REMOVAL OF MANGANESE FROM GROUNDWATER BY OXIDATION AND ADSORPTION PROCESSES

SNIGDHA AFSANA

DEPARTMENT OF CIVIL ENGINEERING
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
DHAKA
AUGUST 2004

REMOVAL OF MANGANESE FROM GROUNDWATER BY OXIDATION AND ADSORPTION PROCESSES

A Thesis Submitted
by
SNIGDHA AFSANA

In partial fulfillment of the requirements for the degree of
Master of Science in Engineering (Civil & Environmental)

DEPARTMENT OF CIVIL ENGINEERING
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
DHAKA
AUGUST 2004

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

DEPARTMENT OF CIVIL ENGINEERING

CERTIFICATE OF APPROVAL

We hereby recommended that the thesis titled "**Removal of Manganese from Groundwater by Oxidation and Adsorption Processes**" submitted by **Snigdha Afsana**, Student No. 100104156 (P) be accepted as fulfilling this part of the requirements for the degree of Master of Science in Engineering (Civil & Environmental).

BOARD OF EXAMINERS

Dr. M. Ashraf Ali
Associate Professor
Dept. of Civil Engineering, BUET

:**Chairman** (Supervisor)

Dr. Sk. Sekender Ali
Professor and Head
Department of Civil Engineering, BUET

:**Member**

Dr. Feroze Ahmed
Professor
Department of Civil Engineering, BUET

:**Member**

Dr. M. A. Jalil
Professor
Department of Civil Engineering, BUET

:**Member**

Dr. M. Shah Alam Khan
Assistant Professor
Institute of Water and Flood Management, BUET

:**Member** (External)

DEDICATIONS

To my Family Members

DECLARATION

It is hereby declared that except for the contents where specific references have been made to the work of others, the studies contained in this thesis titled "Removal of Manganese from Groundwater by Oxidation and Adsorption Processes", is the result of investigation carried out by the author. No part of this thesis has been submitted elsewhere for any Degree, Diploma or other qualification.

(Dr. M. Ashraf Ali)
Counter Signed by Supervisor

(Snigdha Afsana)
Signature of the Candidate

ACKNOWLEDGMENT

First of all, I want to express my deepest gratitude to Almighty Allah for His graciousness, unlimited kindness and with the blessings of Whom the good deeds are fulfilled.

I am delighted to express my heartiest gratitude and sincerest indebtedness to my supervisor Dr. M. Ashraf Ali, Associate Professor, Department of Civil Engineering, BUET, for his continuous guidance, invaluable suggestions, affectionate encouragement and generous help at every stage of this study. His active interest in this topic and valuable advice was my source of inspiration to carry out the study.

Many thanks to the technical staff of the Environmental Engineering Laboratory, BUET, for their assistance and cooperation during the study.

A very special debt to my mother, husband, mother-in-law, father-in-law and other relatives and friends, who are always a constant source of inspiration throughout my life.

ABSTRACT

Although significant research works have been carried out on removal of arsenic and iron from groundwater, relatively little work has been done on the removal of manganese from groundwater in Bangladesh, in spite of its existence at relatively high concentration in many areas of Bangladesh. The primary concern regarding presence of manganese in water stems from its capability to stain sanitary-ware and laundry at concentration > 0.1 mg/L and its deposition in water distribution system, even at concentration as low as 0.02 mg/L. Chemical oxidation followed by filtration, is by far the most widely used manganese removal technique. Although coagulation by iron and aluminum salts has been widely used in Bangladesh for arsenic removal, little information is available on its capability in removing manganese from water. The present study is focused on assessing removal of manganese from groundwater using two chemical oxidants (potassium permanganate and bleaching powder) commonly available in Bangladesh. Besides, manganese removal by simple aeration, a method widely used for iron removal, has also been assessed. In addition possible manganese removal by coagulation with iron salts has also been evaluated.

In this study, it has been found that potassium permanganate is capable to remove manganese from groundwater very effectively over a wide range of initial manganese concentration. In the near-neutral natural pH range of groundwater, maximum manganese removal by permanganate oxidation was achieved at a permanganate dose equal to that required from stoichiometric consideration. However, for an initial manganese concentration of 2.0 mg/L, greater than 95% removal was achieved for a dose fraction equal to 0.8 times that required from stoichiometric consideration. A slightly (20%) higher permanganate dose did not have any significant effect on manganese removal.

Removal of manganese has been found to be highly dependent on pH. In general, removal increased as pH increased. Beyond pH of about 8, removal of manganese with permanganate is almost independent of pH. One drawback of permanganate oxidation is the development of color. It has been found that sand filters, with depths of 10 to 20 cm, are capable to reduce the color below Bangladesh drinking water standard. The sand filters were also found to be very effective in removing oxidized manganese solids.

In case of oxidation by chlorine (bleaching powder), better manganese removal could be achieved only at pH values 10 and above. In the neutral pH range, removal of manganese was relatively poor (less than 50%) for initial manganese concentration ranging from 1.0 to 10.0 mg/L. However, removal increased significantly as pH increased and almost complete removal was achieved at pH 10. Significant manganese removal (over 95%) can also achieved by simple aeration at high pH value (>10). Thus, at higher pH values, oxidation of manganese by air may have contributed to the higher manganese removal by bleaching powder.

In this study, experiments were carried out to evaluate the influence of dissolved iron on manganese removal by oxidation. It was found that when high amount of dissolved iron was present in water, manganese removal by chemical oxidation (with potassium permanganate) was very poor. This is partly due to the fact that a significant part of the oxidizing agent added for oxidation of manganese may have been utilized for oxidation of dissolved ferrous iron. It was also found that when both manganese and iron are present in water, pre-oxidation of iron (e.g., by aeration) prior to the addition of the oxidizing agent would improve manganese removal.

In this study, effectiveness of coagulation by iron salts in removal of manganese was evaluated. Coagulation experiments were carried out with and without the addition of an oxidizing agent (potassium permanganate) in order to ascertain the dominant removal mechanism (either oxidation or adsorption onto iron flocs). From results obtained in this study, it appears that very little manganese could be removed by adsorption onto the coagulated flocs of iron solids. The increased removal of manganese by coagulation with ferric chloride at higher pH values appears to be due the oxidation of manganese by atmospheric oxygen rather than adsorption of manganese on iron solids and their subsequent precipitation.

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 OCCURRENCE OF MANGANESE : LITERATURE REVIEW

CHAPTER 3 CHEMISTRY OF MANGANESE AND MANGANESE REMOVAL TECHNIQUES: LITERATURE REVIEW

CHAPTER 4 MANGANESE REMOVAL FROM GROUNDWATER BY OXIDATION

CHAPTER 5 MANGANESE OXIDATION IN PRESENCE OF IRON

CHAPTER 6 MANGANESE REMOVAL BY COAGULATION-ADSORPTION-COPRECIPITATION

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
AWWA	American Water Works Association
BGS	British Geological Survey
BAMWSP	Bangladesh Arsenic Mitigation Water Supply Project
DFID	Department for International Development
DPHE	Department of Public Health Engineering
MW	Molecular Weight
NHS	National Hydrochemical Survey
rpm	Revolution per minute
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Groundwater extracted through hand pump tubewells is the primary source of safe drinking water for the majority of the rural population of Bangladesh. Urban water supply is also heavily dependent on groundwater extracted through deep tubewells. Groundwater, being free from pathogenic microorganisms, receives wide public acceptance. However, groundwater contains a wide range of dissolved minerals and presence of certain dissolved constituents in excess of quantities recommended for drinking purpose may make it unsuitable or less acceptable as a source of water supply. The most widely reported groundwater-quality problems in Bangladesh include excessive concentration of arsenic, iron and salinity (in coastal areas). However, a close inspection of the available groundwater quality data (e.g., DPHE/ BGS, 2001) suggests that excessive concentration of manganese is also a significant problem in many areas of the country. The DPHE-BGS groundwater survey indicates that in Bangladesh manganese is present in groundwater at relatively high concentration. In the nationwide groundwater-quality survey (DPHE/ BGS, 2001), concentration of manganese up to 10 mg/l has been found, with an average value of 0.5 mg/l.

Presence of excessive manganese in potable water may cause significant adverse health impacts. It may also cause problems related to aesthetics and may cause precipitation in the water distribution system. Evidence of manganese neuro-toxicity has been found in people following long-term exposure to dusts containing manganese (such as people working in mines). The World Health Organization (WHO) has a provisional health-based guideline value of 0.5 mg/l for manganese in drinking water (WHO, 1993). The WHO guideline value fromconsumer acceptability consideration is 0.01 mg/l. Bangladesh Standard for manganese in drinking water is also 0.10 mg/l. At levels exceeding 0.1 mg/l, manganese in water supplies stains sanitary ware and laundry and causes undesirable taste in beverages. 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. In addition, certain nuisance organisms concentrate manganese and give rise to taste, odor and turbidity problems in distribution system. Therefore, the acceptability threshold value of manganese (0.10 mg/l) is five times less than the provisional health-based guideline value (0.5 mg/l)

A large percentage of wells in Bangladesh fail to satisfy the drinking water standard for manganese. Results of DPHE-BGS survey showed that about 39% of shallow tubewells and 2% of deep tubewells exceeded the WHO health-based guideline value (0.01 mg/l), whereas 79% of shallow tubewells and 22% of deep tubewells exceeded Bangladesh Standard value. High concentrations of manganese are found in many areas of the country, 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 concentration of arsenic may not have acceptable concentration of manganese (BGS/WaterAid, 2001). Again similar comparison between iron and manganese shows that water with high manganese concentration may not have high iron content. Distribution of manganese shows a distinctly different pattern from those of arsenic and iron. People of areas with high iron or manganese contents are more inclined to use the unprotected surface water sources, many of which are dangerously contaminated and completely unsuitable for domestic use without any treatment.

1.2 RATIONALE OF THE STUDY

High concentrations of manganese are found in many areas of the country, 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 concentration of arsenic may not have acceptable concentration of manganese (BGS/WaterAid, 2001). Again similar comparison between iron and manganese shows that water with high manganese concentration may not have high iron content. Distribution of manganese shows a distinctly different pattern from those of arsenic and iron. People of areas with high iron or manganese contents are more inclined to use the unprotected surface water sources, many of which are dangerously contaminated and completely unsuitable for domestic use without any treatment (Shahid, 1998).

Although significant research works have been carried out on removal of arsenic and iron from groundwater, relatively little studies (e.g., Ali et al, 2001; BAMWSP/ DFID/ Water Aid, 2001; Tahura et al. 2001) has been done on the removal of manganese from groundwater of Bangladesh. Manganese removal processes include ion exchange, aeration, greensand filtration, chemical oxidation and subsequent filtration, and biological manganese removal (Varner, 1992). Chemical oxidation and subsequent filtration is by far the most widely used technique for manganese removal from water (Raveendran et al, 2001). A number of water quality parameters, such as pH, Eh, iron, organic matter, etc. can affect the efficiency of manganese removal from water (Seeling et al., 1992). Choice of oxidizing agent is also an important consideration. Potassium permanganate and bleaching powder is the most commonly used oxidizing agent in Bangladesh. Although potassium permanganate is widely used, color development due to its presence is a concern. Effectiveness of commonly available oxidizing agents in removing manganese in groundwater and their impact on the overall removal process needs to be studied in more details (Tahura et al, 2001). Moreover, color produced from permanganate oxidation of manganese may be removed by using commonly used color removal techniques (e.g., sand filtration).

It should be noted that processes typically used for arsenic and iron removal, e.g., coagulation-adsorption- coprecipitation (for arsenic), adsorptive-filtration (for arsenic), and oxidation-precipitation-filtration (for iron), can possibly be used to remove manganese from water. In the project conducted by BAMWSP/ DFID/ Water Aid (2001), it has been found that some household treatment methods for arsenic removal (e.g., Aclan Activated Alumina Method, Sono 3-Kolshi Method) were capable to remove manganese in addition to arsenic. But however, in the study areas, manganese concentration in the feed water to this treatment plants were much below 1 mg/L. Where as mentioned earlier in the most of the areas in Bangladesh, manganese concentration is above 1 mg/L. Therefore, applicability of these methods of arsenic and iron removal needed to be assessed further for higher manganese concentrations.

Presence of iron in water can also considerably influence manganese removal from water by the oxidation process. Excess iron present in water can act as a coagulant and thereby may assist the settling of manganese solids in water. Moreover, iron hydroxide flocs

present in water may also act as an adsorbent for dissolved manganese. Thes
to be studied in more details.

1.3 OBJECTIVES OF THE STUDY:

The overall objective of this study was to evaluate the effectiveness of oxidation and adsorption processes in removing manganese from groundwater. The specific objectives of this research work include:

(1) Evaluation of the effectiveness of the commonly available oxidizing agents (potassium permanganate and bleaching power) in Bangladesh in removing manganese from groundwater;

(2) Better understanding of the processes and parameter (e.g., pH, oxidant dose, Eh, settling time etc) affecting removal of manganese from groundwater

(3) Evaluation of the effectiveness of aeration in removal of manganese present in groundwater.

(4) Assessment of the effectiveness of sand filtration in removing color produced due to the presence of permanganate;

(5) Evaluation of effectiveness the of potassium permanganate in removing both dissolved manganese and iron in groundwater; and

(6) Assessment of the effectiveness of coagulation-adsorption-coprecipitation processes (using both Fe(II) and Fe(III) salts) in removing manganese from groundwater.

1.4 ORGANIZATION OF THE THESIS

The study is presented in seven chapters, the first of which is general introduction. Chapter two and three contain a brief and selective review of relevant literature. In these chapters occurrence of manganese in groundwater, problem associated with manganese in groundwater of Bangladesh, manganese chemistry, and commonly used manganese removal techniques are discussed.

In Chapter Four, laboratory studies carried out on oxidation of manganese in groundwater using chemical oxidants (potassium permanganate and bleaching powder) and aeration have been described. Effect of pH, oxidant dose, manganese concentration, and settling and contact times on oxidation processes are explained and discussed.

In Chapter Five, experiments on oxidation of natural groundwater containing both dissolved iron and manganese are described with a view to find out the effect of the presence of iron on manganese removal by chemical oxidation as well as by aeration.

In Chapter Six, laboratory studies conducted to evaluate the effectiveness of iron coagulation (using both Fe(II) and Fe(III) salts) in removing manganese in groundwater are described. Effect of pH, coagulant dose, and manganese concentration in coagulation process are also discussed.

Conclusions and recommendations for future studies are given in Chapter Seven. Attempts are made to draw conclusions from various findings of the study. Recommendations presented in this chapter provide a basis for further study.

CHAPTER 2

OCCURRENCE OF MANGANESE

2.1 INTRODUCTION

Manganese in objectionable concentration has been detected in many water supply sources. Alone or in combination with other elements, manganese is capable to cause serious impairment of water quality. The problem is severe in context of Bangladesh, as groundwater of Bangladesh contains significantly high amount of dissolved manganese and at the same time groundwater is the vital source for safe water supply for drinking as well as other domestic and agricultural purposes. The number of tubewells in Bangladesh is not known but estimates put the number at around 6– 11 million. The vast majority of these are private tubewells, which penetrate the shallow alluvial aquifers to depths typically of 10–60 m. Irrigation boreholes typically tap shallow as well as deeper aquifers in the region of 70– 100 m depth. In some areas, notably the south and the Sylhet Basin of North-East Bangladesh, deep tubewells abstract groundwater from depths of 150 m or more. In the south, the deep tubewells have been installed to avoid high salinity at shallower levels (DPHE/ BGS, 2001). Shallow hand-dug wells occur in some areas, though they are much less common than tubewells. In many areas in Bangladesh, concentration of manganese is at much higher level than the limit acceptable to the rural people. People of such areas generally refuse to use tubewells water and inclined to use unsafe and impure pond and river water (DPHE/ BGS, 2001).

In this chapter, relevant literatures on occurrence and distribution of manganese in groundwater, and some common removal techniques have been reviewed. Possible health and other effects of manganese have also been focused.

2.2 OCCURRENCE OF MANGANESE

2.2.1 Physical and Chemical states

Manganese is a naturally-occurring element that can be found ubiquitously in the air, soil, and water. Manganese is the third most abundant metals on the earth's surface (9.5×10^2 ppm), making up approximately 0.1% of the earth's crust. Manganese is not found naturally in its pure (elemental) form, but is a component of over 100 mine 2004). Manganese is naturally occurring in many surface and ground wa in soils that may erode into these waters. However, human activities are also res for much of the manganese contamination in water in some areas.

