$ ) [influent water prepared with deionized water containing 0.01 M KCl and 10.2 mg/l Mn(II); hydraulic loading rate,  $\text{HLR} = 6 \text{ ml/min.cm}^2$ , Temp= $28^\circ\text{C}$ ]

Both Fig. 4.1 and Fig. 4.2 show that the system approaches the breakthrough point as filter run time increases. This indicates that the removal of Mn is characterized by adsorption, and the removal capacity decreases as the adsorption sites on the media are exhausted with increasing filter run time. These figures also indicate absence of regeneration of Mn-oxide coating on the filter media (e.g., by oxidation of adsorbed Mn on filter media); such regeneration would increase Mn removal by continuously creating new adsorption sites, which is not apparent from the experimental results. Thus, it appears that DO alone cannot regenerate the media by oxidizing Mn(II) under experimental condition applied in this study.

### ***Effect of Bicarbonate:***

As discussed in Chapter 2, bicarbonate can play a role in catalyzing the oxidation of Mn. Bicarbonate could also promote formation of  $\text{MnCO}_3(\text{s})$  solids within the filter media, which would also promote removal of Mn by precipitation (and possibly by creating additional adsorption sites). In order to evaluate these possible mechanisms, column experiments were conducted under conditions similar to those discussed above, but with addition of bicarbonate in the influent water. Figure 4.3 shows removal of Mn in the green sand filter column as a function of filter run time in the presence of 200 mg/l bicarbonate. It shows that effluent Mn concentration gradually increased up to 38% of influent Mn concentration (after 120 minutes of filter run time), but thereafter it did not increase further during the remaining filter run time (up to 300 minutes), showing possible stabilization of effluent Mn concentration (equilibrium condition).



**Figure 4.3:** Effluent Mn concentration as a function of filter run time in the presence of bicarbonate in influent water [ influent water prepared with de ionized water containing 0.01 M KCl, 10.4 mg/l Mn(II), and 200 mg/l bicarbonate; hydraulic flow rate, HLR= 6 ml/min.cm<sup>2</sup>, Temp=28 °C, influent water DO ~8.0 mg/l]

Comparing the results of two similar experiments presented in Figure 4.2 (without bicarbonate in influent water) and Figure 4.3 (with bicarbonate in influent water), it is obvious that Mn removal efficiency is increased in the presence of bicarbonate and the system does not approach the breakthrough point. There are two possible reasons for this phenomenon:

- (1) Possible surface mediated oxidation ( at the surfaces of Mn-oxide coated filter media) of adsorbed Mn by DO in the presence of bicarbonate, which produces insoluble Mn-oxide and regenerates the exhausted media.
- (2) Possible formation of insoluble  $\text{MnCO}_3(\text{s})$  in the presence of bicarbonate which increases removal efficiency by removing Mn within the filter media by precipitation.

To investigate the dominant mechanism among these two possible mechanisms, efforts were made to invoke fundamental concept of solid precipitation and dissolution. Equation 4.1 and Equation 4.2 show formation/dissolution of  $\text{MnCO}_3(\text{s})$  and the mass law expression for formation/dissolution of  $\text{MnCO}_3(\text{s})$ . Equation 4.2 shows that at equilibrium, the product of the molar concentrations of  $\text{Mn}^{+2}$  and  $\text{CO}_3^{-2}$  ions will always be equal to the solubility product,  $K_{sp}$ . If precipitation of  $\text{MnCO}_3(\text{s})$  is the dominant mechanism in presence of bicarbonate, then the change in aqueous concentration of any one of the ions ( $\text{Mn}^{+2}$  and  $\text{CO}_3^{-2}$ ) would cause change in the concentration of the other ion accordingly so that the value of  $K_{sp}$  remains constant.



$$K_{sp} = [\text{Mn}^{+2}] [\text{CO}_3^{-2}] = [\text{Mn}^{+2}] [\alpha_2 C_T] \quad (4.2)$$

where:

$[\text{Mn}^{+2}]$  = molar concentration of  $\text{Mn}^{+2}$  ion in equilibrium

$[\text{CO}_3^{-2}]$  = molar concentration of  $\text{CO}_3^{-2}$  ion in equilibrium

$K_{sp}$  = solubility product

$\alpha_2$  = distribution coefficient, is a function of pH only

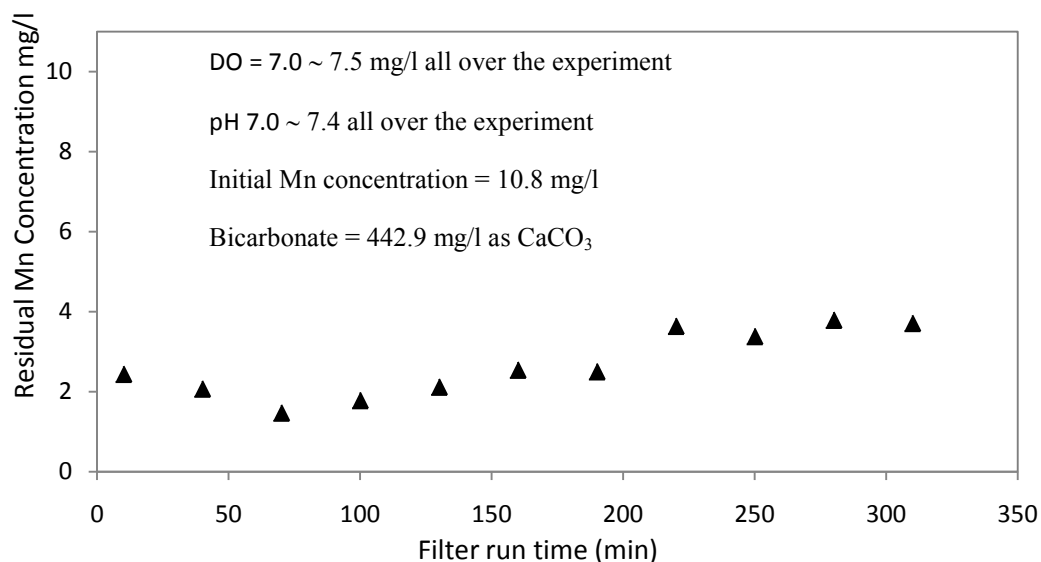
$C_T$  = Total concentration of dissolved inorganic carbon =  $[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{-2}]$

According to Equation 4.2, if bicarbonate concentration is increased at a particular pH (i.e., by changing the total concentration of inorganic carbon,  $C_T$ , in water), more  $\text{CO}_3^{2-}$  will be available in solution, and a lower concentration of  $\text{Mn}^{2+}$  would cause precipitation of  $\text{MnCO}_3(\text{s})$ .

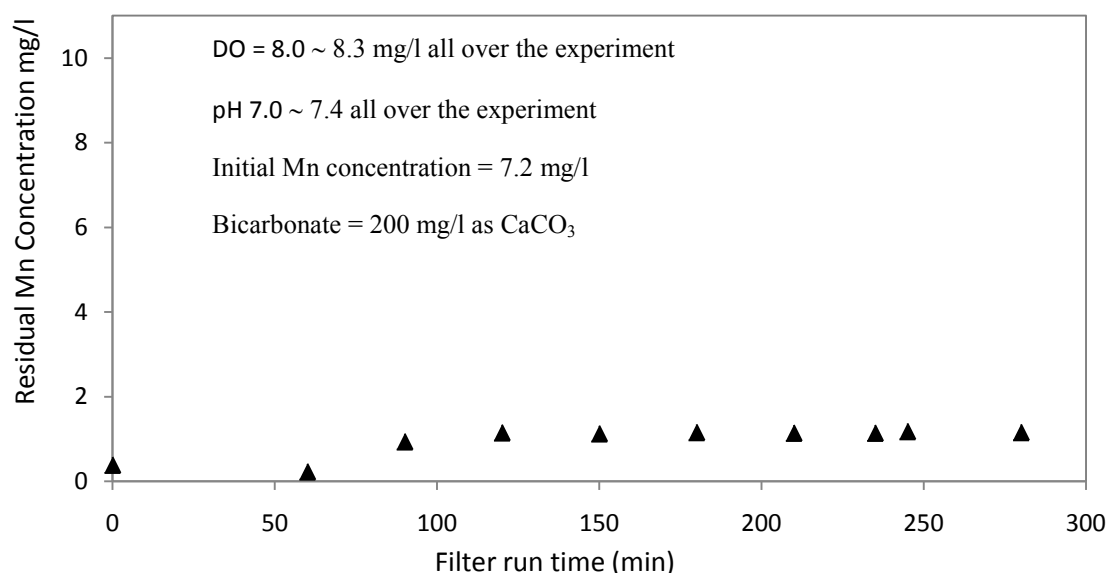
To investigate this, two sets of experiments were conducted; one with increased bicarbonate concentration (442.9 mg/l) and the other with decreased influent Mn concentration (7.21 mg/l), keeping the other water quality and operational parameters (e.g., flow rate) unchanged.

Figure 4.4 shows effluent Mn concentration as a function of filter run time for the column experiment with an increased bicarbonate concentration of 442.9 mg/l and initial Mn(II) concentration of 10.8 mg/l. Therefore, Fig. 4.3 and Fig. 4.4 show removal of Mn under similar conditions, except for the difference in bicarbonate concentration. Figure 4.4 shows that effluent Mn concentration increases gradually from nearly 1.5 mg/l (at 70 minutes of filter run time) to nearly 4 mg/l (at 220 minutes of filter run time), where it gets stable and does not increase further during the rest of the filter run time (up to 320 minutes), indicating an equilibrium condition. If  $\text{MnCO}_3(\text{s})$  precipitation was the dominant mechanism then according to Equation 4.2, effluent Mn concentration would have been lower in this experiment than that of the experiment corresponding to Figure 4.3, since higher bicarbonate concentration (and hence  $C_T$ ) had been used in this experiment.

Figure 4.5 shows results of a similar experiment where Mn(II) and bicarbonate concentration in the influent water were 7.2 mg/l and 200 mg/l, respectively. As shown in Figure 4.5, effluent Mn concentration increases up to 1 mg/l (at filter run time of 100 minutes) and thereafter, and does not increase further during the rest of filter run time (up to 280 minutes), indicating an equilibrium condition. If  $\text{MnCO}_3(\text{s})$  precipitation was the dominant mechanism then according to Equation 4.2, effluent Mn concentration at equilibrium would have been similar to that of the experiment corresponding to Figure 4.3, since in both of these experiments bicarbonate concentration (and hence,  $C_T$ ) was similar. On the other hand, this experimental result agrees well with the concept of surface mediated oxidation of adsorbed Mn by DO in the presence of bicarbonate, since under continuous regeneration and adsorption, equilibrium concentration of adsorbate (i.e., Mn) is proportional to its initial concentration.



**Figure 4.4:** Effluent Mn removal as a function of filter run time in the presence of bicarbonate in influent water [influent water prepared with deionized water containing 0.01 M KCl, 10.8 mg/l Mn(II), and 442.9 mg/l bicarbonate; hydraulic flow rate, HLR= 6 ml/min.cm<sup>2</sup>, Temp=28 °C, influent water DO~8.0 mg/l]



**Figure 4.5:** Effluent Mn concentration as a function of filter run time in the presence of bicarbonate in influent water [influent water prepared with deionized water containing 0.01 M KCl, 7.2 mg/l Mn(II), and 200 mg/l bicarbonate; hydraulic flow rate, HLR= 6 ml/min.cm<sup>2</sup>, Temp=28 °C, influent water DO~8.0 mg/l]



Analysis of the results shown in Figures 4.3 through Figure 4.5 suggest that the possible dominant mechanism for the removal of Mn(II) is continuous regeneration of Mn-oxide coated media (caused by the surface mediated oxidation of adsorbed Mn by DO in the presence of bicarbonate), rather than  $\text{MnCO}_3(\text{s})$  precipitation. This result is supported by the findings of a previous study (Kozlov et. al., 2004; Tang et. al., 2009) which shows that Mn(II) oxidation is favored in the presence of bicarbonate in water. Tang et.al. (2009) investigated the effect of bicarbonate on the binding and oxidation of divalent manganese in bacterial reaction centers and revealed that bicarbonate is able to facilitate the binding and oxidation of the manganese (II) ion between pH 6 and 8 in center where the tight binding in their absence could not otherwise be established.

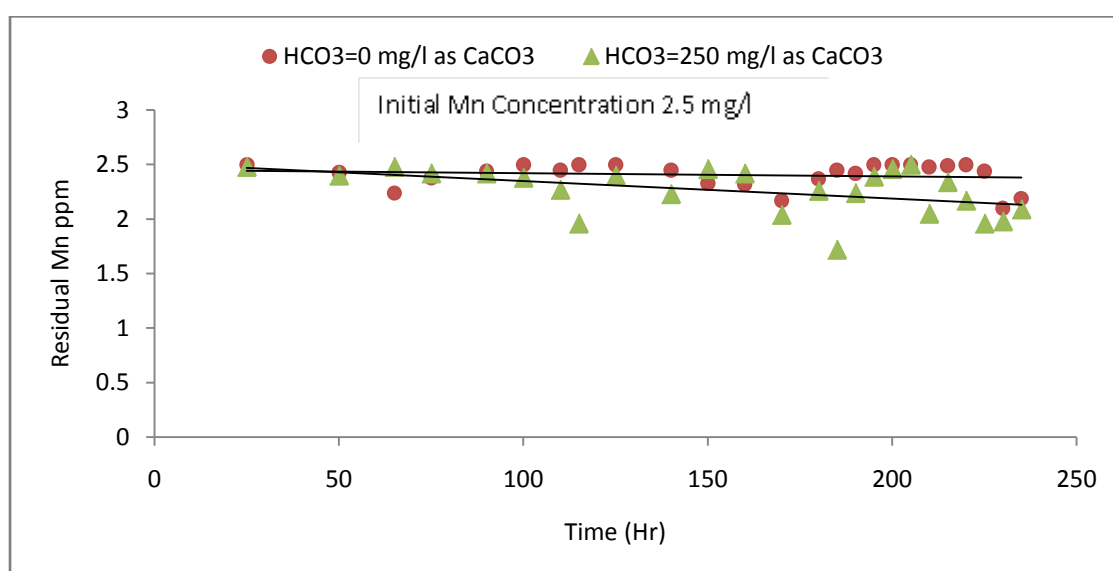
Thus, the dominant mechanism of Mn removal in granular filter media (sand) appears to be adsorption of dissolved Mn(II) onto the filter media, followed by oxidation of Mn(II) to Mn(IV) by dissolved oxygen (DO) in the presence of bicarbonate ion. This process appears to create and regenerate the Mn-oxide coating on the filter media (sand) and regenerates/ increases adsorption capacity of the media. It should be noted that the XRD analysis, carried out as a part of this study, did not provide any useful information regarding the mineral phases of Mn formed on the filter media.

#### ***4.2.2 Effect of Bicarbonate: Verifying the hypothesis for Mn(II) oxidation***

Experiments carried out in “green sand” columns (described in Section 4.2.1) suggest that bicarbonate plays an important role in oxidation/removal of Mn in Mn-coated filter media. In order to confirm the “hypothesis” [regarding role of bicarbonate on oxidation of Mn(II)], additional experiments were therefore carried out to evaluate the effect of bicarbonate ( and also pH ) on oxidation/removal of Mn ( as described in Section 3.2.1) . In these experiments, Mn(II) bearing water, with or without bicarbonate, was passed through a filter column made of Sylhet sand, and residual Mn concentrations were measured.

Figure 4.6 shows residual Mn concentration as a function of filter run time for experiments carried out with initial Mn concentration of 2.5 mg /l; the pH of the influent water was maintained at  $7.0 \pm 0.2$ . It shows that Mn removal by fresh filter

media prepared with Sylhet sand (with very little initial Mn content) was insignificant for in fluent water without bicarbonate. On the other hand, a appreciable Mn was removed from the water with bicarbonate concentration of about 209 mg/l; the Mn removal appears to increase with filter run time. This possibly suggests a process involving adsorption of Mn(II) onto filter media, followed by oxidation of Mn(II) in the presence of bicarbonate, creating/regenerating Mn-oxide coating, thus increasing Mn removal capacity of the media. Figure 4.6 provides strong evidence of the effect of bicarbonate on the oxidation and removal of Mn in filter media.

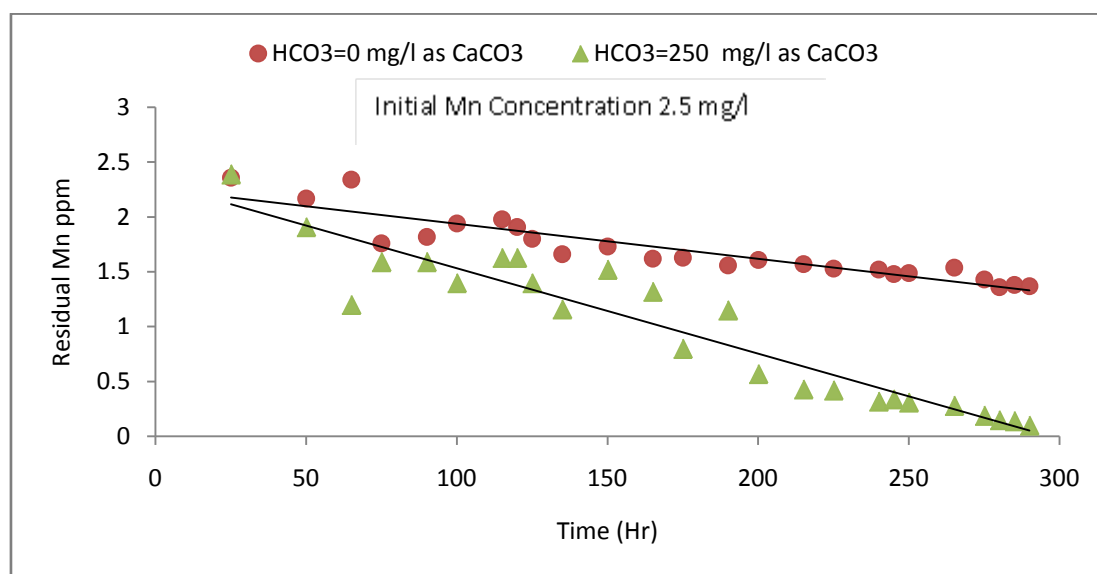


**Figure 4.6:** Effluent Mn concentration as a function of filter run time in the presence and in the absence of bicarbonate in influent water having a pH of  $7.0 \pm 0.2$  [influent water prepared with deionized water containing 0.01 M KCl, 2.5 mg/l Mn(II); flow rate= 1 ml/min.cm<sup>2</sup>]

Figure 4.7 shows residual Mn concentration as a function of filter run time for experiments carried out with initial Mn concentration of 2.5 mg/l; the pH of the influent water was maintained at  $8.0 \pm 0.2$ . It shows that at pH 8, a appreciable Mn removal (by the filter media) is achieved by the Sylhet sand filter media, even in the absence of bicarbonate. However, Mn removal is enhanced significantly in the presence of bicarbonate (present at about 245 mg/l). The figure also shows that Mn removal increases sharply with filter run time, especially in the presence of bicarbonate; Mn removal increased from negligible amount at 50 hours of filter run

time to about complete removal at 300 hours of filter run time. The data presented in Figure 4.7 also provide strong evidence of the significant effect of bicarbonate on the oxidation and removal of Mn in filter media. At the same time, Figure 4.6 and Figure 4.7 show significant effect of pH on the oxidation/removal of Mn in filter media, with higher pH favoring Mn oxidation/removal. While the effect of pH on Mn oxidation is well documented, the data presented in Figures 4.6 and 4.7 clearly demonstrate the role of bicarbonate and pH in the oxidation/removal of Mn in filter media.