Manganese is typically released from the rock strata and enters surface and ground water during mining. Manganese is dissolved in anoxic and acid water. Homogeneous precipitation of Mn(II) as an oxide phase does not occur below pH 8 but Mn(II) oxidation does occur in the presence of different mineral surfaces and/or via bacterial processes between pH 6 and 8. It is also known that bacterially mediated oxidation of dissolved manganese (Davidson et al, 1989).

Manganese is an important component of metals redox chemistry in soils, and marine and fresh water environments (Martin, 2003). Among the microorganisms capable of oxidizing Mn (II) are bacteria, algae, yeast, and fungi (Ehrlich et al, 1996). Because aqueous environments are dynamic, and water chemistry, aquatic plants, and algal communities can change with time, even when manganese (II) precipitates as stable oxide phases, these precipitates can be resolubilized if new reducing Environments form. The chemical and physical properties of elemental manganese and common manganese compounds are presented in Table 2.1 (USEPA, 2001).

Manganese problems are most likely to develop in water from wells with high carbonate and low oxygen as shown in the middle well in Figure 1. 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. However, the Amount of manganese dissolved in water often follows a trend of low to high back to low again as depth of the well increases (Seelig et al, 1992). A typical representation of dissolved manganese concentration with variation in well depth is shown in Figure 2.1.

Table 2.1 Physical and Chemical Properties of Manganese and that of Some Common Manganese Compounds

Name	Manganese	Manganous Chloride	Manganese Sulfate	Manganese (II, III) Oxide	Manganese Dioxide	Potassium Permanganate
Synonyms	Elemental manganese; Colloidal manganese; Cutaval; Magnacat; Tronamang	Manganese chloride; manganese dichloride; manganese bichloride; manganese (II) chloride	Manganese sulfate; Sulfuric acid, manganese (II) salt	Trimanganese Tetroxide; Mangano Manganic oxide; Manganese Tetroxide	Manganese peroxide; manganese binoxide; manganese black; battery manganese; pyrolusite	Permanganic acid; potassium salt; chameleon material
Valence	0	+2	+2	+2 and +3	+4	+7
Chemical Formula	Mn	$MnCl_2$	$MnSO_4$	Mn_3O_4	MnO_2	$KMnO_4$
Molec. Weight	54.9	125.84	151.00	228.81	86.94	158.04
Color		Pink	Pale rose-red	Black	Black	Purple
Physical State	Solid	Solid	Solid	Solid	Solid	Solid
Melting Point(^{0}C)	1244	650	700	1564	535	240
Boiling Point(^{0}C)	1962	1190	Decomposes at 850 °C	-	-	-
Solubility In water (g/100 ml)	Decomposes	723 (25°C)	120 (25°C)	Insoluble	Insoluble	63.8 (20°C)
Taste Threshold	-	-	-	-	-	-
Odor Threshold (air)	-	-	-	-	-	-

- No date available. (Source: USEPA, 2004)

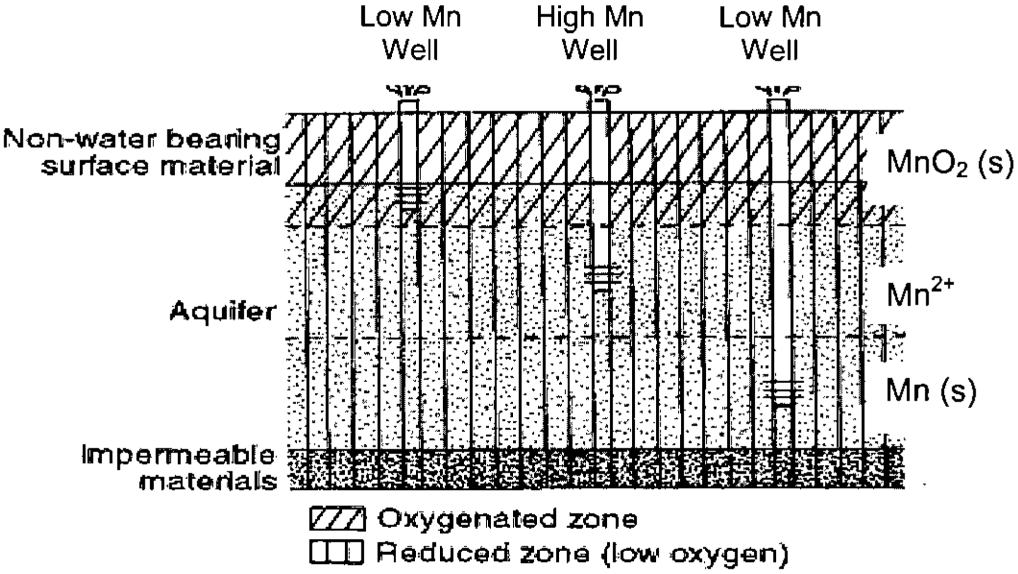


Figure 2.1 Dissolved manganese concentration with variation in depth of well (Seelig et al, 1992)

2.2.2 Sources of Manganese in the Environment

Manganese compounds are widely distributed in air, soil, and water. Sources of atmospheric manganese include industrial emissions, fossil fuel combustion, and erosion of manganese-containing soils.

Water

Manganese is naturally occurring in many surface and ground water sources and in soils that may erode into these waters. However, human activities are also responsible for much of the manganese contamination in water in some areas. Ambient manganese concentrations in seawater have been reported to range from 0.4 to 10 μg/L (ATSDR, 2000), with an average of about 2 μg/L (USEPA, 2004). Levels in freshwater typically range from 1 to 200 μg/L (USEPA, 2004). The United States Geological Survey's National Ambient Water Quality Assessment (NAWQA) has gathered limited data since 1991 on representative study basins around the U.S. This report indicates a median manganese level of 16 μg/L in surface waters, with 99th percentile concentrations of 400 to 800 μg/L (USEPA, 2004). Higher levels in aerobic waters are usually associated with industrial pollution. Manganese can be released to water by discharge from industrial facilities or as leachate from landfills and soil (Gregory et al, 1996). In the USA, reported industrial discharges in 1991 ranged from 0 to 17.2 t for surface water, from 0 to 57.3 t for transfers to public sewage, and from 0 to 0.114 t for underground injection (Barceloux, 1999).

An estimated total of 58.6 t, or 1% of the total environmental release of manganese in the USA, was discharged to water in 1991 (Casale et al, 2001). Overall, the detection frequency of manganese in U.S. groundwater is high (approximately 70% of sites assayed have measurable manganese levels) due to the ubiquity of manganese in soil and rock. In another worldwide survey, manganese is detected in about 97% of surface water sites (at levels far below those likely to cause health effects) and universally in sediments and aquatic biota tissues (at levels which suggest that it does not bioaccumulate (USEPA 1984).

Soil

Manganese constitutes approximately 0.1% of the earth's crust, and is a naturally occurring component of nearly all soils (ATSDR, 2000). Natural levels of manganese range from less than 2 to 7,000 ppm, with a geometric mean concentration of 330 ppm (Shacklette and Boerngen, 1984). Accumulation of manganese occurs in the subsoil rather than on the soil surface (ATSDR, 2000). Land disposal of manganese-containing wastes is the principal source of manganese releases to soil (Barceloux, 1999). An estimated 60–90% of soil manganese is associated with the sand fraction (WHO, 1981, as cited in ATSDR, 2000).

Air

Air levels of manganese compounds vary widely depending on the proximity of point sources such as ferroalloy production facilities, coke ovens, or power plants. The main sources of manganese releases to the air are industrial emissions, combustion of fossil fuels, and re-entrainment of manganese-containing soils (Lioy, 1983; USEPA, 1983, 1984, 1985a, 1985b). Average ambient levels near industrial sources have been reported to range from 220 to 300 ng Mn/m^3, while levels in urban and rural areas without point sources have been reported to range from 10 to 70 ng Mn/m^3 (Barceloux, 1999). Air erosion of dusts and soils is also an important atmospheric source of manganese, but no quantitative estimates of manganese release to air from this source were identified (USEPA, 1984). Volcanic eruptions can also release manganese to the atmosphere (Hasan, 2004).

Food

Manganese is found in a variety of foods including many nuts, grains, fruits, legumes, tea, leafy vegetables, infant formulas, and some meat and fish. Food is the most important source of manganese exposure in the general population (ATSDR, 2000; IOM, 2002; USEPA, 2003a). Particularly green vegetables (2 mg/kg), nuts (14.9 mg/kg), bread (8 mg/kg) and other cereals (6.81 mg/kg) have considerable amount of manganese. Infant formulas contain 50 to 300 µg/L manganese (Collipp et al., 1983), compared to human milk which contains approximately 3.5 to 15 µg/L manganese (ATSDR, 2000; U.S. EPA, 1997). Tea is a rich source of manganese, containing 2.71 mg/kg and is the largest contributor to manganese intake (Kondakis, 1989). Therefore heavy tea drinkers may have a higher manganese intake than the general population. An average cup of tea may contain 0.4 to 1.3 mg manganese (ATSDR, 2000).

Industrial Source of Manganese

Manganese compounds are produced from manganese ores or from manganese metal. Metallic manganese (ferromanganese) is used principally in steel production along with cast iron and superalloys to improve hardness, stiffness, and strength (NTP, 1993; USEPA, 1984). Manganese compounds have a variety of uses. The most common uses of manganese compounds are presented in Table 2.2 (Hasan, 2004).

Table 2.2 Uses of Some Common Manganese Compounds

Compound	Use
Methylcyclopentadienyl manganese tricarbonyl (MMT)	Fuel additive
Manganous carbonate	Ferrites; animal feeds; ceramics etc
Manganese chloride	Catalyst in organic compound chlorination; trace mineral supply for animal feed; brick_colorant; dye; dry-cell batteries; linseed oil drier; disinfecting;
Manganous acetate	Mordant in dyeing; drying agent for paint and varnish;
Manganese ethylenebisdithiocarbamate	Agricultural fungicide
Manganese oxide	Ferrites; ceramics; fertilizer; livestock feed additive
Manganese phosphate	Ingredient of proprietary solutions for phosphating iron and steel
Manganese sulfate	Livestock feed additive; fertilizer; glazes; varnishes; ceramics; fungicides
Manganous trifluoride	Fluorinating agent in organic chemistry
Manganese borate	Drying agent for varnish and oil; linseed oil drier; leather industry
Manganous nitrate	Porcelain colorants; manufacture of reagent grade manganese dioxide
Manganese dioxide (electrolytic manganese, pyrolusite)	Dry-cell batteries; matches; fireworks; porcelain; glass bonding materials; amethyst glass; oxidizer
Potassium permanganate	Oxidizing agent; water and air disinfectant; antialgal agent; metal cleaning, tanning, and bleaching agent; fresh flower and fruit preservative

Sources: U.S. EPA (1994a); ATSDR (2000); Merck (1983).

2.2.3 Environmental Fate

Manganese compounds may be present in the atmosphere as suspended particulates resulting from industrial emissions, soil erosion, volcanic emissions, application of manganese-containing pesticides, and the burning of MMT-containing gasoline (USEPA, 2004). Early analysis of emissions suggested that manganese from combustion of MMT is emitted primarily as manganese tetroxide (Mn_3O_4) (Ter Haar et al., 1975, as cited in ATSDR, 2000). However, more recent testing suggests that when very low levels of MMT are combusted (i.e., concentrations comparable to the currently allowed levels), manganese is emitted primarily as manganese phosphate and sulfate. The reported formal charge of the emitted manganese is +2.2, with a mass median aerodynamic diameter of 1 to 2 microns (Ethyl Corporation, 1997, as cited in Lynam et al., 1999). Uncombusted MMT rapidly decomposes to manganese oxide, carbon dioxide, and organic compounds in the atmosphere and has a half-life of only a few seconds in the presence of sunlight (Lynam et al., 1999; Zayed et al., 1999). Because particle size is small, atmospheric manganese distribution can be widespread. These particles will eventually settle out into surface waters or onto soils via the process of dry deposition. Little information is available on the chemical reactions of atmospheric manganese, but it is expected to react with sulfur and nitrogen dioxide. The half-life of manganese in air is only a few days (ATSDR, 2000).

Transport and partitioning of manganese in water is dependent on the solubility of the manganese form. In surface waters, manganese occurs in both dissolved and suspended forms, depending on such factors as pH, anions present, and oxidation-reduction potential (ATSDR, 2000). Often, manganese in water will settle into suspended sediments. Anaerobic groundwater often contains elevated levels of dissolved manganese. The divalent form (Mn^{2+}) predominates in most water at pH 4–7, but more highly oxidized forms may occur at higher pH values or result from microbial oxidation (ATSDR, 2000). Manganese in water can be significantly can bioaccumulate in lower organisms (e.g., phytoplankton, algae, mollusks, and some fish), but not in higher organisms, and biomagnification in food-chains is not expected to be significant (ATSDR, 2000). Bioconcentration factors (BCFs) of 10000-20000 for marine and freshwater plants, 2500-6300 for phytoplankton, 300-5500 for marine algae, 800-830 for inter-tidal mussels, and 35-930 for fish have been estimated (Folsom et al., 1963; Thompson et al., 1972). The high reported BCFs probably reflect the essentiality of manganese for a wide variety of organisms; specific uptake mechanisms exist for essential elements. Little information is available on the biodegradation of manganese-containing compounds in water, but factors such as pH and temperature are important for microbial activities (Hurley, 1984).

2.2.4 Manganese Intake

Adequate Intake (AI) values have been determined for manganese by the Food and Nutrition Board of the Institute of Medicine has fixed the amount of manganese intake per day for different gourp of people. The tabular form is shown in Table 2.3 (USEPA, 2004)

Table 2.3 Adequate Manganese Intakes for Men, Women and Children

Age Group	Males	Females
Infants, 0-6 months	3 μg/day	3 μg/day
Infants, 7-12 months	0.6 mg/day	0.6 mg/day
Children, 1-3 years	1.2 mg/day	1.2 mg/day
Children, 4-8 years	1.5 mg/day	1.5 mg/day
Boys, 9-13 years	1.9 mg/day	--
Boys, 14-18 years	2.2 mg/day	--
Girls, 9-18 years	--	1.6 mg/day
Adults, 19 years	2.3 mg/day	1.8 mg/day
Women- pregnant (lactating)	--	2 mg/day (2.6 mg/day)

Source: (USEPA, 2004)

2.3 UNDESIRABLE EFFECTS OF MANGANESE

Manganese is one of the most difficult elements to remove from surface waters. Presence of manganese primarily interferes with water uses. In higher concentrations manganese causes the following problems (Seelig et al, 1992):

1. Staining: At levels exceeding 0.1 mg/l, manganese in water supplies stains sanitary ware and laundry. Where the concentration of manganese is high, the color of the staining tends toward more black or gray.
2. Taste: Manganese causes a metallic or vinyl type taste in the water.

3. Appearance: Manganese will often give an oily appearing, "crusty" sheen to the water surface. (Oil does not appear "crusty" when disturbed, but "feathers out" like a rainbow).
4. Sulfur Taste: Hydrogen Sulfide, which causes a characteristic "rotten egg" odor, can also be liberated by the same conditions (i.e. low dissolved oxygen and low pH) that cause manganese to dissolve in water. Hydrogen sulfide is frequently encountered in water with excessive manganese. Some of the treatment methods used to remove iron and manganese will also "remove" hydrogen sulfide gas. Presence in high concentrations, manganese may cause an unpleasant metallic taste to the water (Raveendran et al, 2001).
5. Deposits accumulation: The presence of manganese in drinking water may lead to accumulation of deposits in the distribution system. Even at a concentration of 0.02 mg/l, manganese may form coating on distribution pipes, which may slough off as a black precipitate.
6. Clogging: Manganese supports the growth of manganese bacteria. This non-health related bacteria can clog strainers, pumps, and valves. Periodic or continuous chlorination is the best means to control manganese bacteria. Once present, manganese bacteria are difficult to purge from a well.

In agricultural fields, where groundwater is used for irrigation purpose, presence of manganese in water causes irrigation difficulties. Dissolved manganese in water becomes insoluble either by bacteria mediated oxidation or by atmospheric oxidation. Manganese solids the deposits and results in clogging in different parts of the pump. Oxidized manganese produced by iron bacteria often results in the formation of an ochre sludge or slime mass, which is capable of plugging the entire irrigation system (Boman et al ,1999).

2.4 HEALTH 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 (NRWA, 2004).

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

2.4.1 Short-term Exposure Studies

Neurological

Kawamura et al. (1941) reported health effects resulting from the ingestion of manganese-contaminated well water for an estimated 2-3 months by 25 individuals. The source of contamination was identified as leachate from approximately 400 dry cell batteries buried near the drinking water well. The concentration of manganese in the well water was in average 28 mg Mn/L or higher. Assuming a daily water intake of 2L, with a minimum of 2 mg Mn from food, a dose of at least 58 mg Mn/day is estimated. This exposure level is quite uncertain and it is estimated that it is around 25-30 times the level considered to be safe and adequate by the Food and Nutrition Board of the Institute of Medicine (IOM, 2002).

Health effects reported by Kawamura et al. (1941) included lethargy, increased muscle tonus, tremor and mental disturbances. Out of 25 people examined, 15 had symptoms. Five cases were considered severe, 2 cases were categorized as moderate, and 8 cases were described as mild. The most severe symptoms were observed in the elderly. Younger people were less affected, and symptoms of intoxication were completely absent in young children (age 1 to 6 years) (USEPA, 2004).

2.4.2 Long-term Exposure Studies

Neurological

The neurological effects of inhaled manganese have been well documented in humans chronically exposed to elevated levels in the workplace (ATSDR, 2000; Canavan et al., 1934; Cook et al., 1974; Roels et al., 1999). The syndrome known as "manganism" is caused by exposure to very high levels of manganese dusts or fumes and is characterized by a "Parkinson-like syndrome" including weakness, anorexia, muscle pain, apathy, slow speech, monotonous tone of voice, emotionless "mask-like" facial expression, and slow clumsy movement of the limbs. In general, these effects are irreversible (USEPA, 2004).

By the oral route, manganese is often regarded as one of the least toxic elements, although there is some controversy as to whether the neurological effects observed with inhalation exposure also occur with oral exposure. Several case reports of oral exposure to high doses of manganese have described neurological impairment as an effect, but the quantitative qualitative details of exposure necessary to establish direct causation are lacking. An individual who took large mineral supplements over several years displayed symptoms of manganism (Banta and Markesbery, 1977).

Results from studies of an Aboriginal population in Groote Eylandt have been cited as additional evidence for a relationship between elevated manganese exposure, violent behavior, and adverse health effects (COMA, 1998).

Cancer and Mutagenicity Studies

Mutagenicity

The genotoxic potential of high manganese exposure in humans is not known (IPCS, 1999). Elias et al. (1989) found an increase in the incidence of chromosomal aberration in metal active gas welding workers who had been welding for 10-24 years. Occupational exposure to nickel, as well as manganese, was reported. Since nickel is known to cause chromosomal aberration via inhalation, the results could not be attributed solely to the influence of manganese (USEPA, 2004)

Carcinogenicity

No studies are available on the potential carcinogenicity of high exposure to manganese in humans (ATSDR, 2000). USEPA believes that the available data on occurrence, exposure, and other risk considerations suggest that regulating manganese does not present a meaningful opportunity to reduce health risk. Only the non-enforceable secondary MCL for manganese of 0.05 mg/L will remain in effect (NRWA, 2004).

2.4.5 Standards and Guideline Values for Manganese

The Environmental Protection Agency (EPA) standards for drinking water fall into two categories: Primary Standards and Secondary Standards. Primary Standards are based on health considerations and are designed to protect people from three classes of pollutants: pathogens, radioactive elements and toxic chemicals. Secondary Standards are based on taste, odor, color, corrosivity, foaming and staining properties of water. Iron and manganese are both classified under the Secondary Maximum Contaminant Level (SMCL) standards. The SMCL for manganese in drinking water is 0.05 mg/l (ppm) (Lemley, 1999). The World Health Organization (WHO) has a provisional health-based guideline value of 0.5 mg/l for manganese in drinking water (IOM, 2002). The WHO guideline from aesthetic perspective is 0.10 mg/L. Bangladesh Standard for manganese in drinking water is also 0.10 mg/l.

2.5 OCCURRENCE OF MANGANESE IN GROUNDWATER OF BANGLADESH

The most widely reported groundwater-quality problems in Bangladesh include excessive concentration of arsenic, iron and salinity (in coastal areas). Although Considerable research works have been carried out on occurrence and removal of arsenic as well as of iron, relatively little work has been done on the manganese problem in groundwater of Bangladesh. The National Hydrochemical Survey (NHS) conducted in 2000 by British Geological Survey (BGS) in collaboration with DPHE and DFID (DPHE/BGS, 2001) provides the most comprehensive information on manganese in groundwater of Bangladesh. Using this survey data various aspects of manganese distribution and occurrence in groundwater of Bangladesh has been prepared by Hasan (2004). Groundwater survey indicates that iron and manganese are present in high concentrations. Concentration of manganese in groundwater has been found as high as 10 mg/l, with an average value of 0.5 mg/L. The high values are related to the anaerobic conditions dominant in the aquifers (BGS/ WaterAid, 2001). A large percentage of wells in Bangladesh fail the health guideline value specified by WHO (0.5 mg/L). A total of 938 samples (26.5% of all samples) had manganese concentration below 0.1 mg/L.

Percentile distribution of manganese in groundwater of Bangladesh is summarized in Table 2.4. The table reports the number of well with specific manganese concentration range. Table 2.4 indicates the median concentration of manganese is about 0.3 mg/l. Distribution of manganese in number of wells is shown in Figure 2.2. From Fig. 2.2 it can be noted that the most frequent concentration occurrence of manganese lay within the concentration range of 0.1 to 0.5 mg/L, accounting for about 38.6% of all sample wells. About 35% of sample wells exceed WHO health based guideline value and about 73% exceeds Bangladesh guideline value.

The distribution of manganese in groundwater of Bangladesh is shown in Figure 2.3. From Figure 2.3 it appears that high concentrations of manganese are found all over the country and the distribution are very scattered. It also indicates that groundwater in coastal region of south part of the country has lower manganese concentration (< 0.1 mg/L). However, the regional trends, more precisely shown in Figure2.4, indicate that the central, north and south-east regions of Bangladesh have higher concentrations of manganese.

Table 2.4 Mn Concentration Expressed as Percentile (n=3534)

Percentile	Mn Concentration less or equal to (mg/L)
10	0.03
20	0.068
30	0.123
40	0.185
50	0.287
60	0.428
70	0.613
80	0.892
90	1.365
95	1.9
99	3.697

(Source: Hasan, 2004)

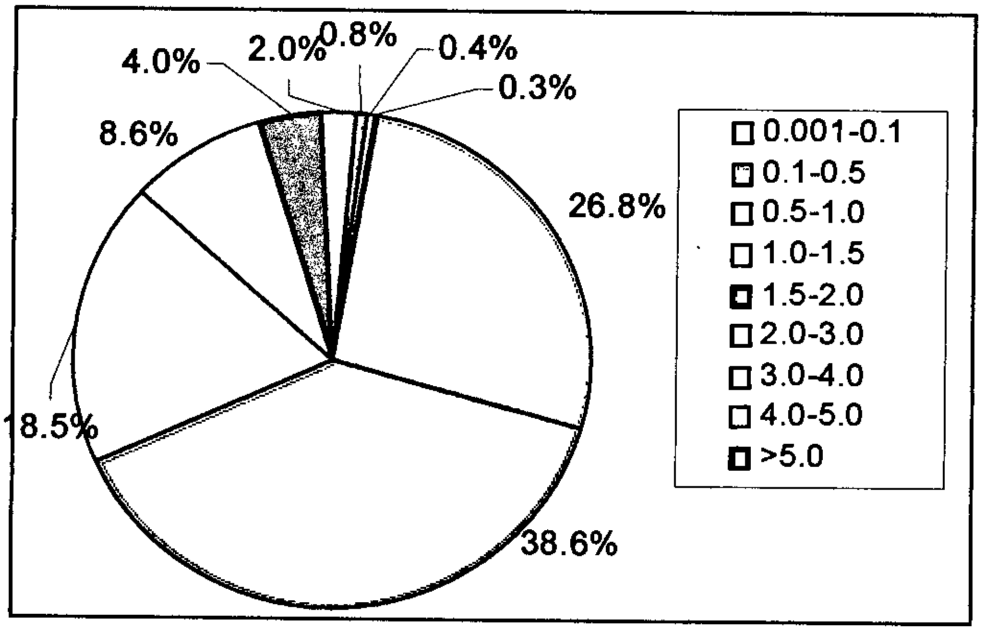


Figure 2.2: Manganese distributions in groundwater

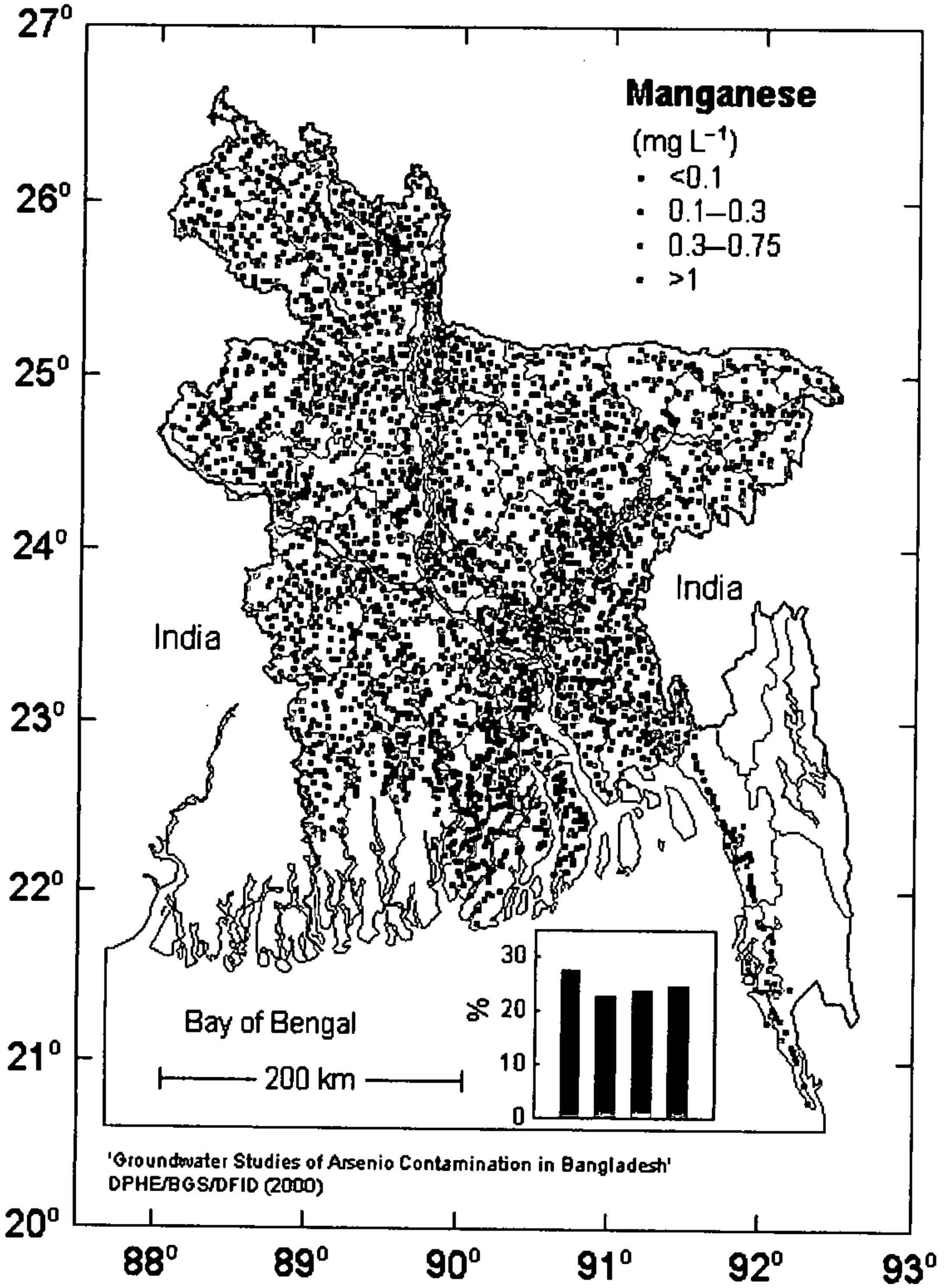


Figure 2.3 Distribution of manganese in groundwater of Bangladesh

(Source: BGS/DPHE, 2001)

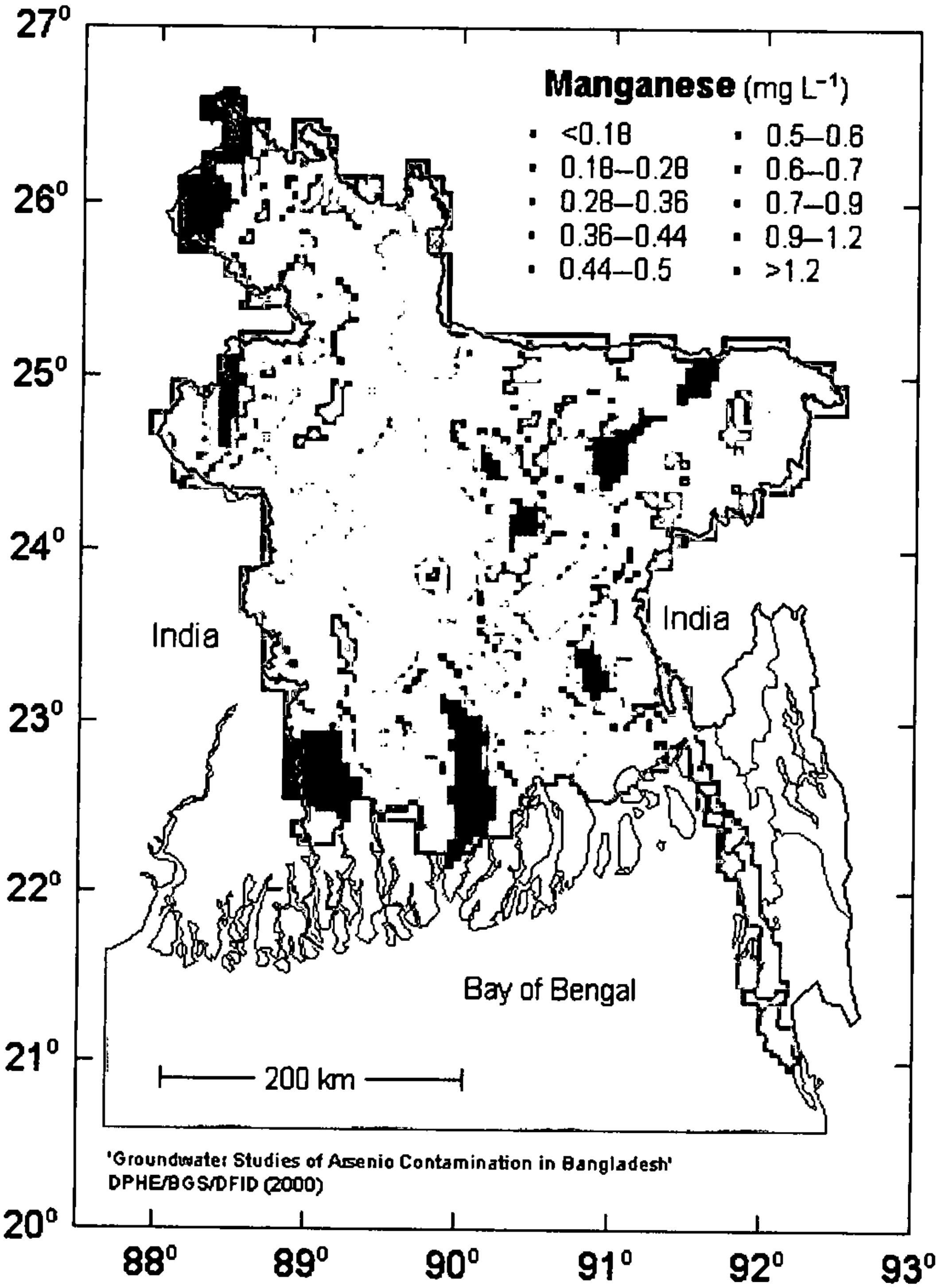


Figure 2.4 Smoothed map of manganese concentration in groundwater

(Source: BGS/DPHE, 2001)

The average manganese concentration distribution for each individual division is presented in Table 2.5. It shows that Rajshahi division has the highest average manganese concentration (0.731 mg/L), where 521 wells among the 1072 wells exceed the WHO health-based guideline value (0.5 mg/L) and 84% of the test wells (about 900 wells) exceed Bangladesh guideline value of manganese. The lowest average manganese concentration is found in Barisal division. The average concentrations for each division above the WHO guideline value lie between 0.738-1.03 mg/L (Hasan, 2004).