It should be noted that flow rate is likely to have an impact on Mn removal by the filter media; lower flow rate would favor higher removal of Mn by allowing greater contact time between Mn bearing water and filter media. However, data presented in Figures 4.6 and 4.7 for experiments carried out with fixed flow rate clearly show that Mn oxidation/removal is significantly enhanced in the presence of bicarbonate, particularly at relatively higher pH values.



**Figure 4.7:** Effluent Mn concentration as a function of filter run time in the presence and in the absence of bicarbonate in influent water having a pH of  $8.0 \pm 0.2$  [influent water prepared with deionized water containing 0.01 M KCl, 2.5 mg/l Mn(II); flow rate = 1 ml/min.cm<sup>2</sup>]

### 4.3 Manganese and Arsenic Removal in Mn-oxide Coated Media

#### 4.3.1 Mn and As Removal in “Prepared Mn-oxide Coated Media”

The removal of Mn and As in filter columns made of “prepared Mn-oxide coated media” was evaluated under a wide range of conditions. This Section presents the results of laboratory experiments carried out to assess the effectiveness of Mn and As removal by the “prepared Mn-oxide coated media”.

##### 4.3.1.1 Manganese removal

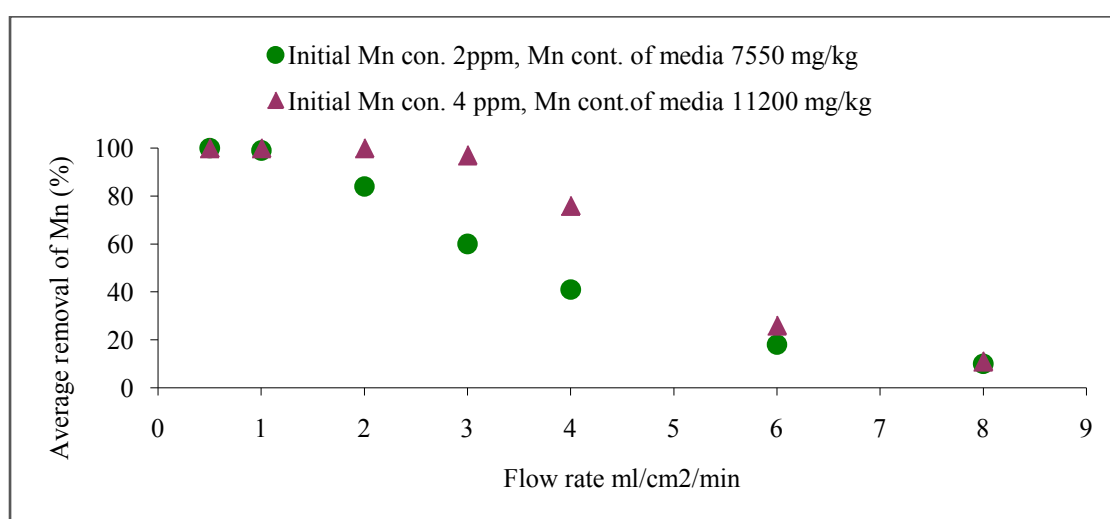
##### *Effect of flow rate/ contact time*

In order to assess the effect of flow rate through Mn-oxide coated filter media (or empty bed contact time with the media) on Mn removal, flow rate of the influent water having an initial Mn concentration of 2 mg/l was varied from 0.5 to 8.0 ml/min/cm<sup>2</sup>. Mn concentration in the effluent water was measured after 90, 120 and 150 minutes. The average Mn-content of the prepared Mn-oxide coated media used in this experiment was about 1,480 mg Mn/kg. However, Mn-content of the top portion (about top 1 cm) of the filter media was much higher, about 7,550 mg Mn/kg of media. The initial pH of the influent water was  $7.0 \pm 0.1$ , which increased gradually up to  $7.55 \pm 0.1$  at the end of 150 minutes of filter run time.

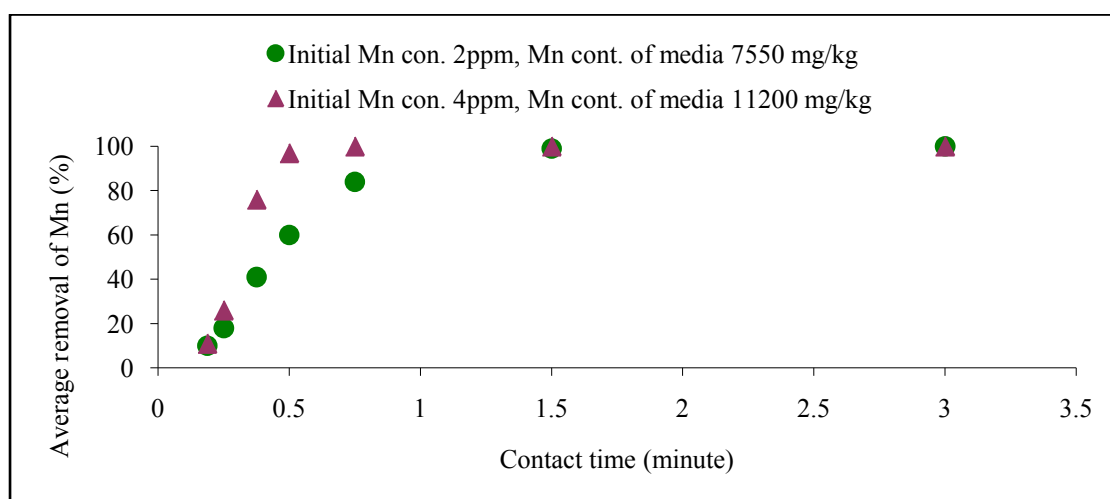
Another set of experiments was carried out under the similar conditions, except that: (a) the pH of the influent water was kept fixed at  $7.0 \pm 0.1$  (with addition of dilute acid/base, as required); (b) Mn concentration of influent water was 4 mg/l; and (c) the average Mn content of the media was about 1800 mg/kg, and Mn content of top 1 cm was about 11,200 mg/l. As before, the Mn concentration in the effluent water was measured after 90, 120 and 150 minutes. In both sets of experiment, the effluent Mn concentration did not vary significantly with filter run time (from 90 to 150 minutes).

Figure 4.8.1 and 4.8.2 show average Mn removal in the “prepared Mn-oxide coated media” as a function of flow rate (Fig. 4.8.1) and contact time (Fig. 4.8.2). It shows that flow rate or contact time has a significant impact on Mn removal; removal increased as flow rate decreased or contact time increased. Figure 4.8.1 and 4.8.2 also show that Mn-content of media also has an impact on Mn removal, with removal

efficiency increasing with increasing Mn-content of filter media. For the first set of experiments (initial Mn of 2 mg/l and Mn content top layer of 7550 mg/kg), Mn removal was only about 10% at a flow rate of 8.0 ml/min/cm<sup>2</sup> (i.e., contact time of about 11 seconds with top 6 cm of media, considering a porosity of 0.25); while removal approached 100% at flow rates less than or equal to about 1 ml/min/cm<sup>2</sup> (i.e., contact time of about 1.5 minutes with top 6 cm of media). As described below, 100% removal of Mn was achieved at a flow rate of 1 ml/min/cm<sup>2</sup> (i.e., contact time of about 2.5 minutes) for initial Mn concentrations of up to 5 mg/l.



**Figure 4.8.1:** Average Mn removal in prepared Mn-oxide coated media as a function of flow rate



**Figure 4.8.2:** Average Mn removal in prepared Mn-oxide coated media as a function of contact time

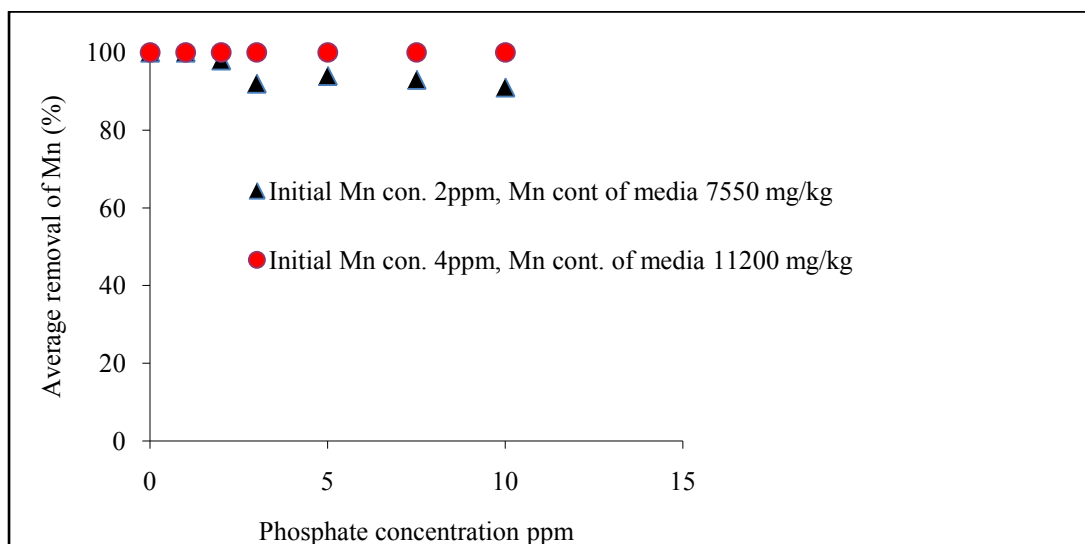
### ***Effect of initial Mn concentration***

In order to assess the effect of initial Mn concentration on Mn removal, influent groundwater with manganese (II) concentrations of 0.50, 1.0, 2.0, 3.0, 4.0, 5.0 and 10 mg/l was passed through the prepared Mn-coated media at a flow rate of about 1 ml/min/cm<sup>2</sup>, and residual Mn concentrations were measured after 90, 120 and 150 minutes. The initial pH of the influent water was  $7.0 \pm 0.1$ , which increased gradually up to  $7.55 \pm 0.1$  at the end of 150 minutes of filter run time. In all cases (i.e., initial Mn concentration varying from 0.022 mg/l to 10.0 mg/l), almost 100% removal of Mn was achieved; filter run time (varying from 90 to 150 minutes) did not have any impact on Mn removal.

These results suggest that the prepared Mn-oxide coated sand media would be able to remove Mn having a wide range of initial concentrations from groundwater to levels satisfying the national standard and WHO guideline value. Tasneem (2010) reported almost complete removal of Mn for different initial Mn concentration, even for short filter run times (about 10 minutes), and that the efficiency of these media in removing Mn improved with time.

### ***Effect of Phosphate***

In order to assess the effect of phosphate on removal of Mn (initial concentration 2 mg/l), phosphate concentration of influent water was varied from 0 to 10 mg/l. No effort was made to adjust pH, and the pH of influent water varied out about 7 to 7.5 during the course of the experiment (150 minutes). Removal of Mn did not vary significantly with filter run time (which varied from 90 to 150 minutes). Figure 4.9 shows average removal of Mn in two different Mn-oxide coated sand filter columns as a function of phosphate concentration. Figure 4.9 shows that Mn removal efficiency increased with increasing Mn content of the filter media. However, effect of phosphate on Mn removal was not significant. For filter media with relatively lower Mn content, Mn removal was about 100% at a phosphate concentration of 1 mg/l, while removal came down to about 91% at a phosphate concentration of 10 mg/l.



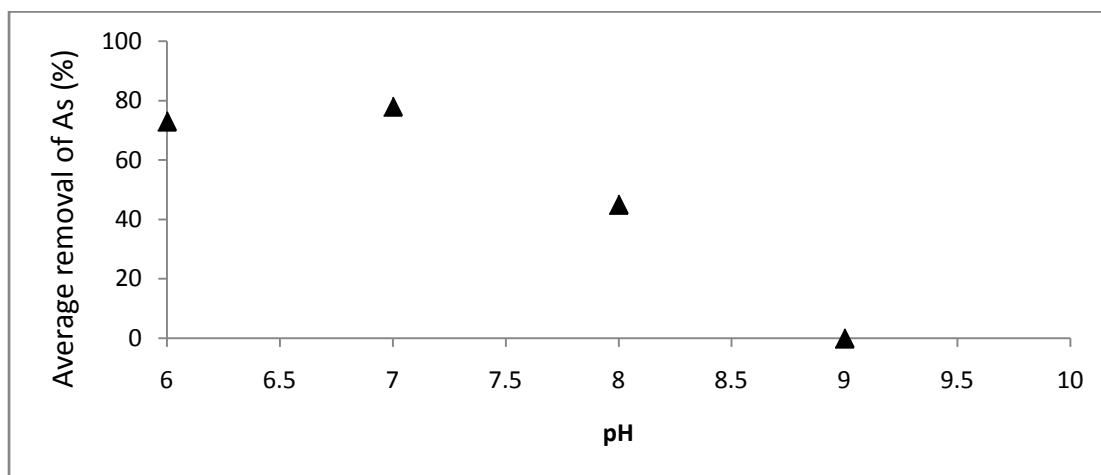
**Figure 4.9:** Average removal of Mn as a function of phosphate concentration

#### 4.3.1.2 Arsenic removal

##### *Effect of pH*

The removal of As in the prepared Mn-oxide coated media has been found to be a strong function of pH. Figure 4.10 shows removal of As(III) (initial concentration 300 µg/l) from groundwater in the prepared Mn-oxide coated media as a function of pH. It shows that As removal decreases from close to 80% at pH of about 7 to almost nil at a pH of 9.0. The strong effect of pH on removal of As in Mn-oxide coated media is supported by Zhang et al. (2011), who showed that pH has a strong influence both on oxidation of As(III) to As(V) and adsorption of As. Zhang et al. (2011) reports that removal of As by Mn-oxide ( $\text{MnO}_2$ ) is governed by oxidation of As(III) to As(V) by  $\text{MnO}_2$  [ $\text{Mn(IV)} + \text{As(III)} = \text{Mn(II)} + \text{As(V)}$ ], and subsequent adsorption of As(V) onto  $\text{MnO}_2$  solids. However, at pH above 6 oxidation of As(III) to As(V) was found to decrease significantly. The pH was found to have more dramatic influence on adsorption of As(V); adsorption of As(V) was found to decrease from about 80% at pH 4 to about 10% at pH 8.0 (Zhang et al., 2011).

It should be noted that the initial alkalinity of influent water was 332 mg/l (as  $\text{CaCO}_3$ ) at pH of about 7.6. Since alkalinity (or bicarbonate ion) also affects removal/adsorption of As (as discussed below), it is difficult to differentiate the effect of pH and alkalinity on As(III) removal from these experimental results.



**Figure 4.10:** Removal of As(III) in Mn-oxide coated media as a function of pH

### *Effect of Alkalinity*

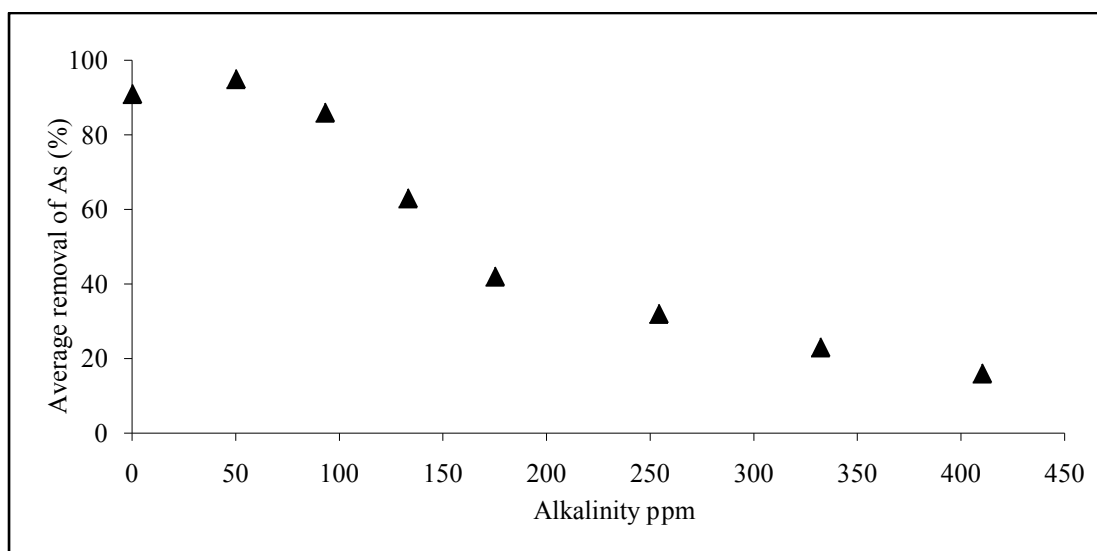
As discussed in Chapter 3, in order to assess the effect of alkalinity on removal of As in Mn-oxide coated media, alkalinity of influent water was varied from 0 to 410 mg/l (as  $\text{CaCO}_3$ ). For this purpose, groundwater with an alkalinity of 216 mg/l (as  $\text{CaCO}_3$ ) was either diluted with deionized water, or amended with  $\text{NaHCO}_3$  solution. A solution of 0.01 M  $\text{KCl}$  was prepared to represent a solution with alkalinity approaching zero. Table 4.1 shows the average pH values of influent water samples with different concentrations of alkalinity. All solutions were spiked to As stock solution to achieve a final As concentration of 300  $\mu\text{g/l}$ .

**Table 4.1:** Initial pH values of influent water with different concentrations of alkalinity

Sl. No.	Alkalinity (mg/l as $\text{CaCO}_3$ ) of influent water	pH value (range)
1	$\approx 0$	6.21
2	50	6.67
3	93	7.01
4	133	7.16
5	175	7.35
6	254	7.48
7	332	7.67
8	410	7.88



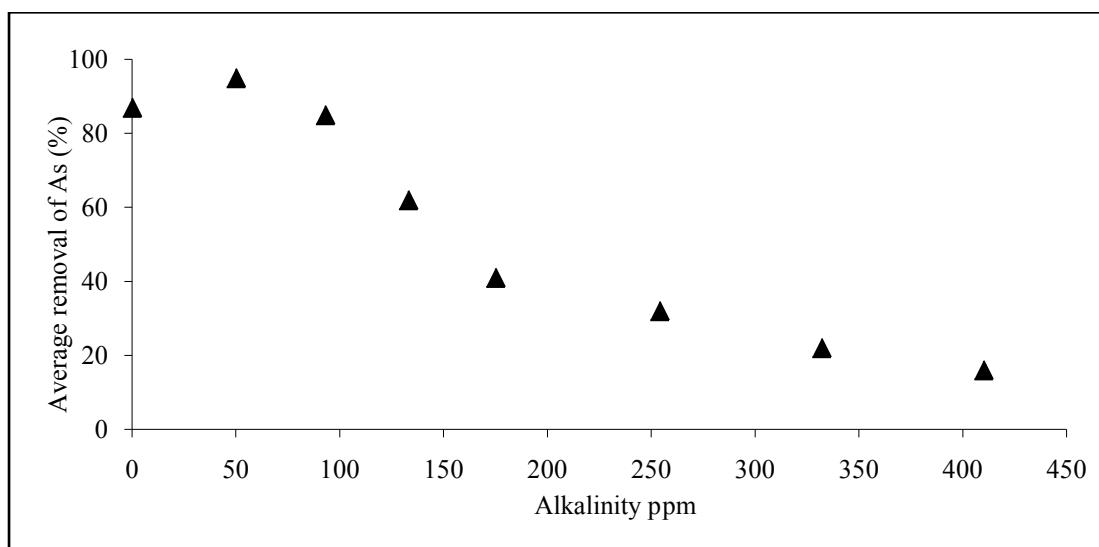
Figure 4.11.1 shows average (up to 150 minutes filter run time) removal of As (initial concentration 300 µg/l) in the prepared Mn-coated media as a function of alkalinity of influent water; the pH of water corresponding to each data point should be read from Table 4.1. The significantly lower removal of As at alkalinity values from 254 to 410 mg/l (as CaCO<sub>3</sub>) could be partly attributed to high pH value of influent water (as explained above; see Fig. 4.10). For alkalinity varying from about 0 to 93 mg/l, Fig. 4.11.1 shows average As removal is in the range of about 90% over a pH range of 6.21 to 7.01. On the other hand, Fig. 4.13.1 shows average As removal (initial concentration 300 µg/l) in the range of 60% in the presence of 216 mg/l (as CaCO<sub>3</sub>) alkalinity over a pH range of 7 to 7.55. Although it is difficult to differentiate the effects of pH and alkalinity on As removal (by Mn-oxide coated media), comparison of Fig. 4.11.1 and 4.13.1 suggest that As removal could be reduced in the presence of higher alkalinity. Since bicarbonate (HCO<sub>3</sub><sup>-</sup>) is the dominant species in the neutral and slightly alkaline pH range; the reduction in As removal could be due to competition with bicarbonate ions for adsorption sites on Mn-oxide coated media.



**Figure 4.11.1:** Removal of As (initial concentration 300 µg/l) in Mn-oxide coated media as a function of alkalinity (Table 4.1 shows pH value for each data point)

Fig. 4.11.2 shows removal (up to 150 minutes filter run time) of As (initial concentration 300 µg/l) as a function of alkalinity of influent water, in the presence of 2 mg/l Mn. These results are similar to those carried out in the absence of Mn (Fig.

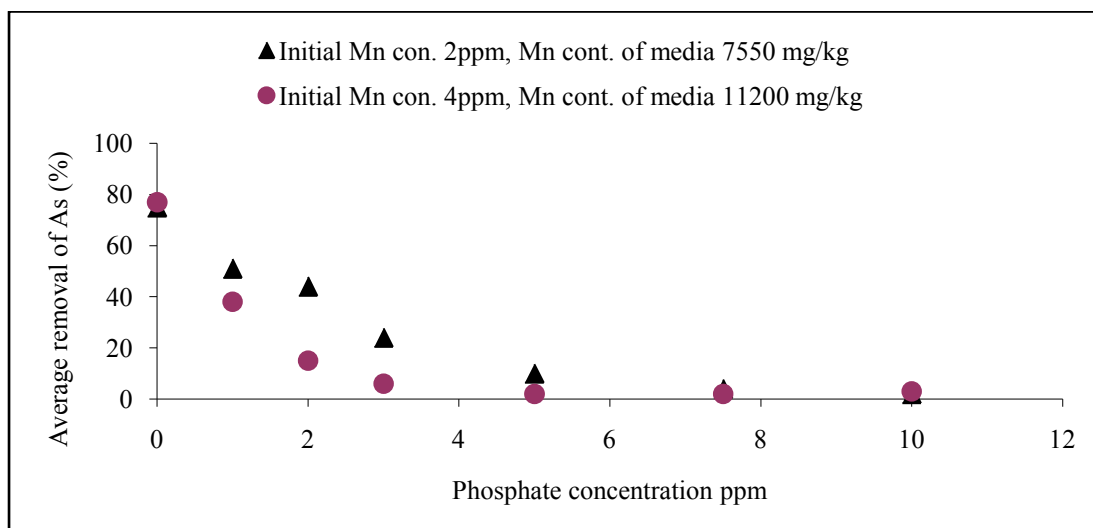
4.11.1). Presence of Mn appears to have little or no effect on the removal of As. Thus, the poor performance of the Mn-oxide coated media in removing As from natural groundwater is related to pH and possible competitive adsorption of bicarbonate ions.



**Figure 4.11.2:** Removal of As (initial concentration 300  $\mu\text{g/l}$ ) in Mn-oxide coated media as a function of alkalinity, in the presence of 2 mg/l Mn.

### *Effect of Phosphate*

Figure 4.12 shows average removal (up to 150 minutes filter run time) of arsenic as a function phosphate concentration. As noted earlier, pH of the influent water sample varied from about 7 to 7.55 during the course of the experiment (up to 150 minutes). However, As concentration of effluent samples collected at 90, 120 and 150 minutes did not vary significantly, indicating that pH (varying from 7 to 7.55) did not have a significant influence on As removal. Figure 4.12 shows very significant effect of phosphate on removal of As in the Mn-oxide coated media. Arsenic removal came down from over 75% in the absence of phosphate to about 2.3% at a phosphate concentration of 10 mg/l due to competitive adsorption.



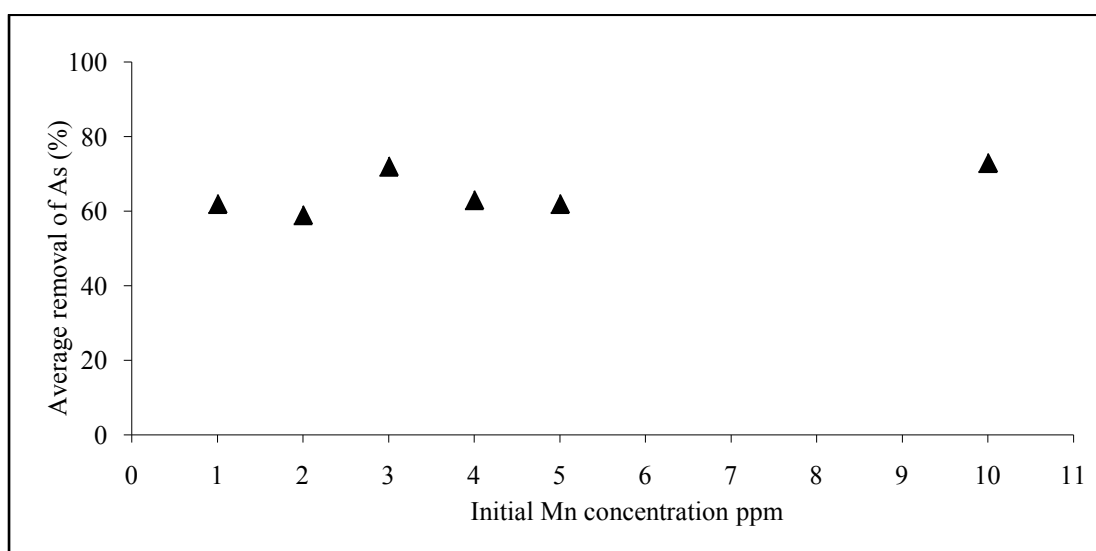
**Figure 4.12:** Average removal of As as a function of phosphate concentration

#### 4.3.1.3 Simultaneous removal of Mn and As

Two sets of experiments were carried out to assess the simultaneous removal of Mn and As in the prepared Mn-oxide coated sand media. In one experiment, As concentration in the influent water was fixed at 300  $\mu\text{g/l}$ , while Mn concentration was varied from 1 to 10  $\text{mg/l}$ ; in another experiment Mn concentration of influent water was fixed at 2  $\text{mg/l}$ , while As concentration was varied from 100 to 1000  $\mu\text{g/l}$ . Removal was determined by measuring As and Mn concentration in the effluent water after 90, 120 and 150 minutes. While no efforts were made to adjust pH, the pH of the influent water gradually increased from about 7.0 at the beginning of the experiment to about 7.55 at the end of the experiment (i.e. after 150 minutes of filter run time). However, no significant differences were observed in effluent As or Mn concentration during the course of these experiments, and the data presented in Fig. 4.13.1 and 4.13.2 represent average of three measurements taken during the course of the experiments.

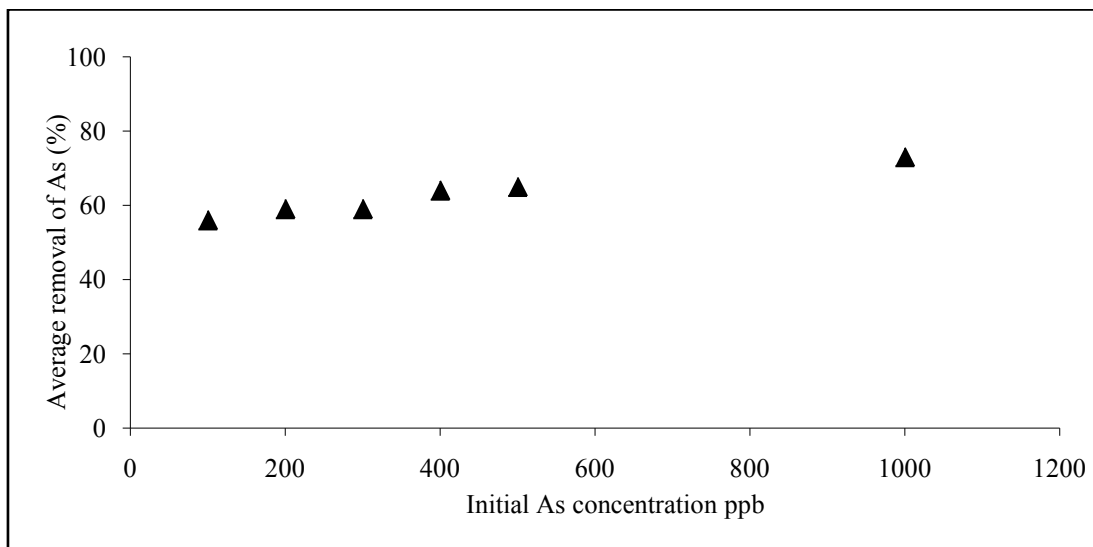
In all experiments, almost 100% removal of Mn was achieved, irrespective of the concentration of As in the influent water. Thus, it appears that the presence of arsenic (up to 1000  $\mu\text{g/l}$ ) does not affect Mn removal. Based on results of similar experiments, Tasneem (2010) also reported that Mn removal was largely unaffected in the presence of As.

Figure 4.13.1 shows average removal (up to 150-minute filter run time) of As, present at an initial concentration of 300  $\mu\text{g/l}$ , as a function of Mn concentration in the influent water in the pH range 7.0 -7.55. It shows that under the experimental conditions (i.e. pH 7.0 to 7.55), average As removal varied from about 63% (in the presence of 1 mg/l Mn) to 72% (in the presence of 10 mg/l Mn). From these results, removal of As appear to increase to some extent in the presence of Mn. Based on results of similar experiments, Tasneem (2010) also reported that As removal increased to some extent in the presence of Mn. As reported by Zhang (2011), this could be due to enhanced oxidation of As(III) to As(V) in the presence of higher concentration of Mn(II) in solution.



**Figure 4.13.1:** Average removal of As (initial concentration = 300  $\mu\text{g/l}$ ) as a function of Mn concentration in the influent water (alkalinity = 216 mg/l as  $\text{CaCO}_3$ )

Figure 4.13.2 shows average removal of arsenic (up to 150-minute filter run time) as a function of initial As concentration in the influent water, in the presence of 2 mg/l Mn. Under the experimental conditions (i.e. pH 7.0 to 7.55), average As removal in the Mn-oxide coated media varied from about 56% (initial concentration 100  $\mu\text{g/l}$ ) to about 70% (initial concentration 1,000  $\mu\text{g/l}$ ); removal efficiency appear to increase slightly with increasing initial As concentration.



**Figure 4.13.2:** Average removal of Arsenic as a function of initial As concentration in the presence of 2 mg/l Mn (alkalinity = 216 mg/l as  $\text{CaCO}_3$ )

### 4.3.2 Mn and As Removal in “Synthetic Mn-oxide Coated Media”

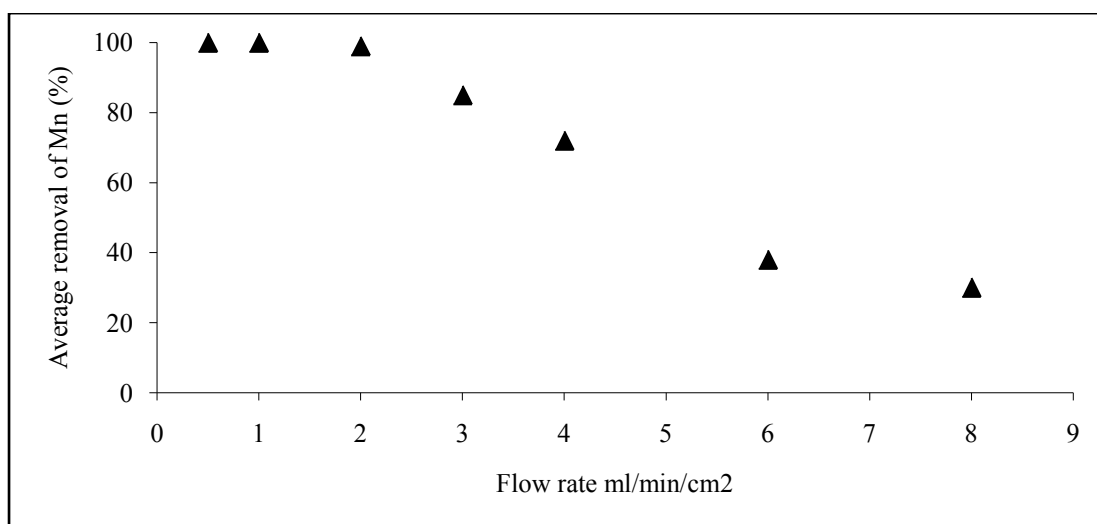
#### 4.3.2.1 Manganese removal

##### *Effect of flow rate/ contact time*

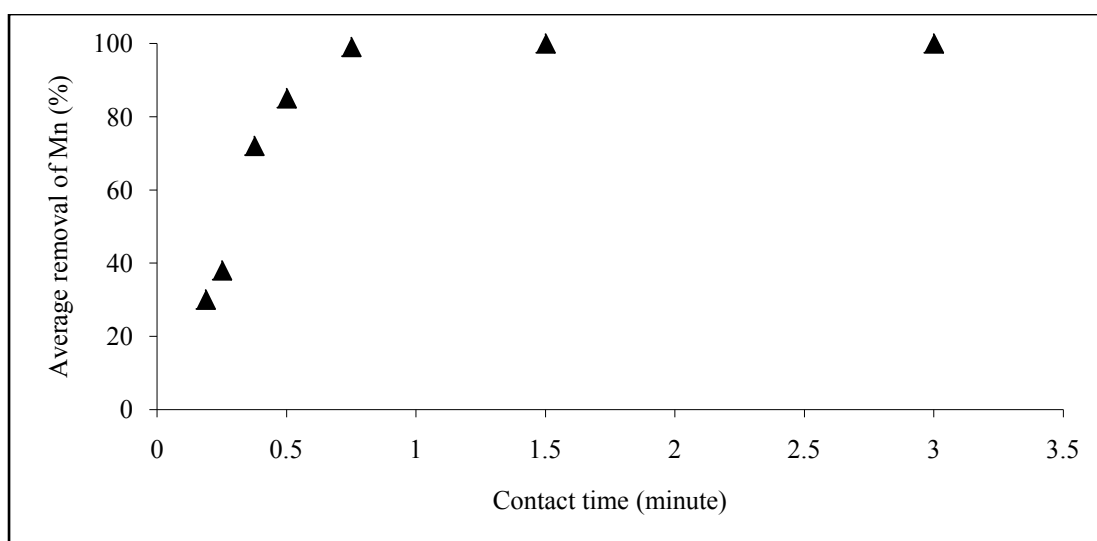
In order to assess the effect of flow rate on Mn removal, flow rate of the influent water having an initial Mn concentration of 2 mg/l was varied from 0.5 to 8.0 ml/min/cm<sup>2</sup>. Manganese concentration in the effluent water was measured after 90, 120 and 150 minutes. As before, no effort was made to adjust pH of the influent water; the initial pH of the influent water was  $7.0 \pm 0.1$ , which increased gradually up to about  $7.5 \pm 0.1$  at the end of 150 minutes of filter run time. The Mn content of the synthetic Mn-oxide coated media at the beginning of the experiments was found to be about 25,250 mg Mn/ kg.

Manganese removal in the media did not vary significantly with filter run time (which varied from 90 to 150 minutes, during this period pH also varied from about 7 to 7.5). Figure 4.14.1 and 4.14.2 show average Mn removal in synthetic Mn-oxide coated media as a function of flow rate and contact time (i.e., empty bed contact time, EBCT). It shows that flow rate or contact time has a significant impact on Mn removal; removal increased as flow rate decreased or contact time increased. At a flow rate of 8.0 ml/min/cm<sup>2</sup> (i.e., contact time of about 11 seconds), Mn removal was about 30%; while removal approached 100% at flow rates below about 1 ml/min/cm<sup>2</sup>

(i.e., contact time of about 1.5 minutes). Under the same experimental conditions, removal of Mn in the “prepared Mn-oxide coated media” (with Mn content of 7,550 mg/kg) was relatively lower (see Fig. 4.8); i.e., the synthetic Mn-oxide coated media with higher Mn content (25,250 mg/kg) is more efficient in removing Mn than the prepared Mn-oxide coated media. About 100% removal of Mn was achieved at a flow rate of 1 ml/min/cm<sup>2</sup> (i.e., contact time of about 1.5 minutes) for initial Mn concentrations of up to 5 mg/l.