Table 2.5 Manganese Occurrence Summaries for Different Divisions

Division	Concentration below WHO health- based guideline value			Concentration above WHO health-based guideline value				Total	
	No of wells	Percent-age (%)	Mean conc. (mg/L)	No of wells	Percent-age (%)	Max. conc. (mg/L)	Mean conc. (mg/L)	No of Wells	Mean Conc. (mg/L)
Barisal	277	7.8	0.055	18	0.5	2.07	1.03	295	0.115
Chittagong	311	8.8	0.19	134	3.8	4.67	1.10	445	0.645
Dhaka	600	17.0	0.175	388	11.0	8.39	1.37	988	0.646
Khulna	330	9.3	0.181	144	4.1	3.24	1.10	474	0.460
Rajshahi	551	15.6	0.202	521	14.7	9.98	1.29	1072	0.731
Sylhet	216	6.1	0.202	44	1.2	2.06	0.74	260	0.292
Total	2285	64.7	0.172	1249	35.3	3.98	1.25	3534	0.554

(Source: Hasan, 2004)

The most contaminated district with respect to manganese Kurigram, with average manganese concentration of 1.336 mg/L, of which about 80% wells have manganese concentration above of WHO health-based guideline value. Manganese concentration distribution in the most contaminated 17 districts is shown in Table2.6. About 80% or more of the tubewells in these 17 districts contain manganese above the Bangladesh standard with average concentrations exceeding the WHO health-based guideline value. The highest manganese concentration (about 10 mg/L) is found in Jaipurhat. But this concentration was found in only one test well.

Table 2.6 Manganese Statistics for the 17 Most Contaminated Districts

District	No. of Wells	Avg Mn conc. (mg/L)	Minimum Mn Conc. (mg/L)		Max Mn conc. (mg/L)	Percentage of wells in specific Mn conc. range (mg/L)				Percentage of wells exceeding	
			Shallow	Deep		<0.1	0.1-0.5	0.5-2.0	>2.0	Bangladesh Standard (0.1 mg/L)	WHO guideline value (0.5 mg/L)
Kurigram	77	1.336	0.015	<.001	5.23	4	19	56	21	96	77
Narayanganj	30	1.276	0.003	0.133	8.39	7	27	43	23	93	67
Sirajganj	89	1.249	0.016	<.001	3.77	4	15	63	18	96	81
Rajbari	34	1.195	0.085	0.943	3.87	3	9	76	12	97	88
Pabna	78	1.083	0.111	<.001	5.54	0	25	65	10	100	74
Narsingdi	56	0.979	0.009	<.001	4.03	18	23	50	9	82	59
Magura	32	0.971	0.087	<.001	3.14	3	25	63	9	97	72
Tangail	91	0.922	0.006	<.001	3.8	12	23	56	9	88	64
Jaipurhat	40	0.907	0.079	<.001	9.98	3	47	42	8	98	48
Manikganj	47	0.868	0.001	<.001	6.03	22	37	28	13	79	40
Rajshahi	78	0.859	0.017	<.001	3.82	13	23	55	9	87	64
Natore	51	0.841	0.145	<.001	2.13	0	24	73	4	100	76
Sherpur	51	0.814	0.032	0.404	7.83	2	53	41	4	98	45
Faridpur	63	0.806	0.008	0.133	3.83	13	35	43	10	87	52
Gaibandha	71	0.787	0.038	<.001	4.59	8	28	61	3	92	63
Jamalpur	63	0.771	0.014	<.001	4.6	10	38	48	5	90	52
Meherpur	15	0.743	0.01	<.001	2.35	7	20	67	7	93	73

(Source: Hasan, 2004)

Distribution and concentration of manganese in groundwater is significantly influenced by the depth of well. From the National Hydrochemical Survey (BGS/DPHE 2001), 39% of shallow tubewells and 2% of deep tubewells exceeded the WHO health-based guideline value. The distribution of manganese concentration with type of well is shown in Table2.7 & Table 2.8.

Table 2.7 Percentages of Wells in Shallow and Deep Wells Above and Below Bangladesh Standard and WHO Health-based Guideline Value

Well type	Bangladesh guideline value (0.10 mg/L)		WHO health-based guideline value (0.50 mg/L)	
	Below	Above	Below	Above
Shallow	21	79	61	39
Deep	78	22	98	2

(Source: Hasan, 2004)

Table 2.8 presents a summary of Manganese concentration in different depth intervals. The highest average concentration (0.717 mg/L) occurs for wells of less than 15m depth. There is little difference in average concentration of manganese for well with depth up to 90m; but for wells above 90m depth, average concentration falls sharply. From Table 2.8, it is evident that shallow wells with depth up to 60m, are the most vulnerable for manganese contamination (Hasan, 2004).

Table 2.9 shows a relationship between year of construction of shallow wells and different manganese ranges. Deep wells have been excluded from this table because most of their manganese concentrations are below the national/WHO standards. From Table 2.9, recent wells appear to be more contaminated.

The trend appears to be alarming because more wells are being constructed recently in areas which are prone to be manganese contaminated. Figure-2.5 shows the distribution of wells with respect of year of construction over the country.

Table 2.8 Manganese Occurrence Summaries for Different Depth Range of Wells

Depth Range (m)	No. of Wells	Percentage of Wells	Avg Mn Conc. (mg/L)	Maximum Mn Concentration (mg/L)	Percentage of Wells > Bangladesh guideline value	Percentage of Wells > WHO guideline value
<15	287	8	0.717	7.83	79	43
15-30	1180	33	0.653	9.98	80	42
30-60	1258	36	0.588	5.54	79	40
60-90	317	9	0.519	8.39	78	29
90-150	165	5	0.293	3.50	76	15
150-200	32	1	0.196	1.04	56	6
>200	295	8	0.073	1.59	18	2
Total	3534	100	0.554	9.98	74	35

(Source: Hasan, 2004)

Table 2.9 Manganese Concentration in Shallow Wells of Different Years of Construction

Year of Construction	Percentage of Total Wells Having Specific Manganese Concentration Range (mg/L)						
	0.001-0.1	0.1-0.5	0.5-1.0	1.0-1.5	1.5-2.0	2.0-3.0	>3.0
Before 1970	25	31	25	15	4	0	0
1970-74	16	41	24	11	5	2	1
1975-79	23	41	16	11	5	2	2
1980-84	24	44	21	4	4	1	1
1985-89	21	43	18	10	5	3	0
1990-95	22	40	20	9	4	3	2
1995 and later	20	39	20	10	5	4	2
All years	21	40	20	9	4	3	2

(Source: Hasan, 2004)

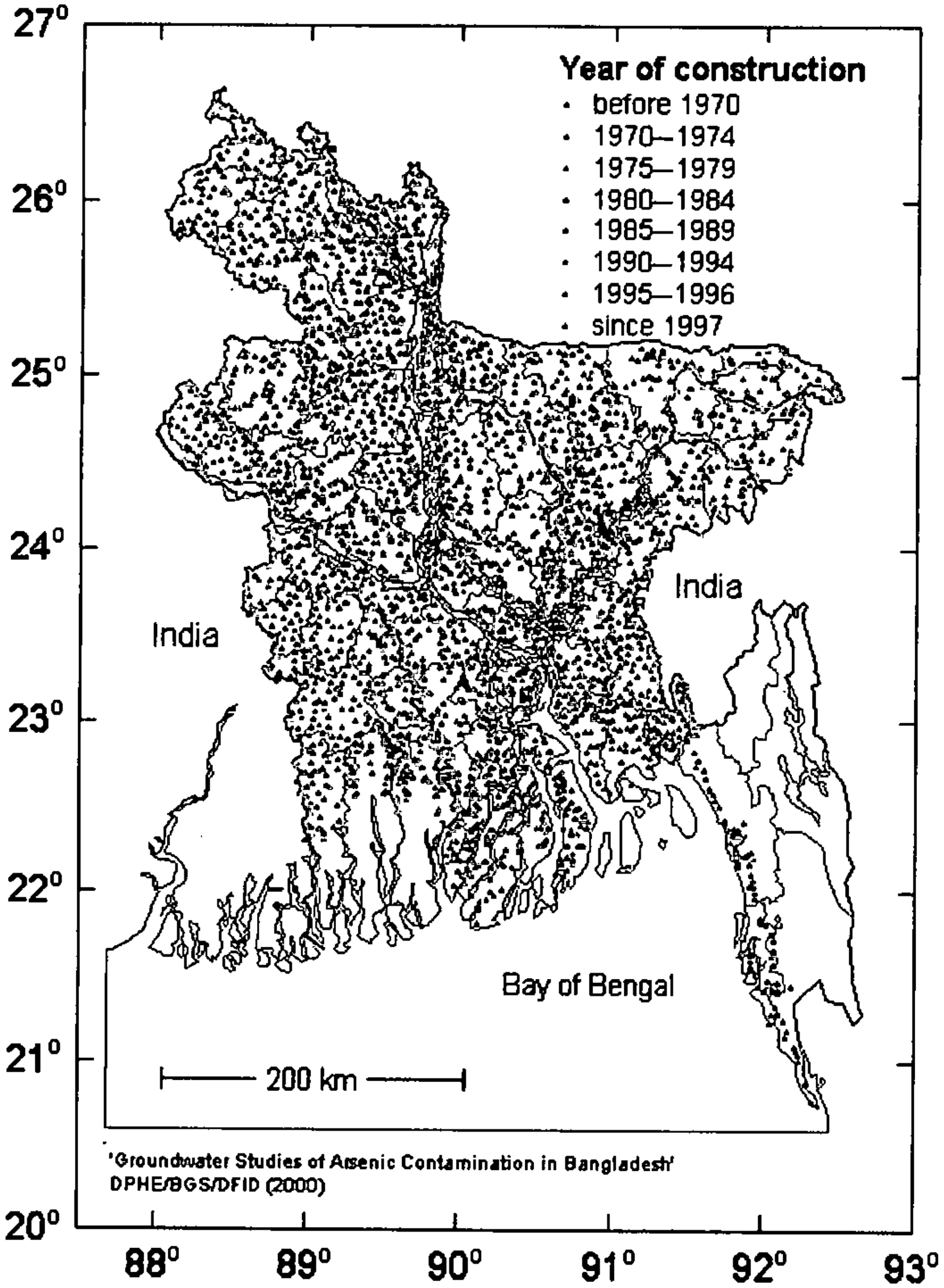


Figure 2.5 Distribution of wells with respect to year of construction
(Source: DPHE/BGS, 2001)

Manganese and Arsenic Ratio

Arsenic is considered to be the most significant groundwater quality problem in Bangladesh. However, available data do not show any correlation between occurrence and distribution of arsenic and manganese in groundwater. This means that groundwater with acceptable concentrations of arsenic may not have acceptable concentrations of manganese Arsenic and manganese showed distinctly different regional pattern that is shown in Figure 2.6. Division wise comparison of the occurrence of manganese and arsenic is shown in Table2.10. Although about 43.5 % of wells in Rajshahi safe for drinking with respect to arsenic concentration, but about 84% of these tubewells fails to satisfy Bangladesh guideline value for manganese. It is notable that groundwater from the deep aquifer contain relatively low concentrations of both arsenic and manganese. Only 33% of shallow tubewells had both arsenic and manganese concentration below the respective WHO guideline value. Whereas about 93% of deep tubewells satisfied respective WHO guideline value (DPHE/BGS, 2001).

Table 2.10 Comparative occurrence of Arsenic and Manganese in different Divisions

Division	As vs Mn									
	As < 50 μg/L Mn < 0.5 mg/L		As < 50 μg/L Mn > 0.5 mg/L		As > 50 μg/L Mn < 0.5 mg/L		As > 50 μg/L Mn > 0.5 mg/L		Total	
	No of wells	Percentage (%)	No of wells	Percentage (%)	No of wells	Percentage (%)	No of wells	Percentage (%)	No of wells	Percentage (%)
Barisal	249	84.4	6	2.0	28	9.5	12	4.1	295	100.0
Chittagong	145	32.6	76	17.1	166	37.3	58	13.0	445	100.0
Dhaka	426	43.1	259	26.2	174	17.6	129	13.1	988	100.0
Khulna	174	36.7	105	22.2	156	32.9	39	8.2	474	100.0
Rajshahi	540	50.4	466	43.5	11	1.0	55	5.1	1072	100.0
Sylhet	162	62.3	42	16.2	54	20.8	2	.8	260	100.0
Total	1696	48.0	954	27.0	589	16.7	295	8.3	3534	100.0

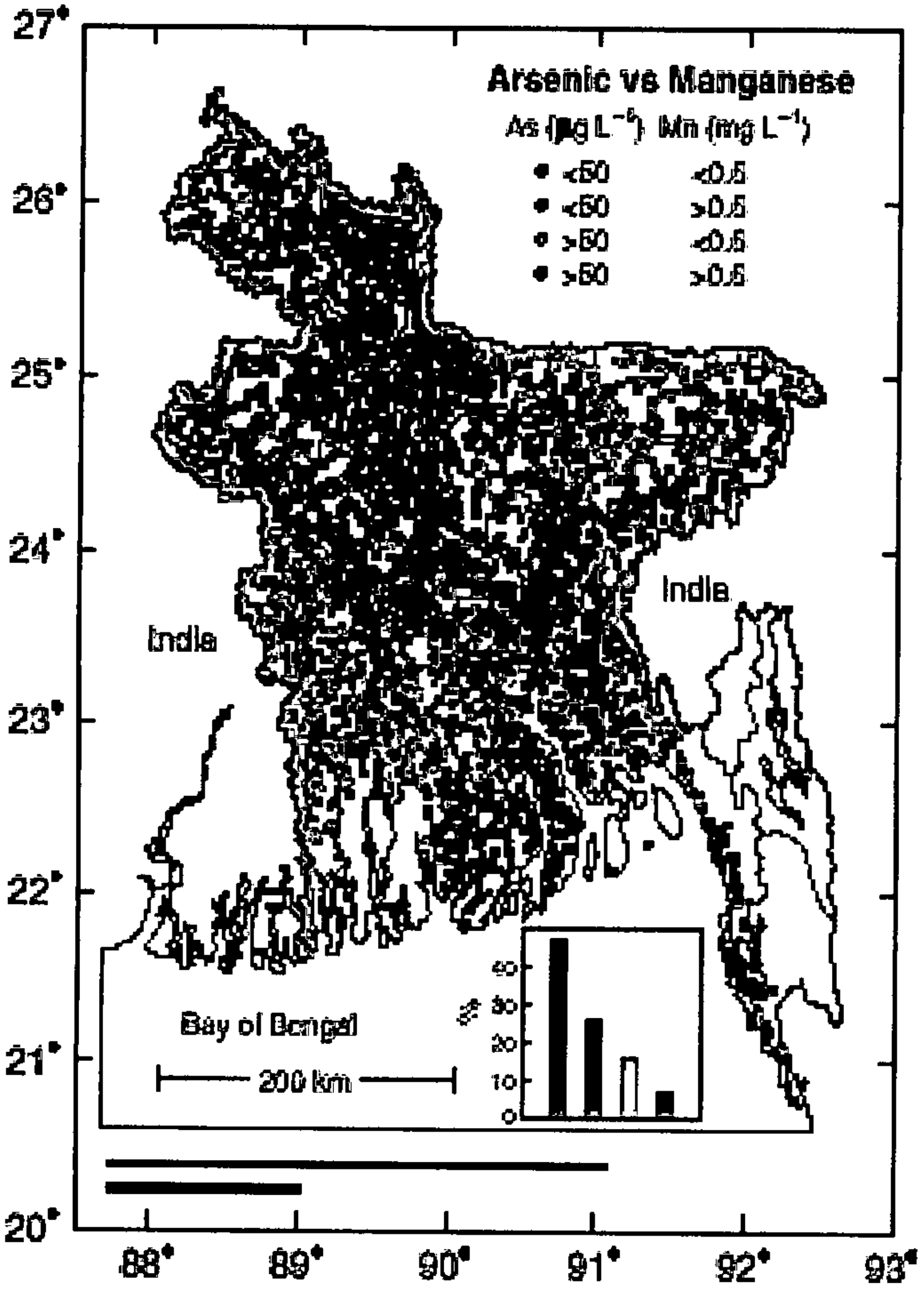


Figure 2.6 Comparative Distributions of Arsenic and Manganese in Groundwater of Bangladesh. (Source: DPHE/BGS, 2001)

Manganese vs Iron

Occurrence of high levels of iron is the most common water quality problems in groundwater of Bangladesh. In many areas iron concentration much higher than WHO standard (0.30 mg/L) as well as Bangladesh guideline value (1.0 mg/L) for iron. Especially the standard limit set by WHO can hardly be maintained in rural water supply in Bangladesh (Shahid, 1998). From National Hydrochemical Survey (NHS), it is found that more than 65% of tubewells had iron concentration greater than WHO guideline value. Therefore assessment of presence of iron in groundwater of Bangladesh has been done with respect to Bangladesh standard value for iron.

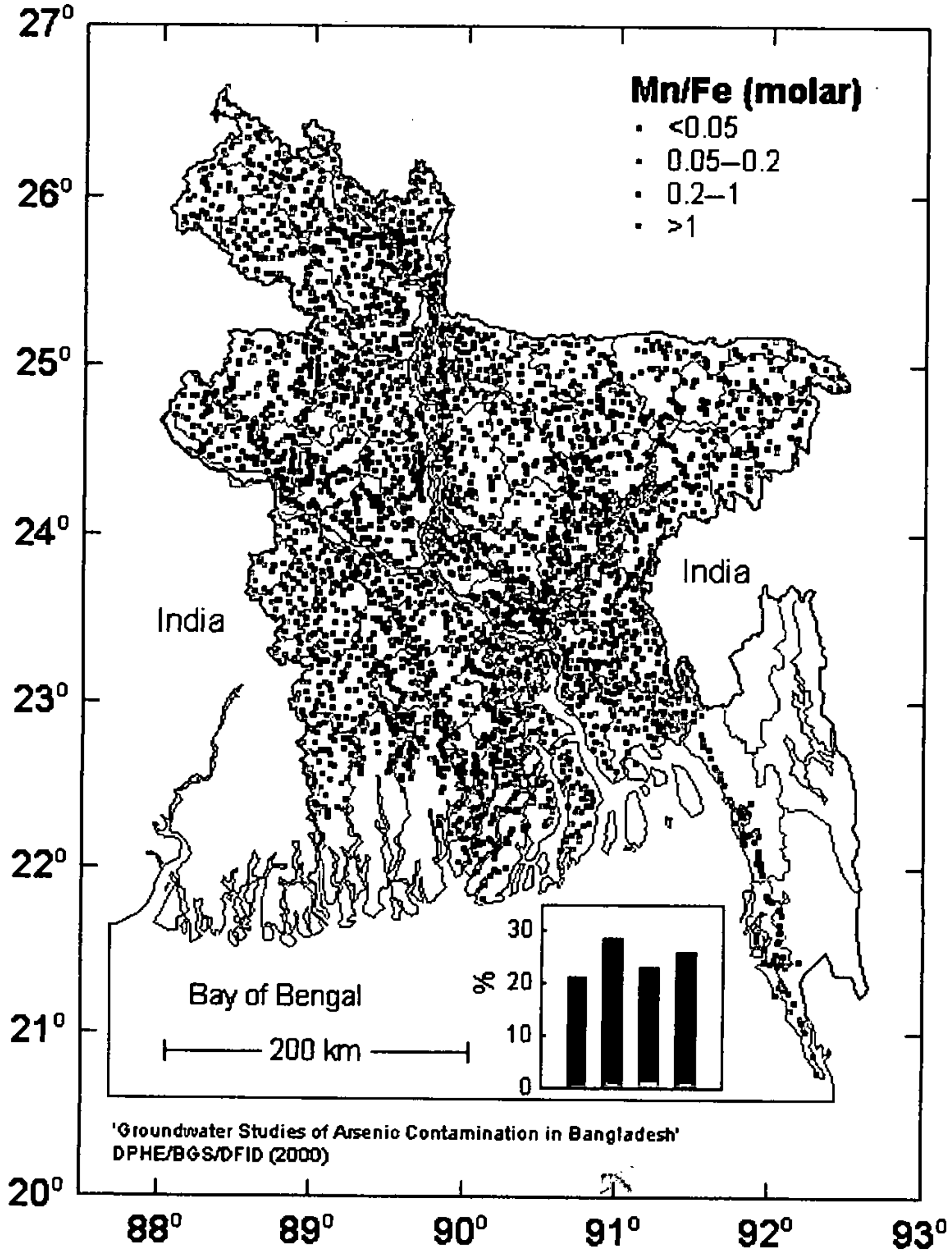
Although both iron and manganese have physical as well as chemical similarities, distribution of these elements in Bangladesh groundwater show very scattered pattern. Figure 2.7 shows relative molar distribution of iron and manganese in Bangladesh groundwater. From figure it is found that in about 25% areas of Bangladesh, Mn/Fe molar ratio exceeds 1 and in about 22% area, the ratio is below 0.05.

Table 2.11 represents a comparative occurrence of manganese and Fe in groundwater of different divisions of Bangladesh. Iron concentration has been evaluated with respect to Bangladesh guideline value and for manganese WHO health-based standard is used. In Chittagong division only 37% of wells had iron concentration below Bangladesh standard value but about 70% wells satisfied the guideline value for manganese. Again in Rajshahi division about 59% and 49% of wells failed to satisfy respective guideline values for iron and manganese. In Dhaka division more than 24% of wells had found to exceed respective standard values of iron and manganese. Barishal division is found to be less affected with respect to these two elements.

From National Hydrochemical Survey (NHS), it is also found that shallow tubewells are more associated with high iron and manganese concentration. More than 65% of shallow tubewells had exceeded Bangladesh guideline value for iron whereas about 61% of that exceeded WHO guideline for manganese. In case of deep tubewells, about 26% had iron concentration and 11% had manganese concentration greater than respective guideline values. Only 27% of shallow tubewells had both iron and manganese concentrations below the standard limits, whereas about 95% of deep tubewells satisfied the respective standard values (DPHE/BGS, 2001).

Table 2.11 Comparative Occurrence of Iron and Manganese in Different Divisions

Division	Mn vs Fe									
	Fe < 1 mg/L Mn < 0.5 mg/L		Fe < 1 mg/L Mn > 0.5 mg/L		Fe > 1 mg/L Mn < 0.5 mg/L		Fe > 1 mg/L Mn > 0.5 mg/L		Total	
	No of wells	Percentage (%)	No of wells	Percentage (%)	No of wells	Percentage (%)	No of wells	Percentage (%)	No of wells	Percentage (%)
Barisal	211	71.5	4	1.4	65	22	15	5.1	295	100.0
Chittagong	123	27.6	42	9.4	188	42.3	92	20.7	445	100.0
Dhaka	300	30.4	148	14.9	301	30.5	239	24.2	988	100.0
Khulna	78	16.5	90	19.0	251	52.9	55	11.6	474	100.0
Rajshahi	381	35.5	279	26.0	170	15.9	242	22.6	1072	100.0
Sylhet	52	20	7	2.7	164	63.1	37	14.2	260	100.0
Total	1145	32.4	570	16.2	1139	32.2	680	19.2	3534	100.0



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

Figure 2.7 Comparative Distributions of Iron and Manganese in Groundwater of Bangladesh. (Source: DPHE/BGS, 2001)

CHAPTER 3

CHEMISTRY OF MANGANESE AND MANGANESE REMOVAL TECHNIQUES

3.1 INTRODUCTION

Manganese is the third most abundant transition metal in the earth's crust (9.5 × 10^2 ppm). The redox chemistries of manganese (I/III/IV) have important roles and impacts in the environment. An important principle to remember about chemical reactions is that, if allowed enough time, it will reach equilibrium with the surrounding environment. When the conditions of that environment are changed, such as pumping water from an underground aquifer, the chemical equilibrium is upset. This will lead to either solution of manganese or its precipitation.

In this chapter relevant literature on chemistry of manganese that influence manganese oxidation and dissolution have been reviewed. Different environmental factors which influence manganese oxidation has also been reviewed briefly. This chapter also provides an overview of manganese removal techniques from water.

3.2 CHEMISTRY OF MANGANESE IN WATER

A general rule of thumb is that oxygenated water will have only low levels of manganese. The reason is that manganese reacts with oxygen to form compounds that do not stay dissolved in water (Varner, 1994). Surface water and shallow groundwater usually have enough dissolved oxygen to maintain manganese in an undissolved state. In surface water, manganese is most likely to be trapped within suspended organic matter particles. Oxidized manganese precipitates are so small sized that complete removal is not possible by settling (Seelig, 1992). Regardless of the removal the basic approach utilized to remove manganese from water involves oxidation of soluble manganese to one of more insoluble forms. Thus the removal chemistry of manganese predominantly includes oxidation chemistry of manganese.

3.2.1 Process Kinetics for Oxidation of Manganese

Although iron and manganese are chemically similar, the rate of manganese oxidation does not follow the same rate law as for Fe (II) oxygenation (Stumm and Morgan, 1981). The chemistry of manganese is substantially more complex than that of iron and only a limited understanding of manganese oxidation exists (Montgomery, 1985).The oxidation and control of manganese is complicated by factors that ranges from misunderstanding of the reaction chemistry to the relatively slow kinetics and the numerous oxidation states that result from this oxidation (Stumm and Morgan, 1981). Various forms of manganese in aqueous solution is shown in Figure 3.1. The oxidation of manganese (II) with molecular with oxygen is an autocatalytic process, that is, the spontaneous oxidation by free oxygen at room temperature. According to Stumm and Morgan (1981), the reaction might be visualized as proceeding to the following pattern:

$$Mn^{2+} + O_2\,(g) \xrightarrow{\text{slow}} MnO_2\,(s) \text{---------------------}(a)$$

$$Mn^{2+} + MnO_2\,(s) \xrightarrow{\text{fast}} Mn^{2+}.\,MnO_2\,(s) \text{---------}(b)$$

$$Mn^{2+}.\,MnO_2\,(s) + O_2\,(g) \xrightarrow{\text{slow}} 2MnO_2\,(s) \text{----------}(c)$$

Although other interpretations of autocatalytic nature of the reaction are possible, the following experimental findings are in accord with such reaction scheme:

i. The extent of manganese (II) removal during oxygenation reaction is not accounted for by the stoichiometry of the oxidation reaction alone ; that is not all the manganese (II) removed from the solution is oxidized. Therefore this mechanism offers a reasonable explanation why a less than stoichiometric oxidant dose may be required in the "oxidation" of manganese (II).

ii. The products of non-stoichiometric oxygenation of manganese (II) show various average degree of oxidation ranging from $MnO_{1.3}$ to $MnO_{1.9}$ (30 to 90% oxidation to MnO_2; commonly expressed as MnO_x) under varying alkaline conditions.

iii. The higher valent manganese oxide suspensions show large sorption capacities for Mn^{2+} in slightly alkaline solutions.

Therefore, this removal mechanism indicates that presence of manganic dioxide generally increases the apparent rate of oxidation of both iron (II) and manganese (II).The integrated form of autocatalytic reaction rate of manganese (II) can be expressed as follows:

$$\frac{-d\,[\mathrm{Mn\ (II)}]}{dt} = k_0\,[\mathrm{Mn\ (II)}] + k\,[\mathrm{Mn\ (II)}]\,[\mathrm{MnO_2}] \qquad (1)$$

where,

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

k_0 = Reaction rate constant [l^2 /mol^2.atm.min]

k = Reaction rate constant [l^3 /mol^3.atm.min]

[Mn (II)], [MnO_2] = Ionic concentration [mol/L]

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

$$\frac{-d\,[\mathrm{Mn\ (II)}]}{dt} = k\,[\mathrm{Mn(II)}]\,[\mathrm{OH^-}]^2 Po_2 \qquad (2)$$

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

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

Where,

OH^- = Hydroxide ion concentration [mol/L]

Po_2 = Partial pressure of oxygen [atm]

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

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

Where,

[Mn(II)] = concentration of Mn(II) (mg/l)

t = time (sec)

k = reaction rate constant (sec^{-1})
$[O_2]$ = oxygen concentration (mg/l)
$[OH^-]$ = concentration of hydroxyl ion (g/l)
$[HCO_3^-]$ = bicarbonate concentration (mg/l)
T = temperature (0 Kelvin)
V_o = Filtration rate (cm/sec)
d_m = mean particle diameter (cm)

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

3.2.2 pE - pH and Eh- pH Diagrams for Manganese in Solution

In order to describe the stability relationships of distribution of various soluble and insoluble forms of aqueous elements, two types of graphical analysis are essential been used: first, equilibria between chemical species in a particular oxidation state as a function of pH and solution composition; second, equlibria between chemical species at a particular pH as a function of pE (or E_H). These diagrams can be combined into pE-pH diagrams. Such pE-pH stability field diagrams show in a comprehensive way how proton and electrons simultaneously shift the equilibria under various conditions and can indicate which species predominate under any given condition of pE and pH (Stumm and Morgan, 1981). Natural waters are in highly dynamic state with regard to oxidation –reduction rather than in or near equilibrium. Most oxidation-reduction reactions have a tendency to be much slower than acid-base reactions, especially in the absence of suitable biochemical catalysis. Nonetheless equilibrium diagrams can greatly aid attempts to understand the possible redox patterns of water (Stumm and Morgan, 1981).

There is an analogy between acid-base and reduction-oxidation reactions. Acid-base reactions exchange protons. Acids are proton donors and bases proton acceptors. Redox processes reactions exchange electrons. Reductants are electron donors and oxidants are electron acceptors. As there are no free hydrogen ions (protons), there are no free electrons. It implies that every oxidation is accompanied by a reduction and vice versa (Jimbo and Goto, 2001). Like pH has been introduced as the proton activity, we may introduce an electron activity defined as:

$$pE = -\log\{e^-\}$$

For as aqueous solution at a given pH each pE value is associated with a partial pressure of H_2 and O_2.

The equilibrium redox equations for these elements can be expressed in logarithmic form:

$$\log P_{H_2} = 0 - 2pH - 2pE$$
$$\log P_{O_2} = -83.1 + 4pH + 4pE$$

These equations can be rewritten as

$$pE = 0 - pH - \tfrac{1}{2} \log P_{H_2}$$
$$pE = 20.78 - pH - \tfrac{1}{4} \log P_{O_2}$$

These equations can be plotted in a pE-pH diagram with a slope d pE/ d pH of -1 for both lines. Similarly, pE-pH diagram for aqueous manganese can be developed using equilibrium equation (Considering solid concentration in pE equations equals 1 μM.):

$$\tfrac{1}{2} MnO_2\,(s) + 2H^+ + e = \tfrac{1}{2} Mn^{2+} + H_2O$$

Then at equilibrium,

$$pE = pE^0 + \log \frac{[Red_1]\,[Ox_2]}{[Ox_1]\,[Red_2]}$$

$$pE = pE^0 + \log \frac{[Mn^{2+}]^{1/2}\,\overset{1}{\cancel{[H_2O]}}}{\underset{1}{\cancel{[MnO_2(s)]^{1/2}}}\,[H^+]^2}$$

$$= 20.58 - \tfrac{1}{2} \log[Mn^{2+}] + 2\log[H^+]$$

pE^0 is the electron activity standard condition of temperature (25^0C) and pressure (1 atm) = 20.58.