**Figure 4.14.1:** Mn removal in Mn-coated synthetic media as a function of flow rate



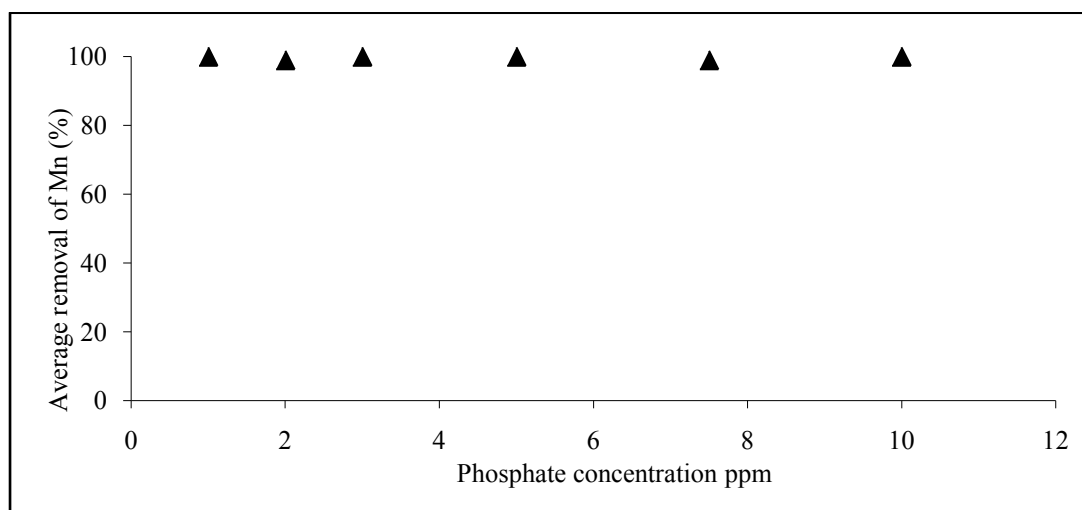
**Figure 4.14.2:** Mn removal in Mn-coated synthetic media as a function of contact time

### ***Effect of initial Mn concentration***

In order to assess the effect of initial Mn concentration on Mn removal, influent groundwater with Manganese (II) concentrations varying from 0.022 mg/l (natural groundwater) to 10.0 mg/l were passed through the Mn-coated synthetic media at a flow rate of about 1 ml/min/cm<sup>2</sup>, and residual Mn concentrations were measured after 90, 120 and 150 minutes. During the experiment (i.e. 150 minutes), the pH of the influent water gradually increased from about 7 to 7.5; however filter run time (varying from 90 to 150 minutes) did not have any impact on Mn removal. In all cases (i.e., initial Mn concentration varying from 0.022 to 5.0 mg/l), about 100% removal of Mn was achieved. These results suggest that the synthetic Mn-oxide coated sand media would be able to remove Mn having a wide range of initial concentration from groundwater to levels satisfying the national standard and WHO guideline value.

### ***Effect of Phosphate***

In order to assess the effect of phosphate on removal of Mn (initial concentration 2 mg/l), phosphate concentration of influent water was varied from 1 to 10 mg/l. No effort was made to adjust pH, and the pH of influent water varied out about 7 to 7.5 during the course of the experiment (150 minutes). Figure 4.15 shows average removal of Mn in the synthetic Mn-coated sand media as a function of phosphate concentration. It shows that almost 100% Mn was removed in the media, irrespective of the concentration of phosphate.

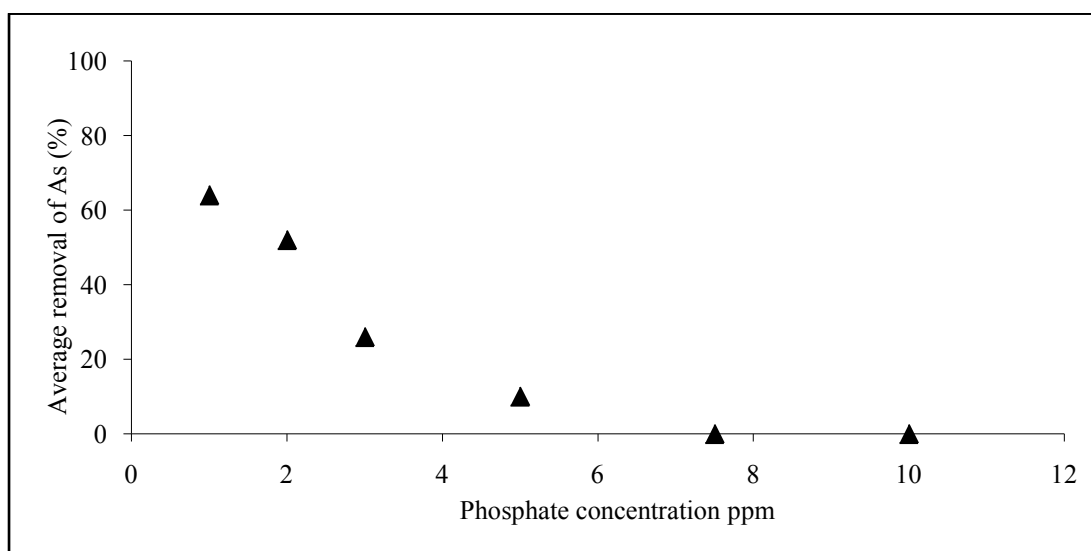


**Figure 4.15:** Average removal of Mn as a function of phosphate concentration

### 4.3.2.2 Arsenic Removal

#### *Effect of Phosphate*

Figure 4.16 shows average removal (up to 150-minute filter run time) of arsenic as a function phosphate concentration. As noted earlier, pH of the influent water sample varied from about 7 to 7.5 during the course of the experiment (up to 150 minutes). However, As concentration of effluent samples collected at 90, 120 and 150 minutes did not vary significantly, indicating that pH (varying from 7 to 7.55) did not have a significant influence on As removal. Figure 4.16 shows very significant effect of phosphate on removal of As in the synthetic Mn-coated sand media. Arsenic removal came down from about 60% in the absence of phosphate to about 0% at a phosphate concentration exceeding 7.5 mg/l due to competitive adsorption.



**Figure 4.16:** Average removal of As (in the presence of 2 mg/l Mn) as a function of phosphate concentration; pH increased from 7.0 to 7.5 during the experiment

### 4.3.2.3 Simultaneous removal of Mn and As

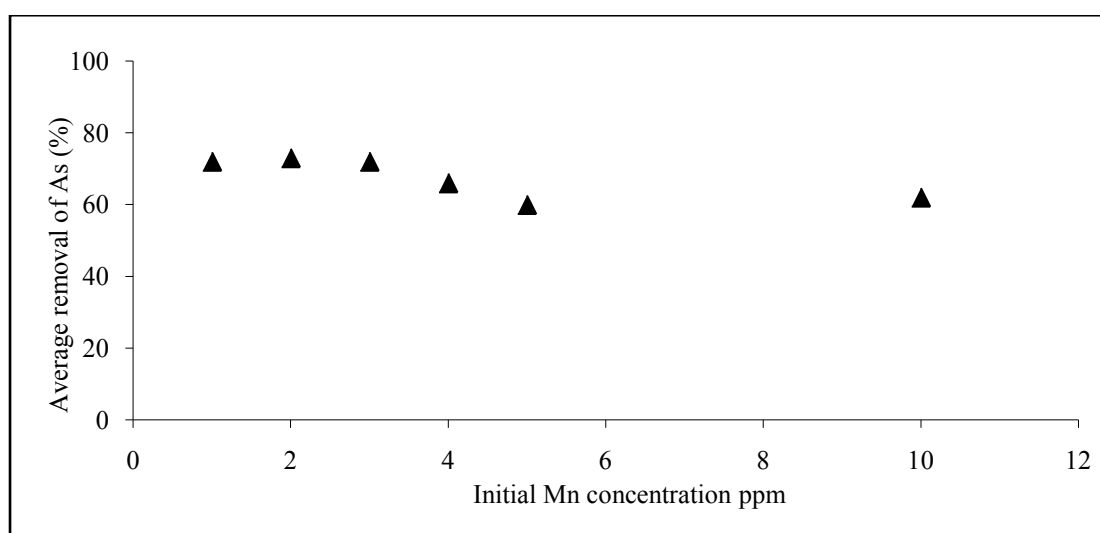
As before, two sets of experiments were carried out to assess simultaneous removal of Mn and As in the synthetic Mn-coated sand media. In one set of experiment, As concentration in the influent water was fixed at 300 µg/l, while Mn concentration was varied from 0 to 10 mg/l; in another set of experiment Mn concentration of influent water was fixed at 2 mg/l, while As concentration was varied from 100 to 1,000 µg/l. Removal was determined by measuring As and Mn concentration in the effluent water



after 90, 120 and 150 minutes. No effort was made to adjust pH of influent water; the pH of influent water gradually increased from about 7 to 7.5 during the course of the experiment.

Removal of Mn was not found to vary significantly with filter run time (which varied from 90 to 150 minutes). In both experiments, 100% removal of Mn was achieved, irrespective of the concentration of As in the influent water. Thus, it appears that presence of arsenic (up to 1,000  $\mu\text{g/l}$ ) in the influent water does not affect Mn removal in either the synthetic Mn-oxide coated media, as was observed for the prepared Mn-oxide coated media.

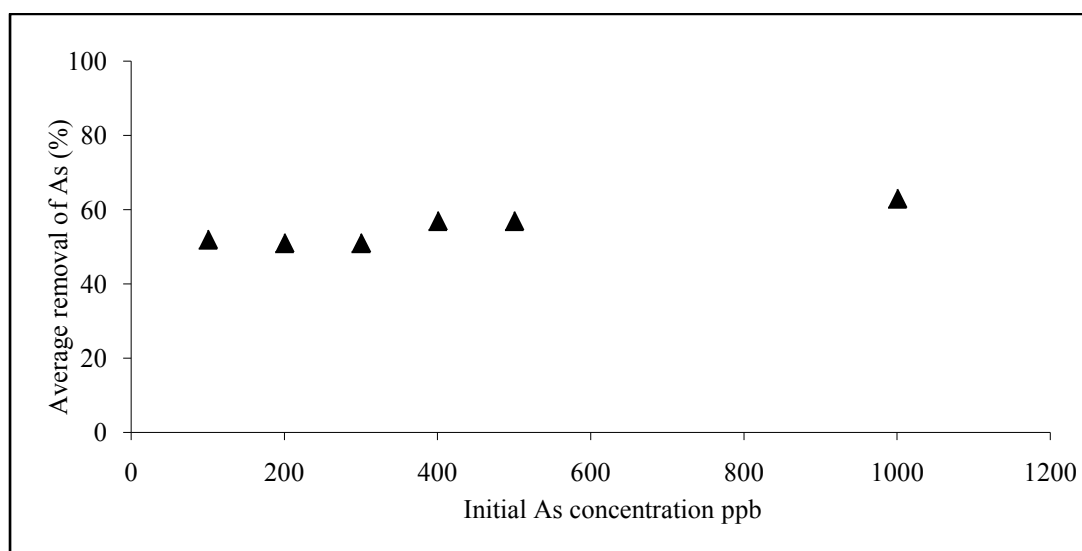
On the other hand, like the “prepared Mn-oxides and coated media”, the synthetic Mn-oxide coated media was not found to be very effective in removing As from influent groundwater. Figure 4.17 shows average removal of As, present at an initial concentration of 300  $\mu\text{g/l}$ , as a function of Mn concentration in the influent water up to 150-minute filter run time. It shows that under the experimental conditions, average As removal varied from about 51% (in the absence of Mn) to 72%.



**Figure 4.17:** Average removal of As (initial concentration = 300  $\mu\text{g/l}$ ) as a function of Mn concentration in the influent water

Figure 4.18 shows removal of Arsenic (up to 150 minute filter run time) as a function of initial As concentration in the influent water, in the presence of 2 mg/l Mn. Under

the experimental conditions, average As removal in the synthetic Mn-coated media varied from about 51% to about 57%; removal efficiency appear to increase slightly with increasing initial As concentration. As explained earlier, pH has a strong influence on removal of Mn in Mn-oxide coated media. However, since pH varied over a relatively narrow range (7 to 7.5) in these experiments (Fig. 4.17-4.18), pH is unlikely to have any significant effect on these results.



**Figure 4.18:** Average removal of As as a function of initial As concentration in the presence of 2 mg/l Mn

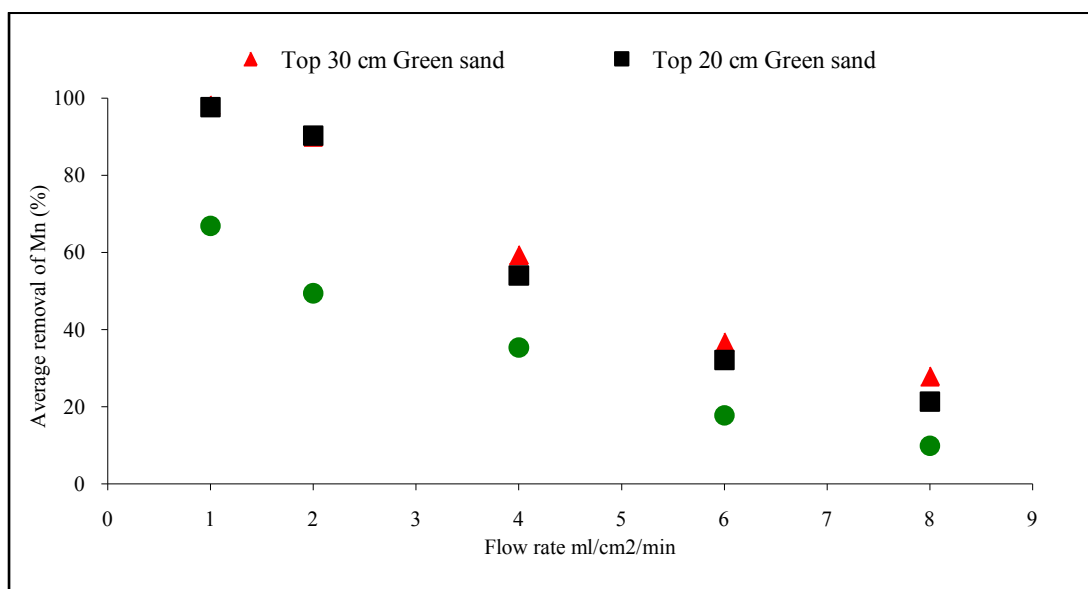
### 4.3.3 Mn and As Removal in “Green Sand”

#### 4.3.3.1 Manganese removal

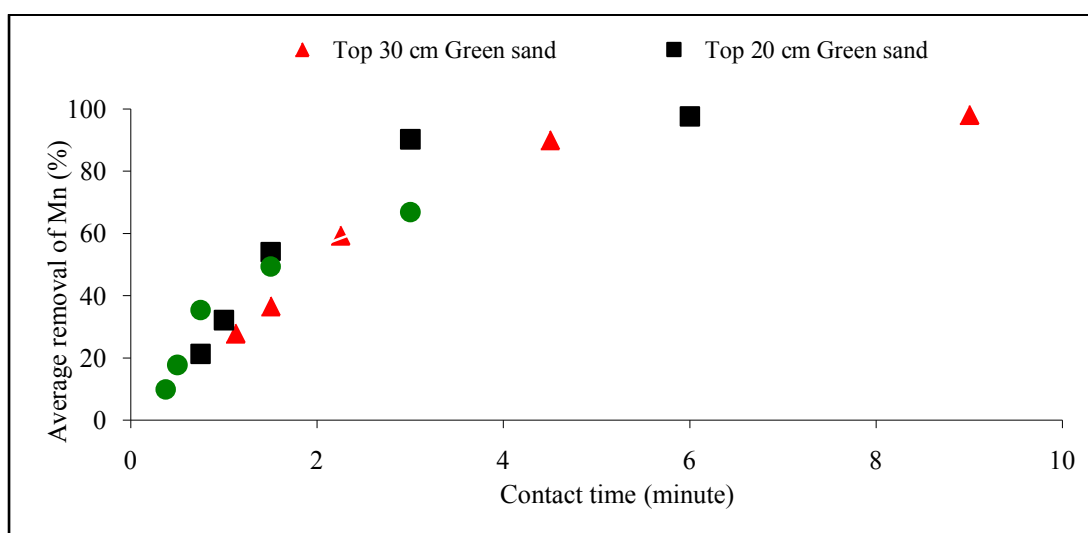
##### *Effect of flow rate/ Contact time*

In order to assess the effect of flow rate (or contact time) on Mn removal, flow rate of the influent water having an initial Mn concentration of 4 mg/l was varied from 1.0 to 8.0 ml/min/cm<sup>2</sup> through each of the three columns (Column 1: top 10 cm “green sand”, Column 2: top 20 cm “green sand”, Column 3: top 30 cm “green sand”). Manganese concentration in the effluent water was measured after 90, 120 and 150 minutes. No effort was made to adjust pH of the influent water; the initial pH of the influent water was about 7.0±0.1, which increased gradually up to about 7.5±0.1 at the end of 150 minutes of filter run time. The initial Mn content of green sand was 14,400 mg/kg.

It was found that Mn removal did not vary significantly with filter run time (which varied from 90 to 150 minutes, during this period pH varied from about 7 to 7.5). Figure 4.19.1 and 4.19.2 show that average Mn removal in three different green sand columns as a function of flow rate and contact time (i.e., empty bed contact time, EBCT).



**Figure 4.19.1:** Mn removal in green sand as a function of flow rate



**Figure 4.19.2:** Mn removal in green sand as a function of contact time

Figure 4.19.1 and 4.19.2 clearly show that removal of Mn depends on both flow rate and depth of “green sand” (that is, depends on contact time between water and “green

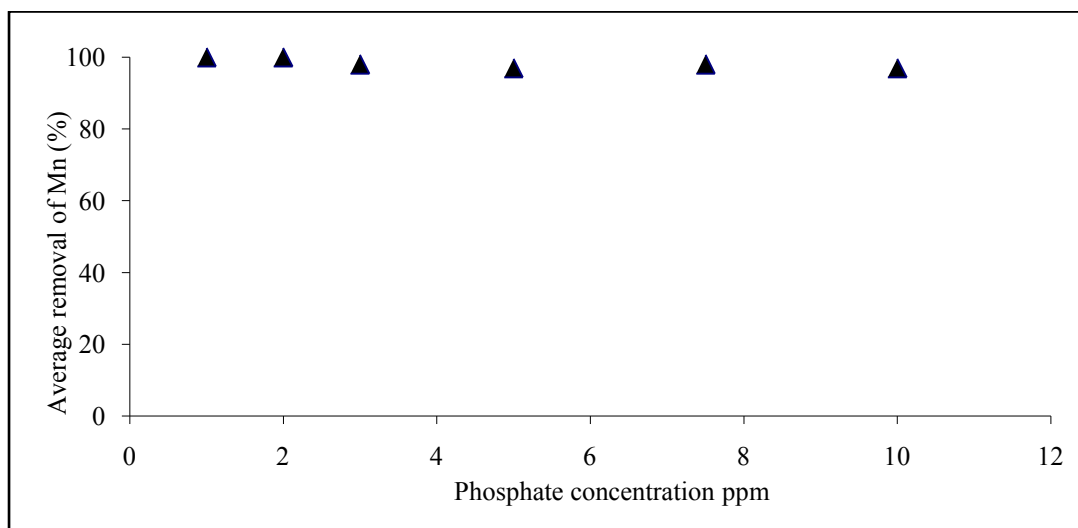
sand”). Removal increased as flow rate decreased or depth of green sand increased (i.e., as contact time increased). The column with 10 cm of “green sand” at the top could remove only about 70% of Mn (initial concentration 4.0 mg/l) even at the slowest flow rate employed (about 1 ml/cm<sup>2</sup>/min; or contact time of about 3.0 minutes, considering a porosity of 0.30), while removal was about 10% at the highest flow rate employed (about 8 ml/cm<sup>2</sup>/min; or contact time of about 22.5 seconds). On the other hand, close to 100% removal was achieved in media with “green sand” depths of 20 cm and 30 cm at a flow rate of 1 ml/cm<sup>2</sup>/min.