Rewriting the above equation,

$$pE = 20.58 - ½\log[Mn^{2+}] - 2pH \qquad (4)$$

Thus pE-pH diagram derived according to equation (4) is shown in Figure 3.2 for a total manganese concentration 10^{-6} M at 25^0C. The dashed lines show the water stability region for 1 atm of gases. Above the top line, water should thermodynamically form O_2 if oxygen partial pressure is below 1 atm. Similarly, below the bottom line, water should thermodynamically form H_2 if hydrogen partial pressure is below 1 atm. Natural environments have a range of pE/pH values: for oceans pE = O_2 saturated, pH = 8), surface waters of lakes and rivers (pE = O_2 saturated, pH = 4 to 6), mine waters (pE = O2 saturated, pH = 1 to 3), groundwater and sediments (pE = 0 to 3, pH = 7 to 9), and swamps (pE = 0 to -3, pH = 5 to 7) (Martin, 2003).

In the aqueous phase in the manganese system, $[Mn(H_2O)_6]^{2+}$ is the unique dominant at the common pE and pH values of natural waters. Hydrolysis begins only for pH > 10, while the stabilization of aqueous Mn(III) requires strong ligands. The white pE-pH regions show where Mn_T is thermodynamically speciated entirely in the aqueous phase. For instance, if the prescription of 10^{-6}M Mn_T initially includes solid species in the white region, then it is predicted that these solids will dissolve. However, the dissolution rate is slow compared to the timescales of days, weeks, and months usually relevant to the environment. The gray pE-pH regions conversely show where some (viz. near the boundary lines) or most (viz. moving inward in the gray region) of 10^{-6} M Mn_T should thermodynamically include solid phases, with a small amount of aqueous manganese species in equilibrium (e.g., 10^{-9} to 10^{-15} aqueous Mn). However, the precipitation rate may be slow. For instance, in the absence of catalysis, aqueous Mn(II) at pE = 10 and pH= 8 persists for years in solution, even though oxidation and precipitation of Mn oxide solid phases is thermodynamically favored. By increasing pH, super saturation increases and Mn(II) oxidizes and precipitates (Martin, 2003).

However, the first solid to form is generally the least favored thermodynamically, a phenomenon described as Ostwald's rule of stages (Martin, 2003). For instance, Mn(III) solids such as MnOOH form initially even when the free energy of formation for Mn(IV) O_2 is greater. The Mn(IV) oxides form only after long aging times of Mn(III)OOH

(Martin, 2003).Stability relationship of aqueous elements can also be expressed by redox potential (Eh) –pH diagram. Redox potential is defined as the oxidation or reduction potential of a particular environment (Douglas, 1994).

The redox potential, a measure of the oxidizing power of a system, is a variable of major importance in characterizing systems containing elements that exhibit more than one oxidation state (Minear et al, 1982). There are some close relationship between Eh and pH. Eh essentially measures the environments ability to supply electrons in an aqueous solution (Jimbo and Goto, 2001). The relationship between pE and the redox potential, Eh can be expressed as follows:

$$pE = \frac{F \times Eh}{2.3\ RT} \qquad (5)$$

Where,

F = Faraday's number = 96485 C/mol = the charge of 1 mol of electrons

R = Gas constant = 8.314 J/mol K = 0.082057 liter atm / mol K.

Nernst Law provides the basis for measurement of redox potential . According to Nernst Law (Jimbo and Goto, 2001):

$$Eh = Eh^0 + \frac{2.3\ RT}{nF} \log \frac{[\,ox\,]}{[\,red]} \qquad (6)$$

Where,

n = Number of electrons gained or lost

Eh^0 = Standard redox potential corresponding to the {ox} = {red} = 1.

From standard redox potential table it is found that for reduction reaction of Mn(II) at room temperature (25^{0}C) is – 0.615 V (for half reaction; as in reduction reaction of manganese two electrons are gained) (Jimbo and Goto, 2001).

Combining equation (5) and equation (6) and putting values of constants a Eh-pH diagram can be developed. Figure 3.3 represents the Eh-pH diagram for manganese at standard condition. In the figure, vertical lines separate species that are in acid-base equilibrium. Non vertical lines separate species related by redox equilibria. Horizontal lines separate species in redox equilibria not involving hydrogen or hydroxide ions. Diagonal boundaries separate species in redox equilibria in which hydroxide or hydrogen ions are involved. Dashed lines enclose the practical region of stability of the water solvent to oxidation or reduction (Douglas, 1994). This diagram is called Pourbaix Diagram.

From Pourbaix diagram for manganese it can be observed that (Douglas, 1994):

- Strong oxidizing agents and oxidizing conditions are found only at the top of Pourbaix diagrams.
- Strong oxidizing agents have lower boundaries that are also high on the diagram. In the diagram it is shown that permanganate is an oxidizing agent over all pH ranges. It is very strongly oxidizing even at low pH.
- Reducing agents and reducing conditions are found at the bottom of a diagram and not elsewhere. Strong reducing agents have low upper boundaries on the diagram and it can be noticed that manganese metal is a reducing agent over all pH ranges and is strongest in basic conditions.
- When the predominance area for a given oxidation state disappears completely above or below a given pH and the element is in an intermediate oxidation state, the element will undergo disproportionation, therefore, MnO_4^{2-} tends to become disproportionate.

3.3 FACTORS AFFECTING MANGANESE OXIDATION

The oxidation and control of manganese reactions is complicated by factors that ranges from misunderstanding of reaction chemistry to the relatively slow kinetics and the numerous oxidation states (Montgomery, 1985). Further adding to the complexity of manganese chemistry is the fact that there are difficulties with analytical techniques used to remove manganese. The gross analytical techniques do not allow for differentiation of the speciation of the manganese. Therefore, presumptions are made with respect to the oxidative states of manganese without through knowledge of its speciation (Montgomery, 1985). However, in general, the removal of manganese is greatly influenced by some environmental parameters, such as pH, dissolve oxygen, temperature etc. Some of these factors are discussed below.

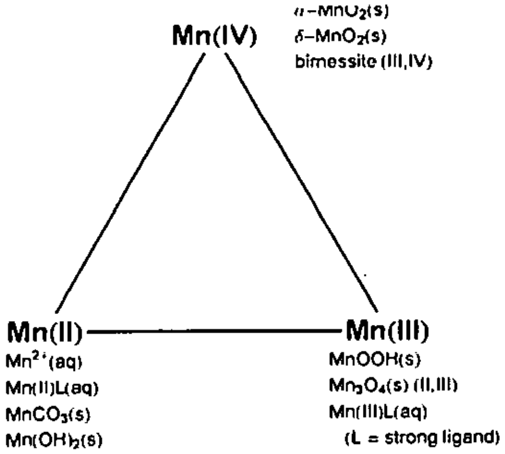


Figure 3.1 Forms of Manganese in aqueous solution
(source : Martin, 2003)

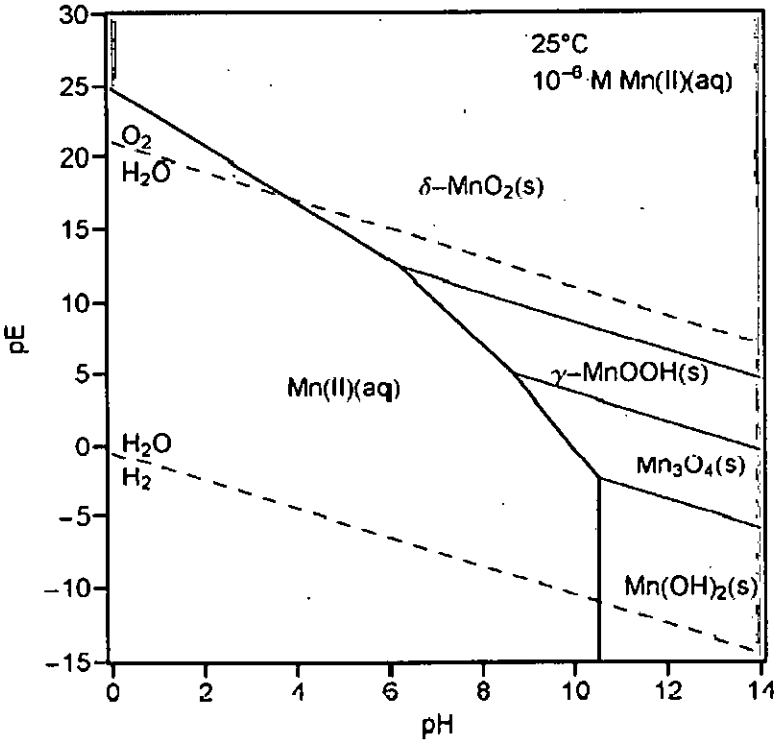


Figure 3.2 pE-pH diagram for the simple ions and hydroxides of manganese at 25°C. (Source: Martin, 2003)

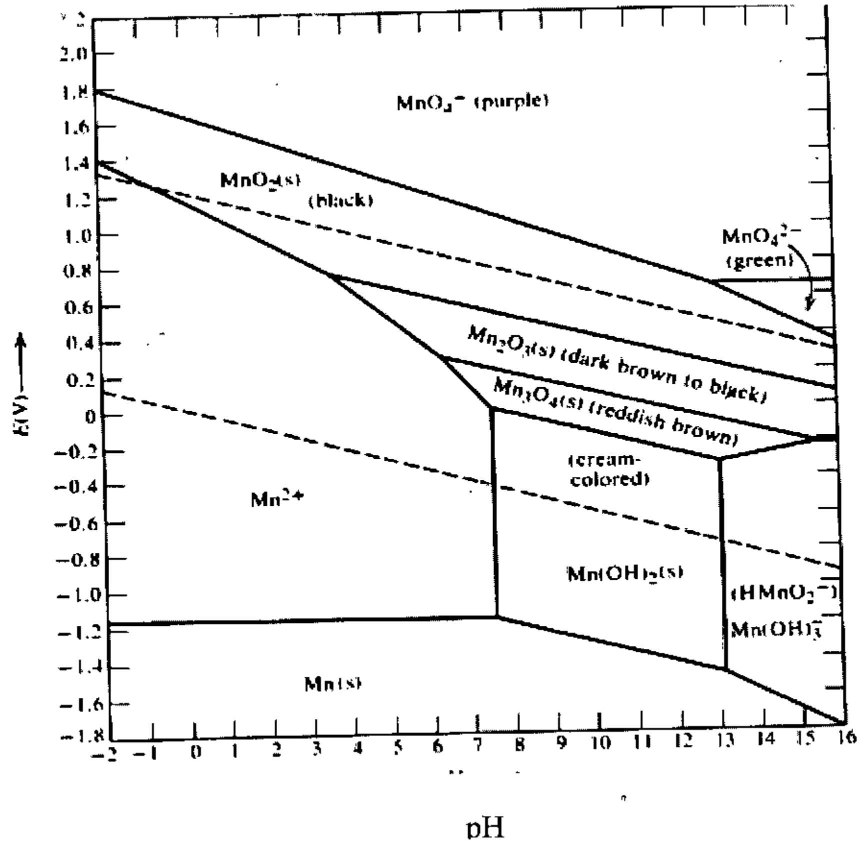


Figure 3.3 Eh-pH diagram (Pourbaix diagram) for manganese at 25^0 C

(Source: Douglas, 1994)

3.3.1 Effect of pH

Oxygenation kinetics equation for manganese (Equation 2) clearly shows that rate of reaction of Mn (II) has a second order relationship with hydroxyl ion concentration which indicate that an increase in one pH unit, cause 100 fold increase in rate of reaction (Stumm and Morgan, 1984). The pH dependence of Mn(II) oxidation is shown in Figure 3.4. Reaction of Mn (II) with O_2 is at least 10^6 times slower than that occurs for iron (II) oxidation at circumneutral pH (Martin, 2003). Only for pH > 8 does the reaction rate become appreciable.

According to Marble et al (1998), overall mass transfer of Mn(II) from solution to active sites at the surface decreases as pH decreases because of competition with H^+. As reported by Benschoten and Lin (1992) sorption of Mn (II) in excess of 0.5 mol of Mn(II) adsorbed per mole of MnO_2 (s), where as the capacity of oxide surface at pH 9 is about 2 mole of Mn(II) adsorbed per mole of MnO_2 (s). However, strong oxidizing agent like permanganate or chlorine dioxide can effectively oxidize manganese at a pH range from 5 to 10 (Samblebe, 2003). But for slow oxidizing agents like chlorine, it is necessary to raise the pH above 8.5 for effective oxidation reaction of manganese (Samblebe, 2003).

3.3.2 Presence 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 (Shahid, 1998). 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 inorganics. Permanganate oxidizes a wide variety of inorganic and organic substances in the pH range of 4 to 9 (Hazen and Sawyer, 1992).

3.3.3 Effect of Temperature

Change in temperature can affect the oxidation reaction rate of manganese. As ionization constant of water is dependent on temperature variation, which in turn effects hydroxyl ion concentration of water. On this basis, from oxidation reaction kinetics it can be found that at a given pH value, the rate increases about 10 fold for a 15^0 C increase in temperature (Shahid, 1998).

A number of research review indicates that oxidation rate gets slower with decrease in temperature (Benschoten and Lin, 1992). As reported by Montgomery (1985), oxidation of manganese by permanganate solution needs a contact time of 5 mins at 20^0 C and a contact time of 10 mins at 1^0 C.

3.3.4 Presence of Dissolved Oxygen

As stated in equation (2), the rate of manganese oxidation is of the first order with respect to the partial pressure of oxygen, Po_2 (Stumm & Morgan, 1981). It is also observed that above about 30% of saturation value of dissolve oxygen, there exhibits no significant dependence on concentration of dissolve oxygen. Below this value the net rate of Mn(II) removal was approximately first-order with respect to DO concentration (Marble et al, 1999) The DO dependence of the observed net rate of removal is presented in Figure 3.5.

Many other researchers [e.g., Graveland, 1975; Tebo and Emerson, 1985; etc] reported no dependence of the rate of Mn(II) removal on DO above concentrations of about 1 mg/L(i.e.~ 12% air saturation, or 0.03 mM) and an approximate linear dependence at lower DO values (Marble et al, 1998).

3.3.5 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. The dependence of the net rate of removal of Mn (II) on Mn(II) concentration is shown in Figure 3.6. However, it is apparent from the Figure that the net rate of Mn(II) removal does not extrapolate to a zero intercept at zero Mn(II) concentration.

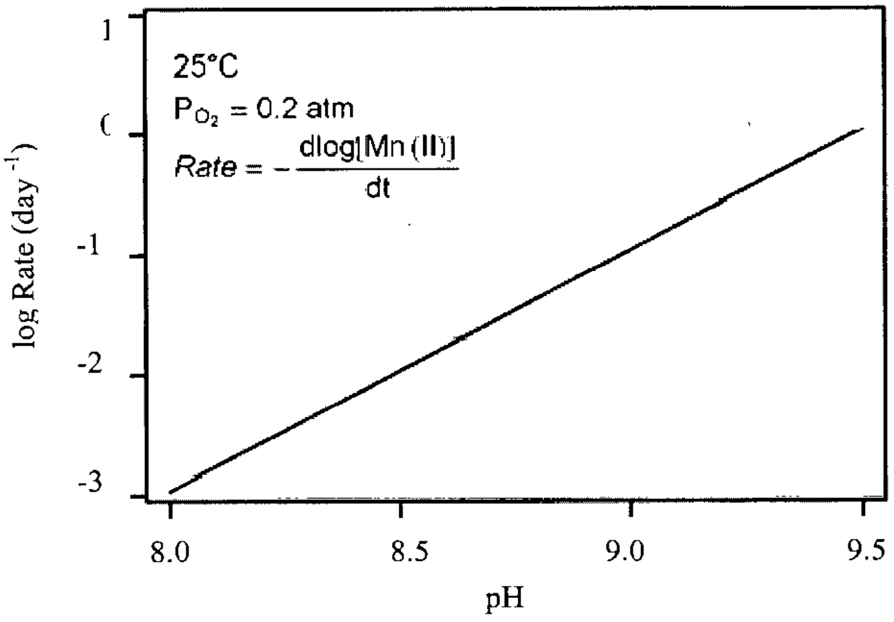


Figure 3.4 Effect of pH on Manganese Rate of Oxidation

(Source: Marble et al, 1998)

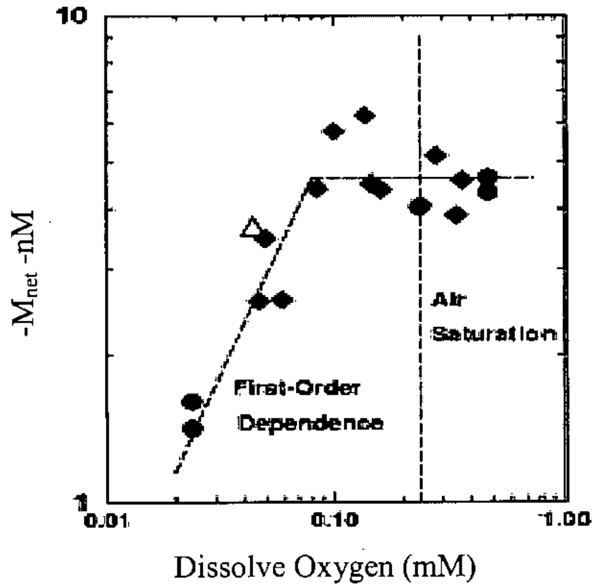


Figure 3.5 Effect of Dissolved Oxygen on Manganese Oxidation

(Source: Marble et al, 1998)

In other studies [e.g., Tebo and Emerson, 1985; Tebo et al, 1997] of Mn (II) removal (oxidation) in microbially active media, it has been demonstrated that the rate of Mn (II) removal is consistent with a Michaelis-Menten-type of rate expression (Marble et al, 1998).

$$\frac{-d\,[\mathrm{Mn\ (II)}]}{dt} = V_m \frac{[\mathrm{Mn\ (II)}]}{[\mathrm{Mn\ (II)}] + K_m} \qquad (7)$$

Where

V_m = maximum rate (nM/sec)
K_m = Michaelis constant

The study by Marble et al (1998) found that it was more difficult to remove Mn when the initial concentration was low, regardless of the oxidant used.

3.3.6 Effect of Alkalinity

As stated in Stumm and Morgan (1985), sorption capacities of Mn (II) increases at slightly alkaline solutions as low alkalinity waters tend to dissolve minerals and metals. Figure 3.7 shows removal of manganese in bicarbonate solution (Stumm and Morgan, 1985). As indicated by Graveland (1975) in his manganese oxidation rate equation that manganese oxidation rate is directly dependent on bicarbonate alkalinity. A review of research involving reactions of permanganate and Mn(II) indicates that experiment often carried out in acid media to avoid complications that arise from precipitation of Mn (II) oxides and heterogeneous oxidation reaction (Benschoten and Lin, 1992). There is lack of clear information about the mechanism of direct effect of alkalinity on manganese removal.

3.3.7 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,

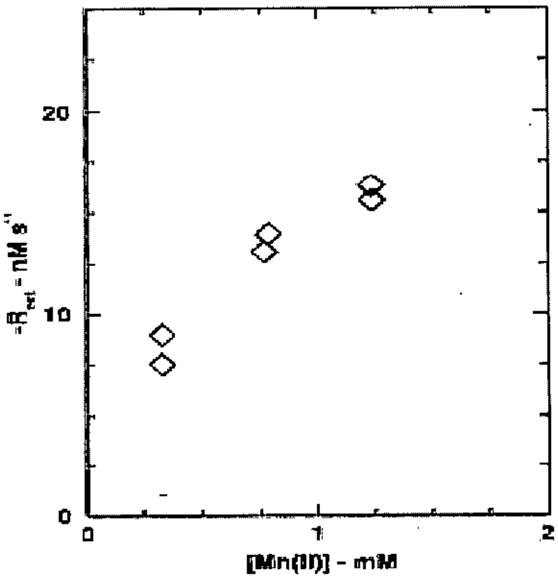


Figure 3.6 Effect of Manganese Concentration in Solution

(Source: Marble et al, 1998)

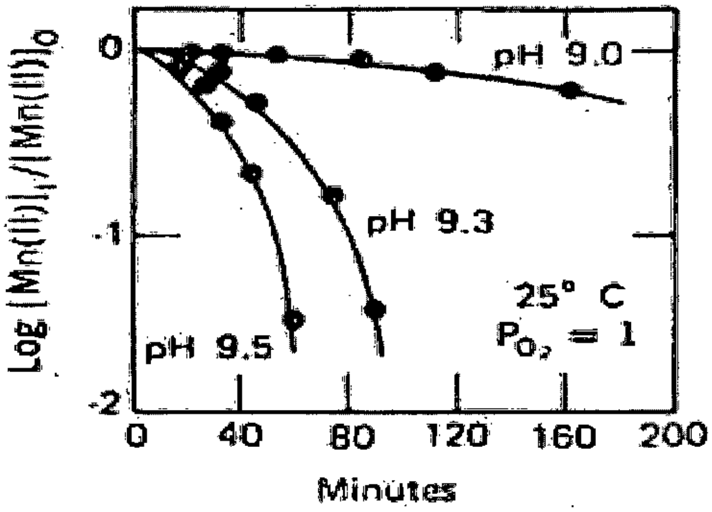


Figure 3.7 Manganese oxidation in Bicarbonate Solution

(Source: Stumm and Morgan, 1981)

e.g., Mn(II) on MnOOH producing additional MnOOH (Martin, 2003). As reported by Bensschoten et al (1992), the kinetics of the reaction rate can be expressed as:

$$\frac{-d\,[\mathrm{Mn\,(II)}]}{dt} = k \times A \times Po_2 \; \frac{(>\mathrm{SOH})\;[\mathrm{Mn\,(II)}]}{[H^+]^2} \qquad (8)$$

Where,

(>SOH) = surface concentration of hydroxyl sites

A = mass solids concentration

Po_2 = Partial pressure of oxygen.

The surface hydroxyl site concentration is hypothesized to be proportional to the concentration of surface Mn(II) species (Bensschoten and Lin, 1992). Reaction rates at surfaces are given either as the conversion rate per unit surface area of the foreign surface (mol/m^2-s) or as the conversion rate per liter of a particulate suspension (M/s). The later is the basic observable in experiments employing particulates, whereas the former is a more intrinsic measure, which can be estimated for a suspension of known loading (g/ L) and specific surface area (m^2/g) (Martin, 2003).

Again in autocatalytic reaction, heterogeneous oxidation occurs when the product of the oxidation further accelerates the reaction rate. For example, the oxidation of Mn(II) produces MnOOH(s), as follows:

$$O_2 + 4\,Mn^{2+} + 6\,H_2O \xrightarrow[\text{or heterogeneous}]{\text{homogeneous}} 4MnOOH\,(s) + 8\,H^+ \qquad (9)$$

As the reaction proceeds, the MnOOH(s) surface area and hence the heterogeneous reaction rate increase. The rate laws of autocatalysis are less precise than those of heterogeneous reactions on foreign mineral surfaces. Detailed descriptions for the autocatalysis pathways are hindered both by the complexities of separating homogeneous from heterogeneous pathways and by limitations in characterizing the increasing mineral surface area and the altering mineral phases during reaction (Martin, 2003).

3.3.8 Presence of Reductive Substances

Reductants rapidly accelerate manganese oxide dissolution. Examples of reductants are ascorbic acid, hydrogen sulfide, and phenols. A reductant typically forms an inner-sphere complex at the surface, though not always so. When an electron is transferred to a Mn(III/IV) oxide, a surficial Mn(II) ion locked inside an oxide lattice is formed. Because Mn(II) oxides are much more soluble than the corresponding higher oxides (Figure 3.2), rapid Mn(II) depolymerization occurs, which is followed by release to the aqueous phase of Mn(II).

3.3.9 Effect of presence of Metal Ions

Unlike iron (II), metal ions like Cu^+ and complex formers do not appear to have any marked effect upon reaction rate of manganese (Stumm and Morgan, 1985).

3.4 MANGANESE REMOVAL TECHNIQUES

If manganese is present in a water source, there would be two basic options – obtain an alternate water supply or use some type of treatment to remove the impurity. Selection of appropriate option for manganese contaminated water depends on various factors, such as concentration of manganese, availability of alternate sources etc. Use of alternate source instead of groundwater is less preferable from cost as well as bacteriological contamination view point. Therefore using groundwater with suitable treatment for manganese removal would be more appropriate.

3.4.1 Factors that must be known when choosing a Treatment Process

Type of Manganese Present

Manganese may be present in any of three different forms ranging from clear to discolored as described below. Not all treatment methods work on all forms of manganese (Varner et al, 1994).

1. Water is totally clear when drawn from the tap: Manganese is present in the dissolved form. The term "Clearwater manganese" is often used to describe this form. The scientific name for clearwater Manganese is called "manganous".
2. Water is rusty colored when drawn from the tap: When exposed to oxygen or other oxygen like chemicals, clearwater manganese will precipitate to form fine blackish (manganic) "rust" particles. The tendency to precipitate is also influenced by changes of water temperature, pressure, pH and other factors. It is this precipitated form which stains water use fixtures and discolors laundry. These rust particles will settle if the water is not disturbed.
3. Water has a yellow tint, but is totally transparent and the color does not settle out with time: In this case the manganese is probably combined with dissolved organic matter in the water. This is commonly called colloidal iron. It is more commonly found in surface water than in groundwater; therefore, you should also have the bacterial quality of your well checked if this form is present. Testing for the organic components of tannins is also suggested.

This form of manganese will not settle out when the water is undisturbed, is too small to be removed by filtration, and cannot be effectively treated by ion exchange (i.e., water softener). Colloidal manganese is very difficult to remove.

Water Quality Tests

In order to determine which treatment process will work for a particular water quality; it is essential to know certain water quality factors. Typically important factors for manganese removal include (Samblebe, 2003):

- The concentrations of manganese.
- pH and hardness.
- Dissolved oxygen for some treatment types; this must be field measured.
- The presence of manganese bacteria.

3.4.2 Overview of All Categories of Treatment

Generally speaking, there are two basic methods for treating water containing manganese either by exchanging manganese with any other cation or by oxidizing soluble manganese to precipitate as insoluble form(s). The diagram below shows the treatment options for manganese removal.

Oxidation processes, both physical-chemical and biological basically involves oxidation-raction and surface adsorption followed by suitable filtration option. Surface adsorption is influenced by autocatalytic behavior of manganese. It is also dependent on the type of oxidation procedure used to remove manganese. A separate explanation for each type of manganese removal processes is summarized in Figure 3.8.

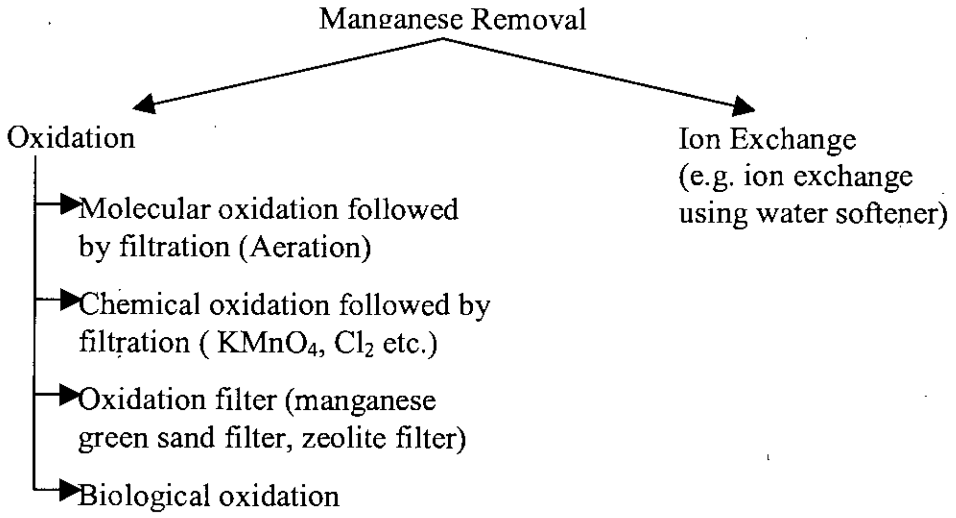


Figure 3.8 : Commonly Used Manganese removal Techniques

3.4.3 Removal of Dissolved Manganese Using Water Softeners

A water softener removes manganese, which is in the dissolved "clearwater" form. Softening also removes calcium (Ca++) and magnesium (Mg++) ions which are the primary minerals responsible for "hard" water. The treatment process consists of passing the water through an ion exchange resin media bed. The manganese ions and also calcium and magnesium ions in the water are "exchanged" for sodium (Na+) ions which have been temporarily stored in the resin material (Kassim, 1994).

As the hardness and manganese are removed from the water, sodium is added proportionally. For every 10 mg/l of hardness and manganese removed, approximately 5 mg/l of sodium will be added to the treated water. For those concerned with elevated sodium levels in their drinking water, potassium chloride (KCl) can be used in place of sodium chloride (NaCl). The cost of potassium chloride is higher than sodium chloride (Ficek, 1985).

Eventually the removal capacity of the ion exchange resin material will become exhausted and the media will need to be rejuvenated. The rejuvenation process begins with a physical backwash of the media. The resin is then immersed in a strong salt brine solution. The sodium from the salt enters the resin and displaces the previously removed manganese and hardness. After a period of time (approximately 20 minutes), the remaining brine, along with the displaced manganese and hardness are flushed out of the device and disposed of into a dry well, septic tank or sewer. Studies by the Water Quality Association (a trade organization of the home water conditioning industry) indicate that waste brine does not injure leach fields or septic tanks (Kassim, 1994).

Ion exchange softening is described as effective for water containing less than 2- 5 mg/L of dissolved (i.e., colorless) manganese. The system will not work at all where the manganese has turned to a rusty color. Other aspects of water quality are not overly important. Where both manganese and hardness are high, softening is an appropriate treatment technique (Seelig, 1992).

Where manganese is bound to organic matter, or concentrations of manganese is very high, manganese bacteria is present, a strong oxidizing substance must be applied before filtration. The most commonly used chemical in these systems is household bleach (hypochlorite) injected ahead of the pressure tank. This procedure disinfects the water and at the same time oxidizes iron (if present), manganese, and organic matter, which will then precipitate. Sedimentation and/or filtration are then needed to remove the precipitants. Activated carbon units or reverse osmosis units should then be used to remove the remaining chlorine and possible halogenated hydrocarbons created from organics. Final choice of the method will depend on manganese concentration, pH of water, and the presence of the bacteria (Sharma et al, 2001).

Advantages of Water Softening

- Softener resin can be rejuvenated and re-used.
- Ion exchange can consistently remove dissolved Fe/Mn from water to extremely low levels.
- There are lower backwash water requirements than oxidizing filters.
- The manganese removal is not appreciably affected by pH.

Disadvantages of Water Softening

- Softening will not operate satisfactorily if manganese bacteria or rusty colored water exists, even if occasionally. If particles are present, a sediment filter is often placed before the resin tank (Samblebe, 2003).
- The softener and iron filter are effective only if the manganese is not bound to organic matter and there are no iron or manganese bacteria in the water. The oxidizing media of the iron filters are not strong enough to break these materials down. In such case it is necessary to pre-oxidize water with appropriate oxidizing agent e.g., permanganate, bleaching powder etc (Sharma et al, 2001).
- A water softener will not remove hydrogen sulfide odor.
- Water softeners produce waste brine that must be disposed off. In absence of a sewer or other suitable drainage system, disposal of the waste brine will likely be into the ground. This creates the potential of polluting the groundwater. This disposal consequence can be lessened by minimizing the number of backwash rejuvenation cycles (Samblebe, 2003).

New water softeners allow the frequency of softener rejuvenation cycles to be reduced. The controls on these devices include: those that measure the water's electrical conductivity or those that measure the volume of water treated. In each case, rejuvenation is triggered based on actual need rather than the passage of time. Excessive backwash needlessly increases salt use and the generation of waste brine (Sharma et al, 2001).

3.4.4 AERATION FOLLOWED BY FILTRATION

Aeration can be used to oxidize manganese ions to manganic dioxide. However, the kinetics of oxidation by oxygen is slow in typical water treatment conditions and so a long detention time is required especially at pH less than 8.5 (Raveendran et al, 2001). Aeration is useful as an option to oxidize manganese in reservoirs. The reaction between manganese and molecular oxygen is:

$$2Mn^{2+} + O_2(g) + 2H_2O = 2MnO_2\,(s) + 4H^+ \qquad (10)$$

The amount of molecular oxygen required to oxidize manganese can be obtained from stoichiometric relation of manganese oxidation as shown in Table 3.1, which shows that 0.29 mg O_2 is required to oxidize per mg of manganese.

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

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

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

Advantages of aeration

- No foreign chemicals are added to the water.
- Low labor cost.
- Can handle a wide range of manganese concentration in water.
- Can often reduce some odor.