### ***Effect of initial Mn concentration***

In order to assess the effect of initial Mn concentration on Mn removal, influent groundwater with manganese (II) concentrations varying from 0.022 to 10.0 mg/l were passed through the 20 cm green sand column at a flow rate of 1 ml/min/cm<sup>2</sup>, and residual Mn concentrations were measured after 90, 120 and 150 minutes. During the experiment (i.e. 150 minutes), the pH of the influent water gradually increased from about 7 to 7.5; however Mn removal did not vary with filter run. Almost 100% removal of Mn was achieved for initial Mn concentration varying from 0.022 mg/l to 10.0 mg/l. These results suggest that green sand would be able to remove Mn having a wide range of initial concentration from groundwater to levels satisfying the national standard and WHO guideline value.

### ***Effect of Phosphate***

To assess the effect of phosphate on removal of Mn (initial concentration 2 mg/l), phosphate concentration of influent water was varied from 1 to 10 mg/l. No effort was made to adjust pH, and the pH of influent water varied out about 7 to 7.5 during the course of the experiment (150 minutes). Figure 4.20 shows average removal of Mn in the 20 cm green sand column as a function of phosphate concentration. It shows that close 100% Mn was removed in green sand, irrespective of the concentration of phosphate.

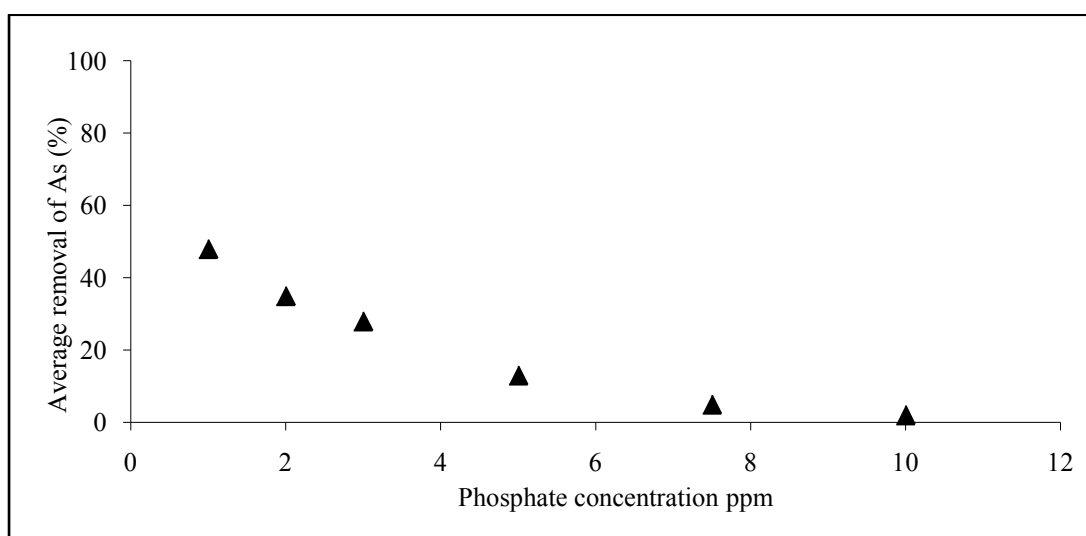


**Figure 4.20:** Average removal of Mn as a function of phosphate concentration

#### 4.3.3.2 Arsenic Removal

##### *Effect of Phosphate*

Figure 4.21 shows average removal (up to 150-minutes filter run time) of arsenic as a function phosphate concentration. The pH of the influent water varied from about 7 to 7.5 during the course of the experiment (up to 150 minutes). However, As concentration of effluent samples collected at 90, 120 and 150 minutes did not vary significantly, indicating that pH (varying from 7 to 7.55) did not have a significant influence on As removal.

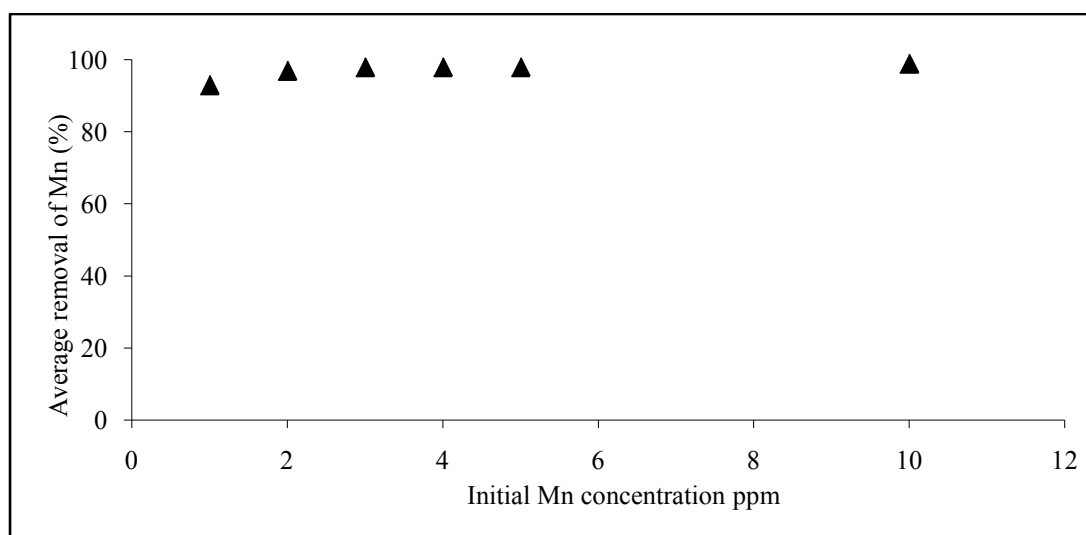


**Figure 4.21:** Average removal of As as a function of phosphate concentration

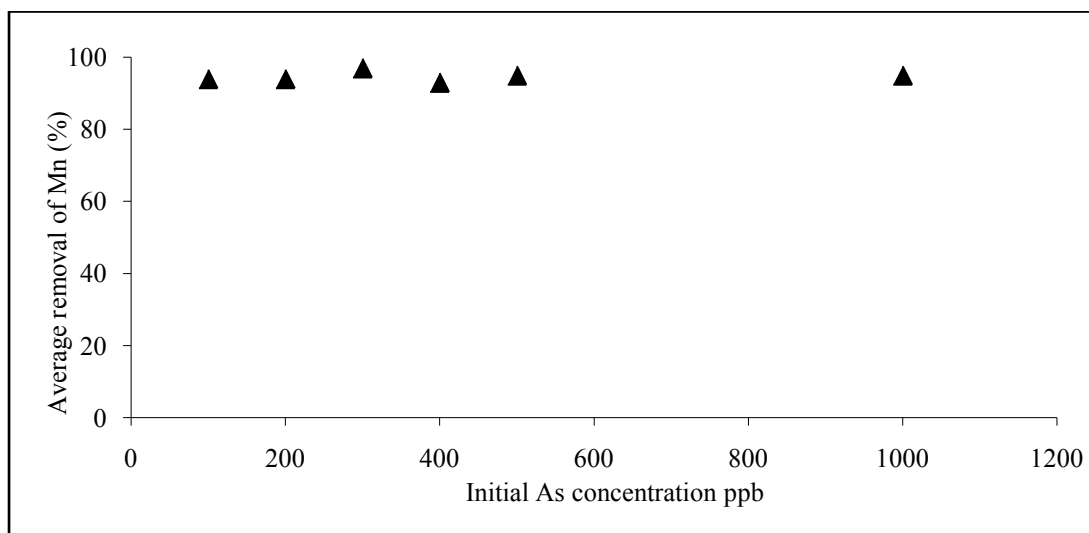
Figure 4.21 shows significant effect of phosphate on removal of As in the green sand media. Arsenic removal came down from about 48% in the presence of 1 mg/l phosphate to about 2.5% at a phosphate concentration exceeding 10 mg/l due to competitive adsorption.

#### 4.3.3.3 Simultaneous removal of Mn and As

As before, two sets of experiments were carried out to assess simultaneous removal of Mn and As in a 20 cm green sand column. In one set of experiments, As concentration in the influent water was fixed at 300 µg/l, while Mn concentration was varied from 0 to 10 mg/l; in another set Mn concentration of influent water was fixed at 2 mg/l, while As concentration was varied from 100 to 1,000 µg/l. Removal was determined by measuring As and Mn concentration in the effluent water after 90, 120 and 150 minutes. No effort was made to adjust pH of influent water; the pH of influent water gradually increased from about 7 to 7.6 during the course of the experiment. Removal of Mn was not found to significant with filter run time (which varied from 90 to 150 minutes).



**Figure 4.22.1:** Removal of Mn in green sand as a function initial Mn concentration

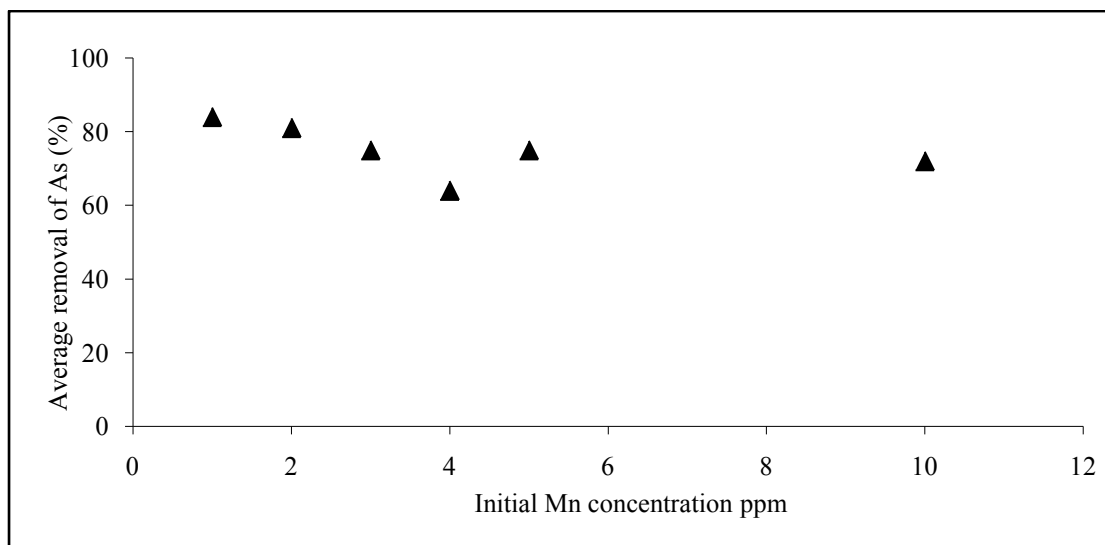


**Figure 4.22.2:** Removal of Mn (initial concentration 2 mg/l) in greensand as a function of initial As concentration

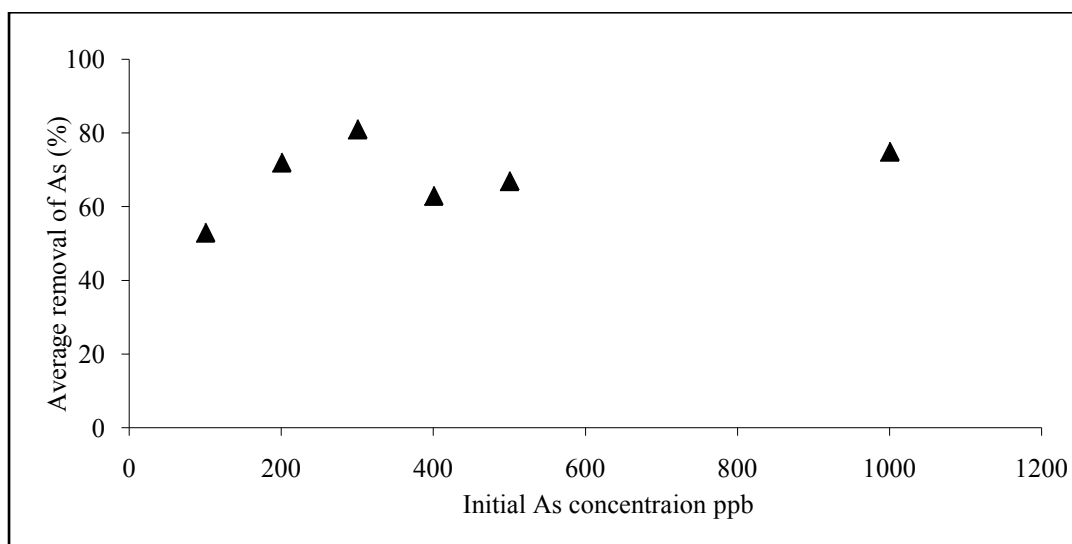
Figure 4.22.1 shows average removal of Mn as a function of initial Mn concentration in the presence of 300  $\mu\text{g/l}$  As. It shows slightly higher removal efficiency of Mn with increasing initial Mn concentration. Figure 4.22.2 shows removal of Mn, present at an initial concentration of 2 mg/l, as a function of As concentration in influent water. It shows very little effect of As on Mn removal efficiency.

Similar to “prepared” and “synthetic” Mn-oxide coated media, greensand was not found to be very effective in removing As from influent groundwater; however the 20 cm green sand column was somewhat more effective in removing As compared to the prepared Mn-oxide coated media and the synthetic Mn-oxide coated media. Figure 4.23 shows average removal of As (up to 150-minute filter run time), present at an initial concentration of 300  $\mu\text{g/l}$ , as a function of Mn concentration in the influent water. It shows that under the experimental conditions, average As removal varied from about 63% to about 84%. Figure 4.24 shows removal of arsenic (up to 150-minute filter run time) as a function of initial As concentration in the influent water, in the presence of 2 mg/l Mn. Under the experimental conditions, average As removal in 20 cm green sand column varied from about 53% to about 82%; removal efficiency appears to increase slightly with increasing initial As concentration. pH could have a strong influence on removal of Mn in Mn-oxide coated media; however, since pH

varied over a relatively narrow range (7 to 7.6) in these experiments (Fig. 4.23-4.24), pH is unlikely to have any significant effect on these results.



**Figure 4.23:** Average removal of As (initial concentration = 300  $\mu\text{g/l}$ ) in green sand as a function of Mn concentration in the influent water

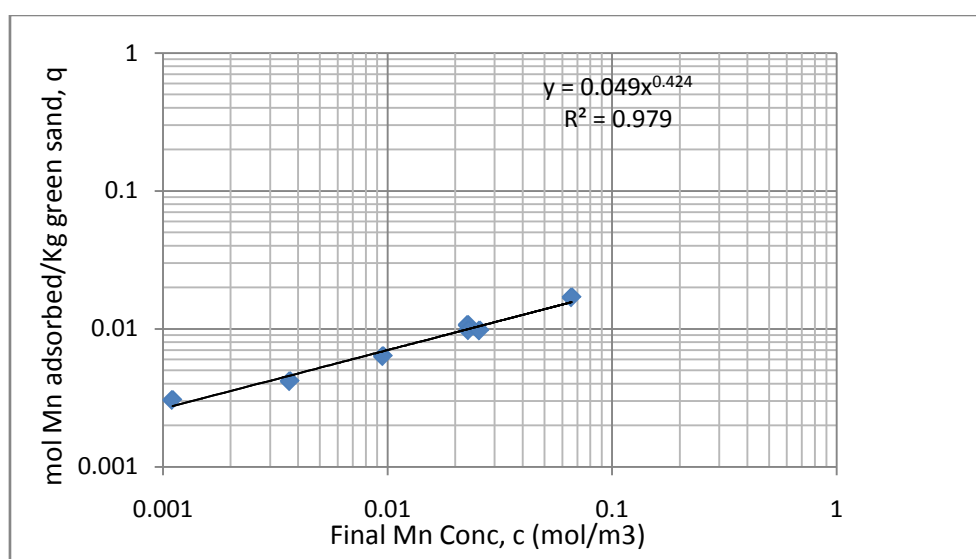


**Figure 4.24:** Average removal of arsenic as a function of initial As concentration in the presence of 2 mg/l Mn; pH varied from 7 to 7.6 during the experiments

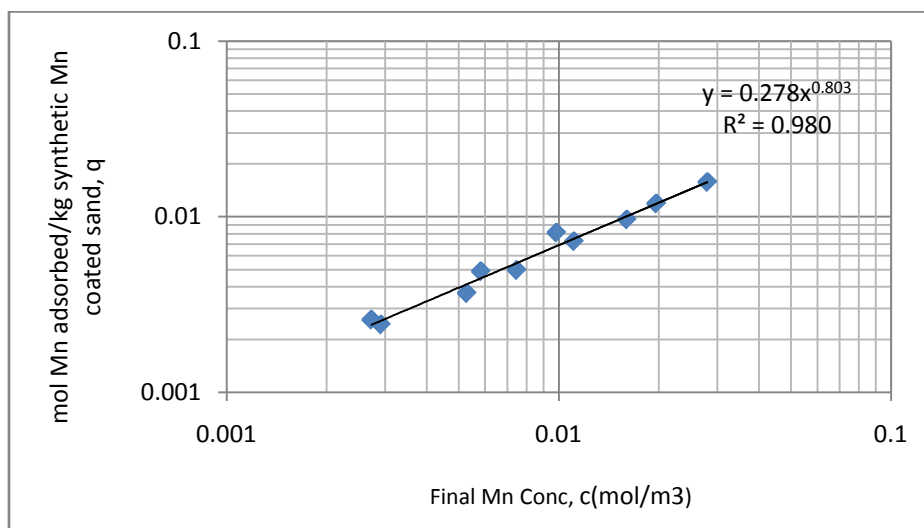


#### 4.3.4 Isotherm Constants for Mn-oxide Coated Media

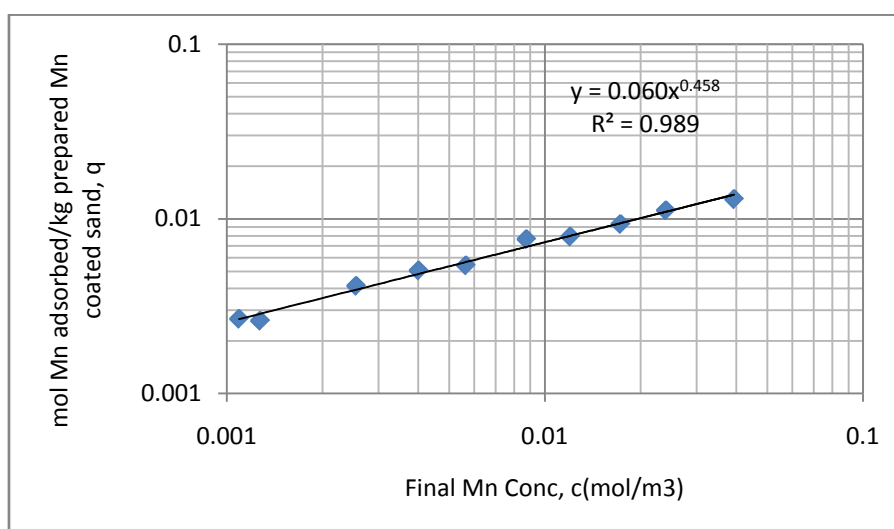
Freundlich adsorption isotherm constants (i.e.,  $K$  and  $n$ ) were estimated using results of batch experiments (discussed in Section 3.3.2.2) where Mn uptake capacity of three Mn-oxide coated media and Sylhet sand was measured at pH of  $7.2 \pm 0.1$  and temperature of  $26.6 - 27.4^\circ\text{C}$ . The data from the batch experiments are presented in Appendix A. Figures 4.25 through 4.28 show log-log plots (quantity of Mn adsorbed versus concentration of Mn in water) of data obtained from batch experiments with three Mn-oxide coated media and Sylhet sand. The estimated  $K$  and  $n$  values (i.e., Freundlich adsorption isotherm constants) for the adsorbents are summarized in Table 4.2. Figure 4.29 shows a plot of isotherm constant  $K$  versus Mn-content of the adsorbent. It shows that  $K$  increases with increasing Mn-content of the media; in other words, adsorption capacity increases with increasing Mn-content of the filter media.



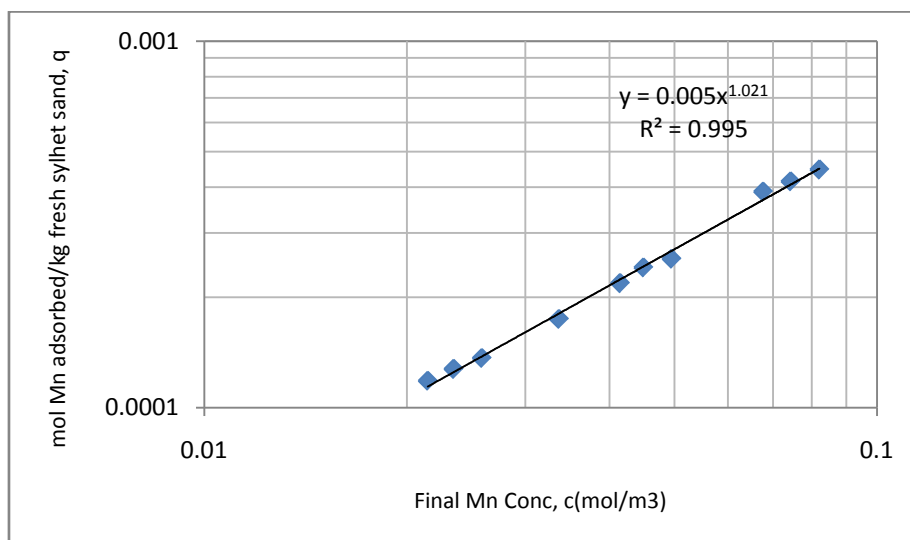
**Figure 4.25:** Log-log plot for estimation of Freundlich adsorption isotherm constants for “green sand”.



**Figure 4.26:** Log-log plot for estimation of Freundlich adsorption isotherm constants for “synthetic Mn-oxide coated media”.



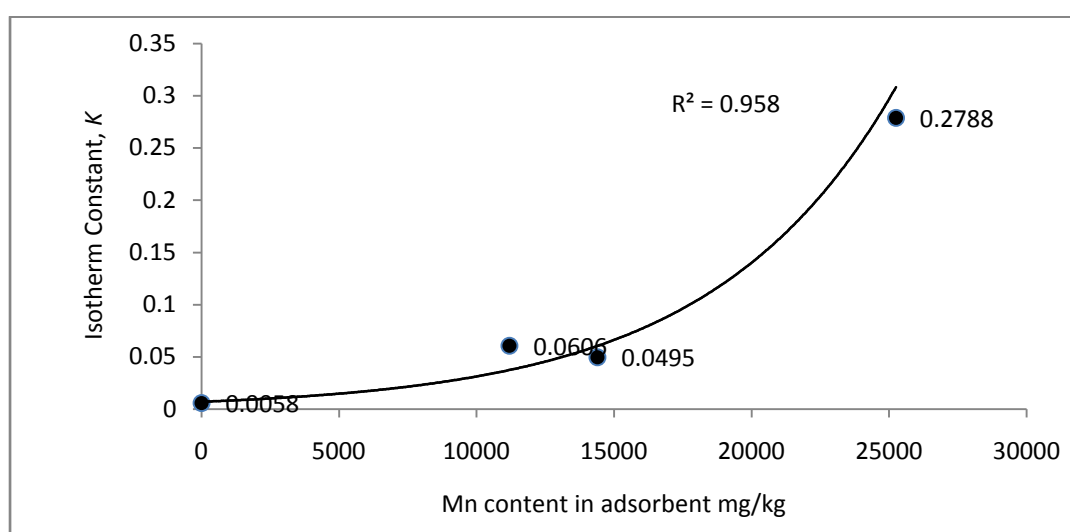
**Figure 4.27:** Log-log plot for estimation of Freundlich adsorption isotherm constants for “prepared Mn-oxide coated media”.



**Figure 4.28:** Log-log plot for estimation of Freundlich adsorption isotherm constants for “Sylhet sand”.

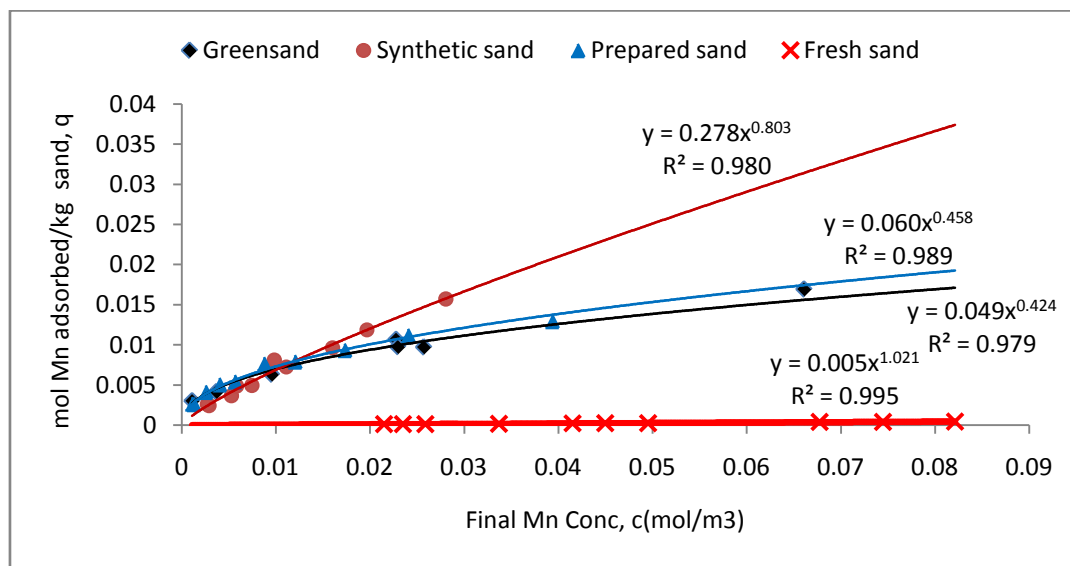
**Table 4.2:** Freundlich adsorption isotherm constants  $K$  and  $n$  for different types of sand estimated from data of batch adsorption experiments

Freundlich isotherm constant	Green Sand	Synthetic Mn-oxide coated sand	Prepared Mn-oxide coated sand	Sylhet Sand
$K$ (mol/kg)/(mol/m <sup>3</sup> )	0.0495	0.2788	0.0606	0.0058
$n$ [dimensionless]	2.358	1.245	2.183	0.979



**Figure 4.29:** Relationship between Freundlich adsorption isotherm constants  $K$  and Mn-content in adsorbent

Figure 4.30 shows calculated removal of Mn on different Mn-oxide coated media, based on the Freundlich adsorption isotherm constants estimated in this study. The experimental data points have also been shown in the figure. It shows that “synthetic” Mn-oxide coated media with very high Mn-content (25,250 mg/kg) has significantly higher adsorption capacity, compared to the other two Mn-oxide coated media.



**Figure 4.30:** Calculated removal of Mn in different Mn-oxide coated media based on estimated Freundlich adsorption isotherm constants

#### 4.4 Leaching of Mn from Mn-coated Media

Experimental results presented above show that under favorable conditions (e.g., higher alkalinity, above neutral pH) dissolved Mn present in water may accumulate in the filter media during passage of water through it. As explained above, Mn retention in the filter media results from adsorption of Mn(II) and subsequent oxidation of Mn(II) by DO in the presence of bicarbonate ions. Thus, filter media employed to remove Mn from water would continue to accumulate Mn. Since dissolution of Mn-oxide is pH dependent and Mn is redox sensitive, changes in pH and redox condition within the filter media could potentially promote release of Mn from the high-Mn filter media. In order to assess the possibility of leaching of Mn from the Mn-oxide rich filter media, batch experiments were carried out to evaluate leaching of Mn under low pH and reducing conditions. This Section presents the results of these batch experiments.

#### 4.4.1 Effects of pH of Mn Leaching

A 50 ml airtight polypropylene tube (headspace-free) was filled with groundwater, collected from a deep tubewell pump station at BUET with Manganese concentration of around 0.022 mg/l. Detailed characterization of groundwater used in the experiments was described earlier in Table 3.1. Initial DO, pH and temperature of the water were 5.06, 6.88 and 27.2°C, respectively. 0.5 g of greensand (with 14,400 mg/kg of Mn), 0.2 g of prepared Mn coated sand (with 11,200 mg/kg of Mn); or 0.2 g of synthetic Mn coated sand (with 25,250 mg/kg of Mn) were added to the tubes, and the solutions were mixed several times by manual shaking. The pH values of the solutions in the tubes were adjusted between pH 4 to pH 10 by addition of acid or base. After 24 hours of equilibration time, the final pH was measured, and the solutions were filtered through a 0.2 µm disk filter and the filtrate samples were analyzed for Mn concentration.

Table 4.3 shows estimated leaching of Mn from three different Mn-oxide coated media at different pH values. It shows that leaching or release of Mn from different Mn-oxide coated media, though not significant, increases with decreasing pH. Release of Mn was relatively higher for the “prepared” and “synthetic” media, compared to green sand.

**Table 4.3:** Estimated leaching of Mn from Mn-oxide coated media at different pH values

***Synthetic Mn coated sand (0.2g): Initial Mn: 5.05 mg***

Target pH	Initial pH	Final pH	Mn(mg/l) in Filtrate	Quantity (mg) of Mn Leached	% Leaching
4.00	3.96	4.56	0.62	0.0310	0.614
5.00	5.00	5.34	0.36	0.0180	0.356
6.00	6.04	6.17	0.12	0.0060	0.119
7.00	7.05	7.05	0.05	0.0025	0.030
8.00	8.00	7.90	0.02	0.0010	0.020
9.00	9.02	8.47	0.01	0.0005	0.010
10.00	10.03	9.97	0.00	0.0000	-
6.88	6.88	7.01	0.04	0.0020	0.040

***Prepared Mn coated sand (0.2g): Initial Mn: 2.24 mg Mn***

Target pH	Initial pH	Final pH	Mn (mg/l) in Filtrate	Quantity (mg) of Mn Leached	% leaching
4.00	3.96	4.32	0.26	0.013	0.580
5.00	5.00	5.24	0.12	0.006	0.268
6.00	6.04	6.03	0.06	0.003	0.134
7.00	7.05	7.05	0.02	0.001	0.045
8.00	8.00	8.01	0.02	0.001	0.045
9.00	9.02	8.58	0.01	0.0005	0.022
10.00	10.03	10.07	0.01	0.0005	0.022
7.37	7.37	7.72	0.02	0.001	0.045

***Greensand (0.5g): Initial Mn: 7.2 mg Mn***

Target pH	Initial pH	Final pH	Mn (mg/l) in Filtrate	Quantity (mg) of Mn Leached	% leaching
4.00	3.96	4.37	0.22	0.011	0.153
5.00	5.00	5.40	0.04	0.002	0.028
6.00	6.04	6.22	0.04	0.002	0.028
7.00	7.05	7.09	0.02	0.001	0.014
8.00	8.00	7.92	0.04	0.002	0.028
9.00	9.02	8.54	0.05	0.0025	0.035
10.00	10.03	9.95	0.00	00	-
6.88	6.88	7.00	0.02	0.001	0.014

**4.4.2 Leaching of Mn under Anoxic Conditions**

A 50 ml airtight polypropylene tube (headspace-free) was filled with groundwater collected from a deep tubewell pump station at BUET. The groundwater was spiked with 1 g/l of glucose ( $C_6H_{12}O_6$ ) and seeded with aerated domestic sewage to induce anoxic condition (due to oxidation of glucose by bacteria). The mixture was aerated by a air diffuser. Initial DO, pH and temperature of the solution are 6.65, 7.53 and 26.5°C, respectively; after 24 hour, DO came down to 0.83 mg/l and after 48 hours, DO came down to less than 0.1 mg/l. Fixed amounts of different types of Mn-oxide coated sand were added to these tubes; 1.0 g of greensand (14,400 mg/kg of Mn), 0.5 g of prepared Mn coated sand (11,200 mg/kg of Mn), or 0.5 g of synthetic Mn coated sand (25,250 mg/kg of Mn) were added and the solutions were mixed several times by manual shaking. One set of experiment was performed without addition of Mn coated sand. After 120 hours of equilibration time, pH and DO were measured. The

suspension was filtered through a 0.2  $\mu\text{m}$  disk filter and the filtrate was analyzed for Mn content.

Table 4.4 shows leaching or release of Mn from different types of Mn-oxide coated media under anoxic condition. It shows that oxidation of organic matter by bacteria results in lowering of pH quite significantly (which is also likely to promote release of Mn). Table 4.4 shows that Mn leaching/ release from freshly “prepared” Mn-oxide coated media is significantly higher compared to the “synthetic” media and green sand (see Fig. 4.31). Anoxic condition resulted in release of up to 18% of Mn-content of this media. This suggests that creation of anoxic condition in a filter bed could result in release of significant Mn from the media.

**Table 4.4:** Estimated leaching of Mn from Mn-oxide coated media under anoxic condition

***Synthetic Mn coated sand (0.5g): Initial Mn: 12.625 mg Mn***

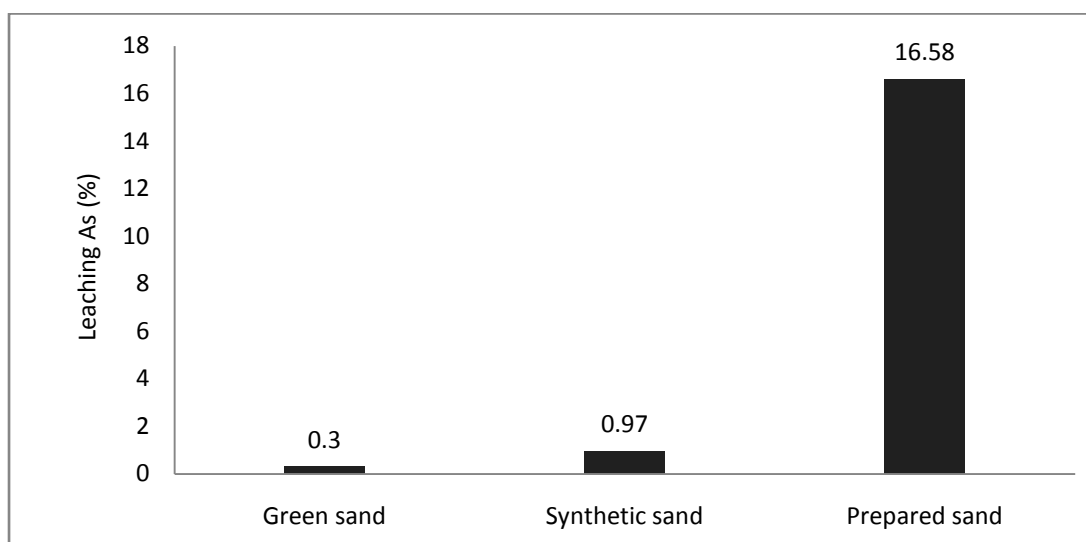
Sl. No.	Initial pH	Final pH	Mn (mg/l) in Filtrate	Quantity (mg) of Mn Leached	% Leaching	Average % Leaching
1	7.53	5.50	2.31	0.1155	0.915	
2	7.53	4.95	2.62	0.1310	1.038	0.97
3	7.53	5.16	2.39	0.1195	0.947	

***Prepared Mn coated sand (0.5g): Initial Mn: 5.6 mg Mn***

Sl. No.	Initial pH	Final pH	Mn (mg/l) in Filtrate	Quantity (mg) of Mn Leached	% Leaching	Average % Leaching
1	7.25	5.18	19.46	0.973	17.375	
2	7.25	5.52	15.96	0.798	14.250	16.6
3	7.25	4.96	20.27	1.014	18.107	

***Green Sand (1.0 g): Initial Mn: 14.4 mg Mn***

Sl. No.	Initial pH	Final pH	Mn (mg/l) in Filtrate	Quantity (mg) of Mn Leached	% Leaching	Average % Leaching
1	7.53	5.48	0.73	0.0356	0.247	
2	7.53	5.23	0.88	0.0440	0.306	0.30
3	7.53	5.03	1.0	0.0500	0.347	



**Figure 4.31:** Manganese leaching (%) under anoxic condition from different types of Mn-oxide coated media



## CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Introduction

In this study, laboratory investigations have been carried out to characterize the mechanisms of Mn(II) oxidation and removal in filter media and to evaluate the effectiveness of Mn and As removal in Mn-oxide coated filter media. Removal of Mn and As in filter columns made up of : (a) “prepared” Mn-oxide coated media, (b) “synthetic” Mn-oxide coated media, and (c) commercially available Mn-bearing “green sand” was evaluated. In addition, possible leaching of Mn from Mn-rich media under low pH, and anoxic conditions has also been assessed. This chapter presents the findings of the work, particularly with regard to mechanism of Mn(II) oxidation and removal in filter media, and ability of different Mn-oxide coated media in removing As and Mn from water. This chapter also presents some recommendations for future study.

### 5.2 Conclusions

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

- (1) The removal of Mn(II) during filtration through a granular media (sand) involves adsorption of Mn(II) onto filter media, followed by oxidation of Mn(II) in the presence of bicarbonate, creating/regenerating Mn-oxide coating, thus increasing Mn removal capacity of the media; the removal/oxidation of Mn(II) is favored at higher pH values and lower flow rates. Thus, removal of Mn(II) during filtration through granular media (sand) could be achieved without the addition of any oxidizing agent [for oxidation of Mn(II) to Mn(IV)], provided the water contains bicarbonate ion.
- (2) Mn-oxide coated filter media are very effective in removing dissolved Mn(II) from groundwater over a wide range of initial Mn concentration and pH. Mn removal efficiency increases with increasing Mn-content of the filter media, increasing Mn in the influent water and increasing pH.

- (3) Synthetic Mn-coated media with Mn content of about 25,250 mg/kg, the highest Mn content among the 3 media, performed best in removing Mn at higher flow rates. However, at lower flow rates, other media (“prepared Mn-oxide coated media” and “green sand”) also performed well. A contact time of about 1.5 minutes was found to be sufficient for almost complete removal of Mn under the experimental conditions employed in this work.
- (4) Removal of arsenic [As(III)] in Mn-oxide coated filter media has been found to be strongly dependent on pH. Removal of As decreased with increasing pH, especially at pH beyond 7.5 and virtually no As removal takes place at pH 9 and beyond. Arsenic removal increased with increasing Mn-content of the filter media.
- (5) At relatively lower pH values (less than 7.5), Arsenic [As(III)] appears to compete with bicarbonate ions for adsorption onto Mn-oxide coated media. Presence of phosphate significantly reduced arsenic removal due to competitive adsorption.
- (6) The leaching or release of Mn from different Mn-oxide coated media, though not significant, increases with decreasing pH. Release of Mn was relatively higher for the “prepared” and “synthetic” media, compared to green sand.
- (7) Under an anaerobic condition created by oxidation of organic matter (which also reduces pH of water significantly), Mn is leached/released from Mn-oxide coated media; Mn leaching/ release from freshly “prepared” Mn-oxide coated media is significantly higher compared to the “synthetic” media and green sand. This suggests that creation of anoxic condition in a filter bed could result in release of Mn from the media.

### **5.3 Recommendations for Further Studies**

As a continuation of the present work, research works should be carried out in the following areas in the future:

- (1) Physicochemical changes in the Mn-coated sand media with filter run time, and its possible implication on Mn removal.
- (2) Effect of process variables (e.g., backwashing, size and depth of media) on Mn/As removal and stability of Mn-coated media.
- (3) Characterization of Mn solids formed on the sand media (e.g., mineral phases of Manganese oxide).
- (4) Development of design criteria for simultaneous removal of Fe, As and Mn in household and community level removal plants.

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## Appendix A

### Data from Batch Experiments Carried out to Estimate Freundlich Adsorption Constants for different Adsorbents

**Table A1:** Batch experiment data for determination of Mn uptake capacity of greensand at pH=7.2±0.1 and temperature of 28°C (data shows the average data of 48, 50 and 52 hours of treatment)

Initial Mn concentration (mg/l)	Green sand (gm)	Sample volume (ml)	Final Mn conc (mg/l)	Final Mn conc, mol/m <sup>3</sup>	mg Mn adsorbed/gm green sand	mol Mn adsorbed/kg green sand
3.39	1.0	50	0.06	0.00110091	0.1665	0.00305504
3.39	0.7	50	0.2	0.00366972	0.2279	0.00418165
3.29	0.4	50	0.52	0.00954128	0.34625	0.00635321
12.91	1.0	50	1.24	0.02275229	0.5835	0.01070642
5.52	0.4	50	1.25	0.02293578	0.53375	0.00979357
12.03	1.0	50	1.4	0.02568807	0.5315	0.00975229
12.91	0.5	50	3.6	0.06605504	0.925	0.01697247

**Table A2:** Batch experiment data for determination of Mn uptake capacity of synthetic Mn coated sand at pH=7.1±0.1 and temperature of 26.6 to 28°C

Initial Mn concentration (mg/l)	Synthetic sand (gm)	Sample volume (ml)	Final Mn conc (mg/l)	Final Mn conc, mol/m <sup>3</sup>	mol Mn adsorbed/kg green sand
1.5	0.5	50	0.16	0.002912374	0.002439113
1.5	0.3	50	0.29	0.005278678	0.003670805
1.5	0.2	50	0.41	0.007462958	0.004960137
3	0.5	50	0.32	0.005824748	0.004878226
3	0.3	50	0.61	0.011103426	0.007250598
3	0.2	50	0.88	0.016018057	0.009647239
5	0.5	50	0.54	0.009829262	0.008118242

**Table A3:** Batch experiment data for determination of Mn uptake capacity of prepared Mn coated sand at pH=7.1±0.1 and temperature of 26.6 to 28°C

Initial Mn concentration (mg/l)	Prepared sand (gm)	Sample volume (ml)	Final Mn conc (mg/l)	Final Mn conc, mol/m <sup>3</sup>	mol Mn adsorbed/kg green sand
1.5	0.5	50	0.07	0.001274164	0.002602934
1.5	0.3	50	0.14	0.002548327	0.004125863
1.5	0.2	50	0.31	0.005642725	0.005415195
3	0.5	50	0.22	0.004004514	0.00506025
3	0.3	50	0.48	0.008737122	0.007644982
3	0.2	50	0.95	0.01729222	0.009328698
5	0.5	50	0.66	0.012013543	0.007899814

**Table A4:** Batch experiment data for determination of Mn uptake capacity of fresh Sylhet sand at pH=7.1±0.1 and temperature of 26.6 to 28°C

Initial Mn concentration (mg/l)	Fresh sand (gm)	Sample volume (ml)	Final Mn conc (mg/l)	Final Mn conc, mol/m <sup>3</sup>	mol Mn adsorbed/kg green sand
1.57	3	50	1.18	0.021478758	0.000118315
1.57	2	50	1.29	0.023481015	0.000127416
1.57	1	50	1.42	0.025847319	0.000136518
3	6	50	1.85	0.033674324	0.000174439
3	3	50	2.28	0.041501329	0.000218428
3	2	50	2.47	0.044959773	0.000241181
3	1	50	2.72	0.049510357	0.000254833

## Appendix B

### B1. Performance of Selected Community Fe-As Removal Plants

As a part of this study, performance of selected community level water treatment plants designed for removal of As, Fe and Mn was assessed. In this study, 7 existing community groundwater plants have been evaluated, all of which use filter media (sand, brick chips, and coal) for removing these constituents. Among the 7 community treatment plants, 5 were located in Manikganj and 2 in Sirajganj. The aim of this exercise was to get insights about removal of Mn in adsorptive filtration based removal systems under actual field conditions.



**Figure B1:** Three-chamber SEDA IRP in Manikganj

The community treatment plants (SEDA-IRPs) located in Manikganj have been designed for removal of both arsenic and iron. These five plants, all connected to shallow tubewells, are of two types. Three plants (plant No. M1, M4 and M5) consist of three chambers – aeration chamber, filtration chamber and storage chamber (see Figure B1). The up-flow filtration chamber has a cross-sectional area of  $8500 \text{ cm}^2$  and

depth 45 cm. The filter material in the filtration chamber consists of sand, brick chips and coal (exact composition and depth of filter material unknown).

The other two plants (plant No. M2 and M3) consist of two chambers – aeration chamber and filtration chamber. Here the filtration chamber is used for storage of water. The up-flow aeration chamber has x-sectional area of  $4500 \text{ cm}^2$  and depth 35 cm (see Figure B2). The same filter materials, e.g., sand, brick chips and coal have been used in these two plants; however, as before, the exact composition and depth of filter material are unknown.



**Figure B2:** Two-chamber SEDA IRP in Manikganj

The two community treatment plants (ITN-BUET MSF) in Sirajganj have been designed as Fe-As-Mn removal plants (see Figure B3). Both plants consist of three chambers. Plant No. 1 in Sirajganj consists of an aeration chamber (connected to a shallow tubewell), an up-flow filtration chamber (x-sectional area  $22,300 \text{ cm}^2$ ), and a down-flow filtration chamber (x-sectional area  $5600 \text{ cm}^2$ ). The depth of the filtration chambers is 30 cm and brick chips have been used as filter material (gradation unknown).

Plant No. 2 in Sirajganj also consists of an aeration chamber, an up-flow filtration chamber (x-sectional area 14,000 cm<sup>2</sup>), and a down-flow filtration chamber (7000 cm<sup>2</sup>). The depth of the filtration chambers is 30 cm and brick chips have been used as filter material (gradation unknown).

Table B1 shows the time of installation of the 7 community groundwater treatment plant as assessed in this study. For assessment of performance, raw and treated water samples were collected from these 7 treatment plants during February to October 2010; Table 3.3 shows the sampling dates. From the Manikganj treatment plants, water samples were collected 7 times, roughly once a month. From the Sirajganj, water samples were collected 6 times, also roughly once a month. From Sirajganj treatment plants, water samples were also collected from the up-flow and down-flow filtration chambers. The water samples were analyzed for a wide range of parameters, including pH, CO<sub>2</sub>, As, Mn, Fe, phosphate and alkalinity.



**Figure B3:** ITN-BUET multistage filtration unit in Sirajganj

**Table B1:** Installation and sampling dates for the 7 treatment plants assessed in this study

Location	Plant Identification No.	Installation Date	Sample Collection Dates
Manikganj	SEDA M1	05/11/2007	10/02/2010
Manikganj	SEDA M2	05/01/2004	09/03/2010
Manikganj	SEDA M3	10/02/2009	16/04/2010
Manikganj	SEDA M4	10/04/2001	13/05/2010
Manikganj	SEDA M5	10/01/2010	08/06/2010 08/07/2010 06/10/2010
Sirajganj	ITN-BUET S1	03/06/2008	26/02/2010
Sirajganj	ITN-BUET S2	28/04/2009	04/04/2010 06/05/2010 04/06/2010 09/07/2010 05/10/2010

Apart from water samples, solid (i.e., filter media) were also collected from the filtration units of the Manikganj treatment units (SEDA-IRPs) during second and last sampling. Solid (i.e., filter media) samples were also collected from the top of the up-flow and down-flow filter chambers of the Sirajganj filter units (ITN-BUET MSFs) during first sampling. The Mn contents of these solid media were determined after extraction with hydroxylamine hydrochloride.

Apart from these measurements, information were gathered on different operation and maintenance issues, e.g., use of the treatment plants, flow rate through the plants, and washing/ back-washing practices. This information along with the test results of collected water and solid samples were analyzed for assessing the performance of the community groundwater treatment units.

### ***Performance of SEDA Treatment Plants in Manikganj***

Performance of five different SEDA Plants of two different designs was evaluated in this study. For this purpose, raw and treated water samples were collected at 7



different times from these five plants. The major findings from the analysis of test results and other information gathered from the field are summarized below.

### **Iron Removal:**

Concentration of Iron (Fe) in raw water for all the five plants was relatively high, varying from about 7 to 13 mg/l. All five plants have been found to be very efficient in removing Fe from groundwater. Aeration followed by up-flow filtration has been found to be effective in removing Fe from groundwater. It should be noted that pH of raw water at the five plants varied over a narrow range of 6.95 to 7.16; alkalinity also varied over a relatively narrow range of 320 to 384 mg/l.

### **Arsenic Removal:**

The mechanism of Arsenic removal in the SEDA plants is adsorption onto Fe hydroxide flocs and co-precipitation with Fe hydroxides. Except for SEDA M5, arsenic concentration in the raw water of for the 4 SEDA plants varied from about 60 to over 120 µg/l. Since raw water Fe concentration for these 4 plants was relatively high, in all cases As was removed to levels below the Bangladesh standard of 50 µg/l. However, removal efficiency varied to some extent among these 4 plants, possibly due to the degree of aeration achieved. Although significant As was removed in the SEDA M5 plant, because of high initial concentration of As (over 600 µg/l), treated water did not satisfy the Bangladesh drinking water standard of 50 µg/l. Thus, raw water Iron (Fe) concentration and the effectiveness of the aeration chamber are the principal factors determining As removal in the SEDA treatment plants.

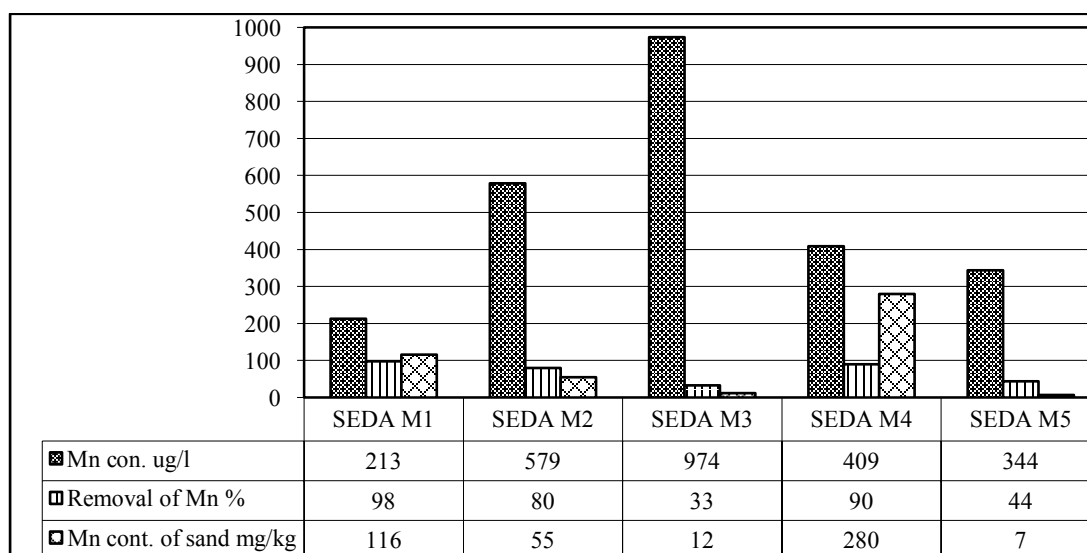
### **Manganese Removal:**

Table B2 shows Mn concentration in the raw and treated water samples collected from the five SEDA plants during the 7 sampling campaigns. Manganese concentration in raw water samples varied from 0.157 to 1.163 mg/l. Table B2 shows that Mn removal varied not only from plant to plant, but it also varied with time for a particular plant. For example, SEDA M1 plant showed very good Mn removal during the first 6 samplings, but showed very poor performance during the last sampling in October 2010. Manganese removal in SEDA M2 plant varied significantly over the 7 sampling periods. Mn removal was poor for the recently installed (2009) SEDA M3

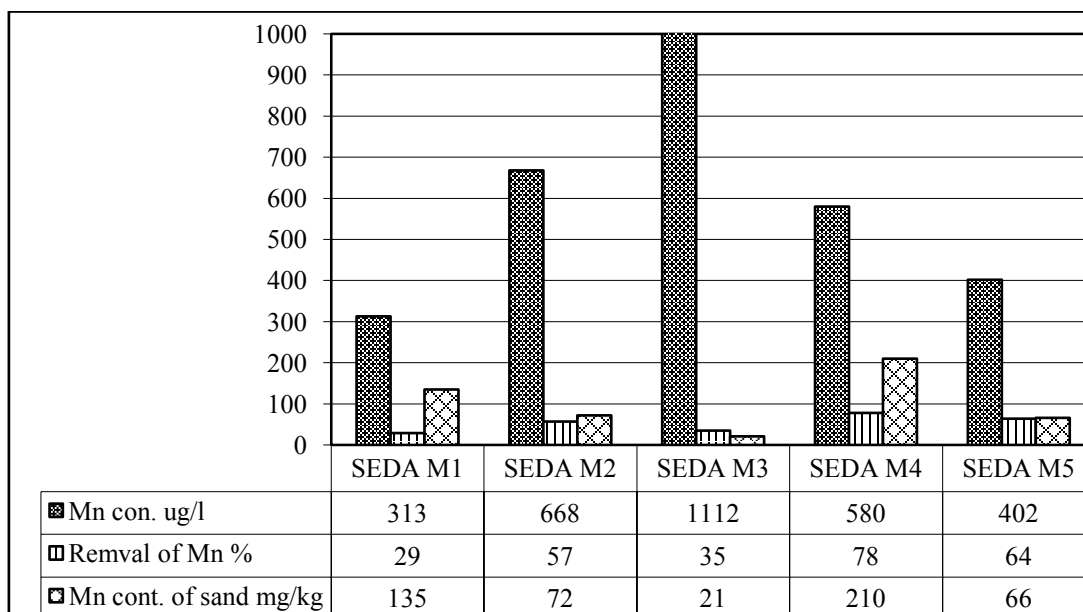
plant. Performance of SEDA M5 plant (installed in 2010) varied significantly over the assessment period. SEDA M4 plant (installed in 2001) showed good Mn removal up to March 2010, but Mn removal performance deteriorated to some extent during April to October 2010. Figure B4.1 and B4.2 show Mn removal performance of the 5 SEDA plants during 2<sup>nd</sup> sampling (9 March 2010) and 7<sup>th</sup> sampling (6 October 2010); it also shows the Mn contents of the filter media collected from the plants.

**Table B2:** Mn concentration (mg/l) in raw and treated water samples of SEDA plants

ID	R/T	Sampling Date						
		10/02/2010	09/03/2010	16/04/2010	13/05/2010	08/06/2010	08/07/2010	06/10/2010
M1	R	0.157	0.213	0.213	0.213	0.213	0.213	0.313
	T	0.004	0.005	0.080	0.003	< 0.001	< 0.001	0.222
M2	R	0.716	0.579	0.579	0.579	0.579	0.579	0.668
	T	0.235	0.116	0.077	0.141	< 0.001	--	0.290
M3	R	1.163	0.974	0.974	0.974	0.974	0.974	1.112
	T	0.914	0.648	0.439	0.182	0.630	0.850	0.721
M4	R	0.329	0.409	0.409	0.409	0.409	0.409	0.580
	T	0.038	0.042	0.175	0.186	0.116	0.179	0.128
M5	R	0.339	0.344	0.344	0.344	0.344	0.344	0.402
	T	0.146	0.193	0.084	0.027	0.168	0.005	0.144



**Figure B4.1:** Mn removal performance of SEDA plants on 9 March 2010 (2<sup>nd</sup> sampling)

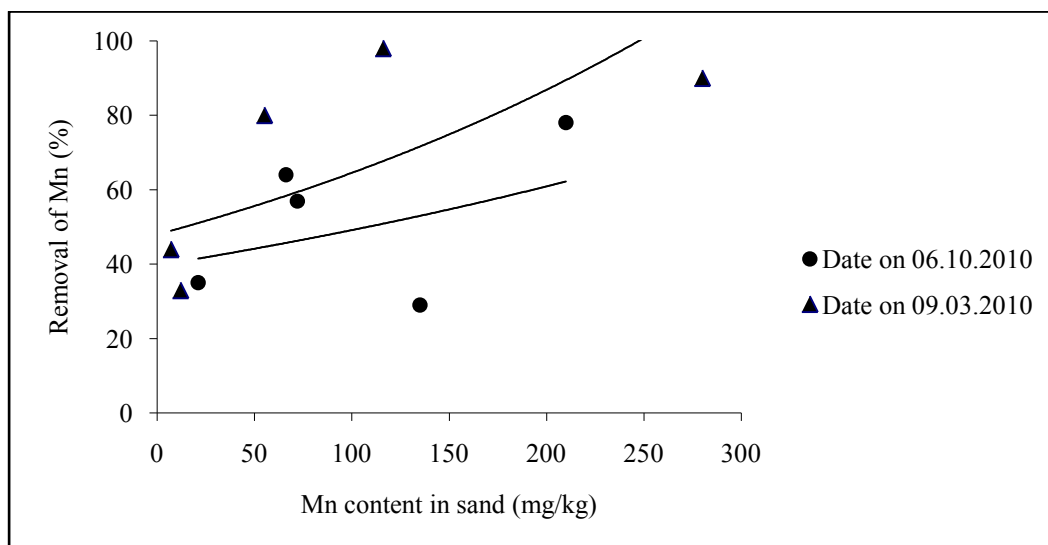


**Figure B4.2:** Mn removal performance of SEDA plants on 6 October 2010 (7<sup>th</sup> sampling)

Based on the raw and treated water quality, Mn content of filter solids and information gathered from the field on operation and maintenance of the plants, the following issues have been identified for the variable performance of the SEDA plants in removing Mn from groundwater.

- (a) Manganese content of the filter media is an important parameter for Mn removal; increasing Mn-content of filter media improved Mn removal efficiency. The Mn-content of the media, however, depend on Mn content of the raw water, filter run time/ contact time, and filter media washing practices.

Figure B5 shows Mn removal in the SEDA plants as a function of Mn-content of filter media. It shows that in general, Mn removal is positively correlated with the Mn content of the filter media.



**Figure B5:** Mn removal performance of SEDA plants as a function of Mn-content of media

- (b) Mn content of the filter media in the SEDA plants appear to depend mainly on filter run time and media washing practices (not so much on Mn content of raw water). The highest Mn content was found in the filter media of M4 plant, which is operational since 2001. On the other hand, Mn content was relatively lower for the M3 (installed in 2009) and M5 (installed in 2010) plants, which have been installed recently. Thus, it is apparent it takes a long time for the formation of Mn-coating on filter media under field conditions.

It was gathered from the field that the filter media of M2 and M3 plants are washed frequently, approximately once every 15 days. This washing practice probably also contributed to the relatively low Mn content of media of these two plants. On the other hand, the media of the M5 plant were not washed during the assessment period, and Mn content of the media increased relatively quickly from 7 mg/kg in March to 66 mg/kg in October.

Formation of Mn coating is likely to be affected significantly by the flow rate of water. However, it was not possible to determine flow rate of water through the media in the SEDA plants; flow rate in the plants varied with use of the plants. Therefore, it was not possible to quantitatively assess the effect of flow rate with Mn content of media of the SEDA plants.

(c) Filter media washing appear to significantly affect Mn removal performance. For example, the M1 plant performed well in removing Mn during the first 6 samplings, but performance deteriorated during the 7<sup>th</sup> sampling in October 2010. It was revealed during field visit that the media of the M1 plant was washed sometime in September 2010. The poor performance of the plant in October appears to be related to the washing of the filter media. This is because of the fact that during washing, the entire media is placed on a polythene sheet and washed with tubewell water, and then placed back into the filtration chamber. This practice removes/disturbs the Mn-rich top media layer that plays the major role in removing Mn. The washing practice also has the potential to remove some of the Mn coatings from the media.

The relatively poor performance of M2 and M3 plants and relatively low Mn-content of the media in M2 plant (compared to M1, which has been installed later) could also be related to the frequent washing of the media (approximately twice a month) of these two units. The relatively poor performance of M4 plant during April to October 2010 could also be related to the washing of the media of this plant in early April 2010.

### ***Performance of ITN-BUET MSF Treatment Plants in Sirajganj***

Performance of two ITN-BUET MSF Plants (identified as S1 and S2) was assessed in this study. For this purpose, raw and treated water samples were collected at 6 different times from these plants. The major findings from the analysis of test results and other information gathered from the field are summarized below.

#### **Iron Removal:**

Average concentrations of Iron (Fe) in raw water of S1 and S2 were about 13.2 mg/l and 34.2 mg/l, respectively. Average pH values of the plants were 6.8 and 6.5, respectively; while average alkalinity was about 140 for both plants. Both plants have been found to be very efficient in removing Fe from groundwater. Most of iron (Fe) was removed in the aeration chamber and up-flow filter chamber. Thus, aeration followed by up-flow filtration has been found to be effective in removing Fe from groundwater.

### **Arsenic Removal:**

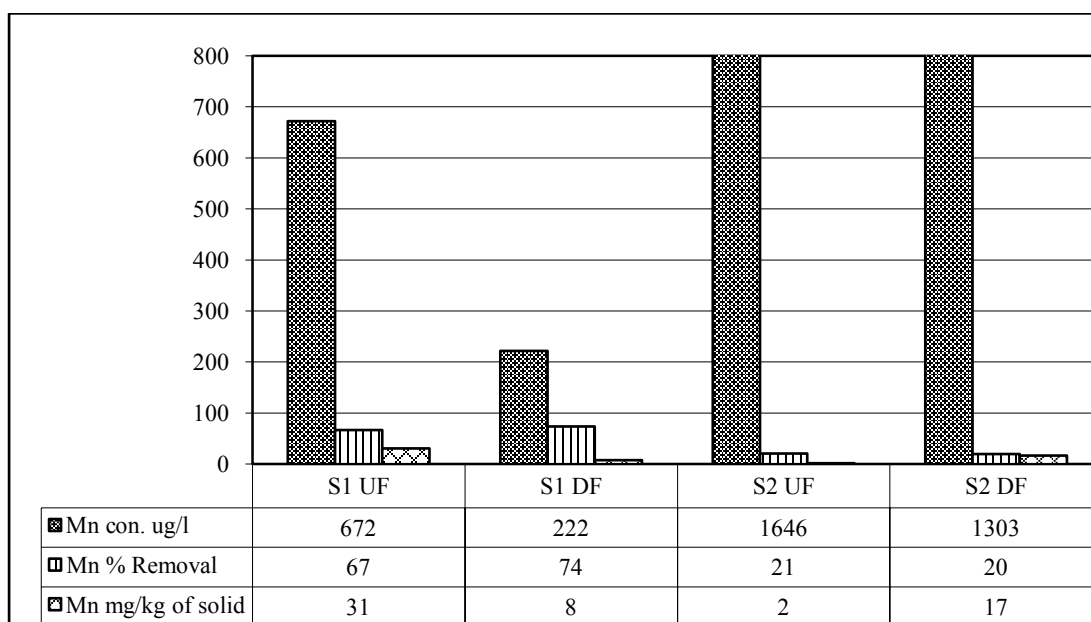
The average As concentrations in raw water of S1 and S2 plants have been found to be about 92 and 35  $\mu\text{g/l}$ , respectively. As shown in Table B3, As removal in the ITN-BUET plants is adsorption onto Fe hydroxide flocs and co-precipitation with Fe hydroxides. Both plants have been found to be very efficient in removing As from groundwater. Arsenic concentration in raw water was relatively low, and in most cases As concentration came down to be low the WHO guideline value of 10  $\mu\text{g/l}$ . Similar to Fe, most of As was removed in the aeration chamber and up-flow filter chamber. Thus, raw water Iron (Fe) concentration and the effectiveness of the aeration chamber are the principal factors determining As removal in the ITN-BUET treatment plants.

### **Manganese Removal:**

Table B3 shows Mn concentration in the raw water, after up-flow filter (limited data) and after down-flow filter (i.e., treated water) of the two ITN-BUET plants during the 6 sampling campaigns. Average Mn concentrations of raw water in S1 and S2 were about 0.58 and 1.477  $\text{mg/l}$ , respectively. In plant S1, significant removal of Mn was found during 5 out of 6 sampling campaigns. Available data (see Table B3) suggest that in most cases most of Mn was removed in the up-flow filtration chamber. In plant S2, overall Mn removal performance was very poor during the first two sampling campaigns; however, Mn removal was found to be very good during the last four samplings. Available data show poor Mn removal in the up-flow filtration chamber; the down-flow chamber was found to be more effective in removing Mn from groundwater. Figure B6 shows Mn removal performance of the two ITN-BUET plants (S1 and S2) on 26 February 2010; it also shows the Mn contents of the up-flow and down-flow filter media collected from the plants.

**Table B3:** Mn concentration (mg/l) in raw and treated water samples of ITN-BUET plants

Plant ID	Sample ID	Sampling Date					
		26/02/10	04/04/10	06/05/10	04/06/10	09/07/10	05/10/10
S1	Raw	0.672	0.570	0.566	0.552	0.492	0.649
	After UF	0.222	--	0.120	< 0.001	0.088	0.075
	After DF	0.036	0.046	0.120	< 0.001	< 0.001	< 0.001
S2	Raw	1.646	1.526	1.411	1.537	1.476	1.609
	After UF	1.303	--	0.609	1.461	0.526	0.278
	After DF	1.048	1.011	0.041	< 0.001	< 0.001	< 0.001

**Figure B6:** Mn removal performance of ITN-BUET plants on 26 February 2010 (1<sup>th</sup> sampling)

Based on the raw and treated water quality, Mn content of filter solids and information gathered from the field on operation and maintenance of the plants, the following issues have been identified for the variable performance of the ITN-BUET plants in removing Mn from groundwater. These findings are somewhat similar to those found for the SEDA plants.

- Manganese content of the filter media is an important parameter for Mn removal; increasing Mn-content of filter media improved Mn removal

efficiency. However, flow rate was also found to be very important in Mn removal; as found in laboratory experiments, higher flow rates resulted in poor Mn removal.

- Data in Table B3, Figure B6 and information gathered from field suggest that both Mn-content of media and flow rate through the media affected performance of the plants. The relatively better performance of the S1 plants in removing Mn appears to be related to the higher Mn-content of the up-flow filter media and relatively slow filtration rate.
- The poor performance of the S2 plant during the first two sampling campaign appears to be related to the low Mn-content of the up-flow filter (also the down-flow filter), and the relatively faster flow rate of water through the filter; the higher flow rate also appears to be responsible for the low Mn content of the filter media.
- The relatively better performance of the S2 plant during the subsequent 4 samplings appear to be due to long residence time/ contact time of water in/ with the filter media. During field visits for sample collection during the last 4 samplings, it was found out that the plant remained out of operation for long periods of time (from morning to afternoon). Therefore, the water samples that were collected in the afternoon were in contact with the filter media for a long time. This appears to be responsible for the good Mn removal performance of the plant.

## **B2. Removal of Mn-As-Fe from Natural Groundwater in Laboratory Filter Columns**

The efficiency of Mn-coated filter media in removing Mn, As, and Fe from natural groundwater collected from Manikganj and Sirajganj was also evaluated. Natural groundwater samples were collected from tubewells of SEDA M4 and M5 plants in Manikganj, and from the tubewells of ITN-BUET MSF S1 and S2 plants in Sirajganj. The characteristics of these groundwater samples are presented in Table B4. The pH value of the water samples are in the neutral range. Manganese concentrations vary from 0.344 mg/l (Manikganj M5) to 1.646 mg/l (Sirajganj S2). Arsenic concentrations



vary from a low of 34  $\mu\text{g/l}$  (Sirajganj S2) to vary high of 600  $\mu\text{g/l}$  (Manikganj M5). Iron concentrations of the two samples from Manikganj and one sample from Sirajganj were in the same range (varying from about 9 to 13  $\text{mg/l}$ ); iron concentration of one sample from Sirajganj was very high, over 35  $\text{mg/l}$ .

**Table B4:** Characteristics of natural groundwater used in laboratory experiments

Parameter	Unit	Manikganj: Plant M4	Manikganj: Plant M5	Sirajganj: Plant S1	Sirajganj: Plant S2
pH	--	7.06	7.05	6.97	6.67
Manganese	$\text{mg/l}$	0.442	0.344	0.672	1.646
Arsenic	$\mu\text{g/l}$	75	600	90	34
Iron	$\text{mg/l}$	10.89	8.78	12.66	35.63
Phosphate	$\text{mg/l}$	3.77	5.75	3.95	4.68
Alkalinity as $\text{CaCO}_3$	$\text{mg/l}$	322	375	142	156



**Figure B7:** Experimental set up for assessing performance of different Mn-coated media in removing Fe, Mn and As from natural groundwater from Manikganj and Sirajganj

In order to simulate conditions of the treatment plants, the groundwater samples were first passed through an up-flow filter column made up of stone chips, before passing

through different types of Mn-coated columns. A transparent acrylic column with a cross-sectional area of  $28.2 \text{ cm}^2$  was used to prepare the up-flow filter column; the column was fitted with flow control arrangements (see Figure B7). The total depth of stone chips in the column was 40 cm. The flow rate through the filter column was maintained between 0.6 to  $0.8 \text{ ml/cm}^2/\text{min}$ . Removal of Mn, As and Fe was evaluated in both the up-flow stone chips column and the down-flow Mn-coated column (prepared Mn-oxide coated media or synthetic Mn-coated media or Green sand).

The efficiency of Mn-coated filter media in removing Mn, As, and Fe from natural groundwater collected from Manikganj (tubewells of SEDA M4 and M5 plants) and Sirajganj (tubewells of ITN-BUET S1 and S2 plants) was evaluated. In order to simulate conditions of the treatment plants, the groundwater samples were first passed through an up-flow stone-chips filter column, before passing through different types of Mn-coated columns.

It should be noted that during transportation and storage of natural groundwater, some Fe present in the groundwater samples precipitated; Fe precipitation increased with increasing storage time. This phenomenon could not be avoided. As a result, significant arsenic present in water had the opportunity to adsorb onto and co-precipitate with Fe hydroxide solids; it is also possible for some Mn to adsorb onto Fe hydroxide flocs. These processes would lead to enhanced removal of arsenic and Mn in the up-flow stone chips column (which retains significant Fe flocs). The following section describes the major findings from the experiments.

### **Iron Removal:**

Concentration of Fe in groundwater from M4 and M5 plants were 10.9 mg/l and 8.8 mg/l, respectively; while those in groundwater from S1 and S2 plants were 12.7 mg/l and 35.6 mg/l, respectively. Significant removal of Fe was achieved in all experimental setups; in most cases removal exceeding 95% was achieved. Both filters, that is the up-flow stone chips filter and the down-flow Mn-coated filter, have been found to be effective in removing Fe. This suggests that Fe flocs that escaped the up-flow stone chips filter were captured by the down-flow filter column.

### **Arsenic Removal:**

Concentration of As in groundwater from M4 and M5 plants were 75 µg/l and 600 µg/l, respectively; while those in groundwater from S1 and S2 plants were 90 µg/l and 34 µg/l, respectively. Significant removal of As was achieved in all experimental set ups, and in all cases As concentration of the treated water was below the Bangladesh standard of 50 µg/l. Significant removal of As was achieved in the up-flow stone chips column (by adsorption onto and co-precipitation with Fe hydroxide flocs, which were retained by the column). Significant As removal was also achieved in the down-flow columns, possibly through retention of As-rich Fe flocs, which were not captured by the up-flow filter column.

### **Manganese Removal:**

Concentration of Mn in groundwater from M4 and M5 plants were 0.442 mg/l and 0.344 mg/l, respectively; while those in groundwater from S1 and S2 plants were 0.672 mg/l and 1.646 mg/l, respectively. Complete removal of Mn was achieved in all experimental set ups. Most of Mn was removed in the down-flow Mn-coated columns. Mn removal in the up-flow filter columns varied from a low of about 6% to a high of about 36%. Higher removal in the up-flow column is possibly an artifact of longer storage time of natural groundwater in the laboratory (as explained earlier).

## **B3 Possible Design Criteria for Optimal Removal of Mn and As**

Based on the laboratory experimental results and the assessment of community groundwater treatment plants, the following criteria could be suggested for the design of groundwater treatment plant for simultaneous removal of Fe, As and Mn.

- (1) A treatment plant for simultaneous removal of Fe, As and Mn should consist of three chambers – Aeration chamber, Up-flow roughing filter chamber, and Down-flow filter chamber.

The first chamber is to be designed for aeration of groundwater for oxidation of Fe(II) to Fe(III) [and possibly oxidation of some As(III) to As(V)] and subsequent precipitation of Fe(III) hydroxides. Adsorption of As onto Fe(III) hydroxides and co-precipitation of As with Fe(III) hydroxides will also take

place in this chamber. A portion of Fe and As will be removed in this chamber as a result of precipitation of Fe(III) hydroxides.

The Up-flow roughing filter chamber is to be designed for continued oxidation of Fe(II) to Fe(III) hydroxide and adsorption/ co-precipitation of As, and retention of Fe(III) hydroxides flocs. Most of Fe and As are likely to be removed in this up-flow chamber. A small portion of Mn may also get removed in the up-flow chamber, as a result of adsorption onto Fe(III) hydroxides and oxidation and surface precipitation. The current design practices (e.g., those used in the ITN-BUET MSF design) may be followed for the design of aeration chamber and up-flow roughing filter.

The Down-flow filtration chamber should be designed primarily for removal of Mn, and for removal of the portion of Fe and As that escapes the Up-flow roughing filter. The top layer of this down-flow chamber should consist of Mn-oxide coated media, for efficient removal of Mn.

- (2) The Down-flow filter chamber should have a layer of Mn-oxide coated media (preferably synthetic Mn-coated sand or green sand) at the top. Since it takes a long time for the formation of Mn-coating on filter media under field conditions, it is essential to provide Mn-coated sand media (i.e., synthetic media or green sand) at the top of the Down-flow filter. Based on the results of this study, a Mn-content of 7000 mg/kg and above should perform well.

The depth of the Mn-oxide coated sand media should be such that the contact time with this media is greater than about 1.5 minutes. The bottom of the Down-flow filter may consist of natural sand; the depth of this layer should be governed by the surface area of the filter and water storage requirements.

- (3) It is important to make sure that the Mn-oxide coated sand media at the top of the Down-flow filter is not disturbed or mixed with the rest of the filter media during washing/ backwashing. Therefore, it is proposed that the Mn-oxide coated media is placed separately, e.g., on a perforated tray at the top of the Down-flow filter.

- (4) It is important to keep the flow rate through the filter media (especially in the Down-flow chamber) as low as practicable, in order to ensure efficient removal of Mn. Slower flow rates would also improve removal of Fe and As. As noted above, the flow rate should be such that the contact time with Mn-oxide coated media at the top of the Down-flow filter chamber is at least 1.5 minutes.
- (5) It would be better to design the Down-flow filter chamber in such a way that the top layer of the filter does not remain submerged in water when the plant is not operational. Submerged condition may lead to reduction of Mn-oxide in the top layer, resulting in possible release of Mn.
- (6) There should be provision of effective backwashing of the Up-flow roughing filter chamber for efficient removal of Fe and As.
- (7) If the pH of groundwater increases to values approaching or exceeding 8, the effluent should be checked specially for arsenic, as arsenic removal by Mn-oxide coated media becomes very poor at higher pH values.