Disadvantages of aeration

- Aeration is not recommended for water containing organic complexes of manganese or manganese bacteria that will clog the aspirator and filter.
- Generally aeration involves high capital costs and high running costs.
- Aeration alone cannot completely oxidize all manganese at pH less than 10 (Seelig, 1992) and without longer detention time.

3.4.5 OXIDIZING FILTER

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

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

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

Manganese greensand is a specially processed medium for iron, manganese, and hydrogen sulphide removal. Manganese greensand is a premium non-proprietary filter medium which is processed from glauconitic greensand on which a shiny, hard finite thickness manganese oxide coating is formed and is firmly attached on every grain by a controlled process. This process utilizes the ion exchange properties of greensand to form a manganese base material which is converted to manganese oxides by oxidation with potassium permanganate. Manganese greensand contains 0.3% manganese or 0.45% manganese dioxide.

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

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

Advantages of oxidation filter

- The manganese greensand process requires no detention time, no secret expensive filter media, no high concentration of chlorine, and no sulphur dioxide (Gregory, 1996)
- Optimum grain size and shape to retain oxidation precipitation products of iron and manganese (Gregory, 1996)
- Unequalled oxidation-reduction buffer capacity. Can tolerate slight over or underfeed of continuously fed oxidants (Gregory, 1996).
- Manganese oxide coating is not removed during backwashing (Gregory, 1996).

Disadvantages of oxidation filter

- High level of dissolved oxygen must be present for effective removal.
- Oxidizing filter size should be suitable to source water output. Where well output is low and the required filter size is large, two smaller filters might be substituted so that each can be backwashed separately. This isolation would be expensive however.
- Backwash requirement is greater than that for softening process (Kassim, 1994).

3.4.6 Chemical Oxidation Followed by Filtration

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

Chlorine

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

$$Mn^{2+} + Cl_2 + 2H_2O = MnO_2(s) + 2Cl^- + 4H^+ \qquad (11)$$

Stoichiometric relation indicates that (Table 3.1) about 1.29 mg of Cl_2 dose is needed for per mg of manganese removal. Even though, the stoichiometric requirement of chlorine is less than potassium permanganate, in practice the chlorine requirement has been found to be much higher due to the chlorine demand by organic carbon (Raveebdran, et al, 2001).

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

Pre-chlorination has a higher potential to react with organic compounds and to produce trihalomethane (THM) which is carcinogenic. Chlorinators and appropriate safety equipment are required to dose chlorine (Samblebe, 2003). When chlorine is used, the treated water can have an unpleasant taste if a particle filter of calcite, sand, anthracite, or aluminum silicate is used. To overcome this problem, use of an activated carbon filter can remove both excess chlorine and solid manganese particles. The insoluble materials produced by chlorination may be highly dispersed and therefore coagulation and filtration is required (Montgomery, 1986). Frequent backwash is needed for effective removal (Singer, 1988).

Sodium Hypochlorite

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

Potassium Permanganate

Although oxidation of manganese by KMnO4 is slower than ClO_2 and ozone, it is most extensively used in oxidation purposes as it is easily available in almost everywhere (Minear et al, 1982). Potassium permanganate is a stronger oxidant than chlorine and sodium hypochlorite. Whilst it is effective in oxidizing manganese, it has also been used for the treatment of taste and odor problems in water supplies (Boman et al, 1999). Unlike chlorine, the reaction of potassium permanganate with organic compounds will not produce trihalomethanes but will actually reduce them (Singer, 1988). The stoichiometric equation for manganese ion oxidation by potassium permanganate is given as below.

$$3Mn^{2+} + 2KMnO_4 + 2H_2O = 5MnO_2\,(s) + 2K^+ + 4H^+ \qquad (12)$$

This reaction shows that alkalinity is consumed through acid production at the rate of 1.21 mg/L as $CaCO_3$ per mg/L of Mn^{+2} oxidized. This consumption of alkalinity should be considered when permanganate treatment is used along with alum coagulation, which also requires alkalinity to form precipitates. According to the stoichiometric equation (Table 3.1), it would require 1.92 mg of potassium permanganate to oxidize 1 mg of manganese ion. In practice, the actual amount of potassium permanganate used has been found to be less than that indicated by stoichiometry. It is thought that this is because of the catalytic influence of MnO2 on the reactions (O'Connell, 1978).

Permanganate being highly reactive oxidant, adsorption of Mn(II) to the oxide surface is the rate-limiting step that is rapid surface oxidation reaction is less effective for low manganese concentration (Benschoten et al, 1992). Where as in contrast for less reactive oxidants like chlorine, surface adsorption is rapid relative to solution and surface oxidation reaction. Generally a detention time of 5 to 15 minutes is recommended for manganese removal (O'Connell, 1978).

According to a study by Desjardins, oxidation of manganese by potassium permanganate occurred in less than 5 minutes where the manganese was not in a complexed form

(Graveland and Heertjes, 1975). As permanganate is very strong oxidizing agent, it is capable to remove manganese over a wide pH range of 5-10 (Samblebe, 2003). But for rapid oxidation it is preferable to raise pH above 7.0 (Benschoten et al, 1992). Slight overdosing of permanganate (up to 0.1 mg/L) has been found not to cause any adverse effects (Raveendran et al, 2001), but presence of excess permanganate produce pink color to the water. Although the cost of permanganate is more than that for chlorine, it has been reported to be as efficient and may require considerably less equipments and capital investment (Montgomery, 1986).

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

Chlorine Dioxide

Chlorine dioxide or ozone is extremely rapid under most solution conditions (Benschoten, and Lin 1992). ClO_2 has relatively higher oxidation potential than ozone and potassium permanganate. ClO_2 is capable to reduce residual manganese concentration to a level less than 10 ug/L within 60-120 sec when manganese concentration is within 1,000 μg/L (Gregory and Carlson, 1996). The stoichiometric equation for manganese ion oxidation by ClO_2 is given as below (Benschoten and Lin, 1992).

$$5Mn^{+2} + 2ClO_2 + 6H_2O = 5MnO_2 + 12H^+ + 2Cl^- \quad (13)$$

From this equation it can be found that about 2.45 mg of ClO_2 is needed to oxidize 1 mg of soluble manganese. However, as ClO_2 is a strong oxidizing agent, during oxidation, relatively less amount of dose is required (Gregory and Carlson, 1996). Best results are obtained when the pH is greater than 7 (Stevens, 1982). Chlorine dioxide has also been reported to oxidize organically bound manganese (Masschelein, 1979). One important advantage of chlorine dioxide oxidation is that it does not produce THMs during oxidation like chlorine (Stevens, 1982).

However, excessive dosing may lead to increase in Cl^- concentration especially at pH less than 7 (Benschoten and Lin, 1992). The chlorine dioxide is a so strong oxidant that reacts with organic material to produce a variety of oxidized by-products. Practicing indicated that ClO_2^- produced hemolytic anemia at lower exposure levels than those required to produce significant increases in methemoglobin. Additional studies extended these findings to chlorine dioxide and ClO_3^-. Chlorite remained the most potent of the three chemical species for causing signs of hemolytic oxidative stress in animals (Cao rui yu et al, 2001). These factors often limit the use of Chlorine dioxide as oxidant in removal of manganese and iron (Cao rui yu et al, 2001).

Ozone

Ozone is 12.5 times more soluble in water than is oxygen, leading to better mixing in water treatment (Evans, 1972). Also, the products of its reaction with organics are oxygen, carbon dioxide, and water. This prevents the incomplete disinfection products that could lead to trihalomethanes (THMs) in drinking water. Ozone is effective against odor-producers because it can easily oxidize these unsaturated compounds. Although ozone is extremely rapid under most solution conditions, it is rarely practiced for oxidation of manganese (Benschoten and Lin, 1992). Ozone may not be effective for oxidation in presence of humic or fulvic materials. When ozone is applied to water, excess air or oxygen is applied in sufficient quantities to supersaturate the dissolved oxygen content of the water. The excess transferred oxygen is of concern due to its effect on accelerating corrosion rates and out gassing via effervescence. The stoichiometric equation for manganese ion oxidation by ClO_2 is given as below (Benschoten and Lin, 1992).

$$2Mn^{2+} + O_3\,(g) + 2H_2O = 2MnO_2\,(s) + 4H^+ \qquad (14)$$

From stoichiometric relation it can be found that about 0.44 mg ozone is reqired for 1 mg manganese oxidation. Oxidation with ozone often results in Mn^{2+} greater than 20 ug/L and increasing TOC concentrations causes increasing Mn^{2+} residuals (Gregory and Carlson, 1996). It is necessary to control appropriate dosing of ozone as overdosing due to ozone's ability to oxidize Mn^{2+} to Mn^{7+} or permanganate. The formation of permanganate and the resulting pink water are drawbacks to the use of ozone for manganese removal (Montgomery, 1985).

Table 3.1 Stoichiometry of Manganese Oxidation

Oxidizing agent	Dose required per mg of Mn	Hydrogen ion produced as H^+ per mg of Mn removal	Alkalinity destroyed as $CaCO_3$ per mg of Mn removal
Oxygen	0.29 (as O_2)	0.04	1.80
Permanganate, $KMnO_4$	1.92 (as $KMnO_4$)	0.02	1.21
Chlorine, Cl_2	1.29 (as Cl_2)	0.07	3.64
Chlorine Dioxide, ClO_2	2.45 (as ClO_2)	0.06	0.73
Ozone, O_3	0.44 as (O_3)	0.05	1.82

- Not given (Source: Raveendran, 2001; Benschoten and Lin, 1992; Gregory and Carlson, 1996)

3.4.8 Biological Oxidation

When manganese is in complexed with substances like humic acids, polyphosphates, silica etc., removal of manganese by simple physical-chemical processes may become ineffective. In such condition biological oxidation can be utilize to remove manganese from water. In biological oxidation process manganese is oxidized by several types of bacteria, such as Lepothrix, Crenothrix, Siderocapsa, Mettallogenium Pseudomonas etc (Sharma et al, 2001). These bacteria which can remove iron or manganese are referred to as 'Iron Bacteria'. In general, these bacteria are found wherever there is a detectable level of iron or manganese in water.

Similar to chemical oxidation, biological oxidation of manganese is highly dependent on pH and redox potential of water. Manganese oxidation by 'iron bacteria' requires higher oxidation - reduction potential (ORP) values (Eh > 300 mv) than that for iron and pH of water should be greater that 7.5 for effective removal. Oxidation occurs according to some variation of the following three step reaction (Gage et al, 2001):

$$Mn^{2+} + O_2 = MnO_2 + \text{Energy}$$

$$Mn^{2+} + MnO_2 = MnO_{2o}Mn^{2+}$$

$$MnO_{2o}Mn^{2+} + O_2 = 2MnO_2$$

Once a biological iron or manganese removal plant is constructed, the system must be given time to 'seed' with bacteria naturally present in the water source. This seeded biomass is naturally and continuously regenerated during the life of the plant and is periodically partially removed through backwashing. For manganese removal plants the seeding time can be considerably longer, anywhere from 3 weeks to 3 months (Gage et al, 2001).

Advantages of biological oxidation process

- Smaller sized plants can be used because of higher applied filtration rates, (sometimes in excess of 50 m/hr versus 10 – 15 m/hr) or because aeration and filtration can take place simultaneously in the same vessel.
- Longer filter runs because manganese retention in the filter due to the formation of more dense precipitates and the use of a more course media
- Produce denser backwash sludge that is easier to thicken and de-water
- Higher net productions due to less water being required for backwashing and being able to use raw water for the backwash; less frequent backwashing is needed
- Require no chemical addition; and no deterioration of water quality over time;
- Lower capital and operating costs through the elimination of chemicals.

Disadvantages of biological oxidation process

- Difficult to control as the process occurs naturally
- Responsible bacteria require more stringent conditions for effective oxidation
- Not suitable for small scale removal

3.4.8 Filtration

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

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

There are two basic operations associated with filtration. They are described below:

(a) Rate of Flow

The filtration step includes application of water uniformly to the top of the filter. Often the rate of water application is described in relation to the area of the filter surface. The application rate can be expressed in cubic meters per hour of water per square meter of area (meters per hour) or gallons per minute per square foot. The rates that can be appropriately used will depend on the raw water quality, the pretreatment provided and the media used in the filter.

A typical rate for filtration would be 6 meters per hour (m/hr) or 2 gallons per minute per square foot (2 gpm/ft^2) although some filters may have been designed for higher rates. Normally, the lower rate will permit a better operation and subsequently less treatment and filter problems. The under drain system should be so designed that the water can be collected evenly from the filter. This type of system can be either a hub or lateral system which has a spoke type configuration or it could be a system of evenly spaced nozzles or collectors on a false bottom. The use of fine porous plates is normally not recommended for manganese removal since the small pore size is susceptible to clogging.

(b) Backwashing

The cleaning or backwashing of a filter is one of the most important aspects of filter operation. The process is to reverse the flow upwards from the under drain or distribution system up through the filter and waste that water. The cleaning action arises from the expansion of the bed and the rubbing of the filter particles so that all of the deposits become free and pass out in the wastewater. For effective backwashing, it is important that the rate of water applied be sufficiently large to permit a good expansion of the bed. This rate is also expressed as a water flow per unit area of filter. Typical backwash rates would be in the order of 60 to 70 meters per hour or 10 to 12 gallons per minute per square foot.

It is important that the distribution water be uniformly applied so that the entire filter bed is expanded evenly. Backwashing is normally carried out until the wastewater turns clear. The backwash water is then stopped and the filter is rinsed to waste before placing it into service. For manganese greensand, an air scour or air wash system is also useful to ensure the media becomes clean. This air wash is normally used during the backwash cycle after the filter has been initially flushed. It is also important that treated water is used to backwash and clean the filter media, particularly in the case of manganese greensand.

A brief description of common manganese treatment options and their suitability is shown in tabular form in table 3.2.

3.5 TREATMENT TYPES NOT RECOMMENDED

3.5.1 Magnetic manganese Removal Devices

The Water Quality Association (the professional association representing the home water treatment industry) has indicated that there is no proof that magnetic manganese removal devices are effective (Cameron an Bourgin, 1995).

3.5.2 Electrodialysis

This process will become clogged by any rust particles, manganese bacteria, silt etc. The treatment membranes cannot be rejuvenated and new membranes will be necessary. This equipment is very expensive to purchase and operate (Cameron and Bourgin, 1995).

Table 3.2 Treatment of Manganese and Iron in Drinking Water

Indication	**Cause**	**Treatment**
Water clear when drawn but red-brown or black particles appear as water stands; red-brown or black stains on fixtures or laundry	Dissolved iron or manganese	• Water softener (<5 mg/l combined concentrations of iron and manganese) • Oxidizing filter (manganese greensand or zeolite) (<15 mg/l combined concentrations of iron and manganese) • Aeration (pressure) (<25mg/l combined concentrations of iron and manganese) • Chemical oxidation with potassium permanganate or chlorine; followed with filtration (>10 mg/l iron/ manganese)
Water contains black particles when drawn; particles settle out as water stands	Oxidized manganese due to exposure of water to air prior to tap	Particle filter (if quantity of oxidized material is high, use larger filter than inline; e.g., sand filter)
Black slime appears in toilet tanks or from clogs in faucets	manganese bacteria	Kill bacteria masses by shock treatment with chlorine or potassium permanganate, then filter; bacteria may originate in well, so it may require continuous feed of chlorine or potassium permanganate, then filter
Black color that remains longer than 24 hours	Colloidal manganese; organically complexed manganese	Chemical oxidation with chlorine or potassium permanganate; followed with filtration

(Source: Varner et al, 1994)

3.5.3 Reverse Osmosis

This process will become clogged by rust particles, manganese bacteria, silt, etc. and cannot be rejuvenated. New membranes would be required. Like eletrodialysis process, this method is also expensive to operate (Cameron and Bourgin, 1995).

3.5.4 Bag Filtration

This method uses chemicals to cause formation of rust particles. The particles are removed from the water by passage through bag filters. The cost of this system is comparatively low. However, the bags must be manually cleaned which creates higher operational costs (Cameron and Bourgin, 1995).

3.6 SEQUESTERING PROCESS: PHOSPHATE TREATMENT

Sequestering of soluble manganese is the opposite of oxidation. It means to bind up or complex forming so as to prevent natural chemical reaction (Montgomery, 1986). Chemical used for sequestering is sodium hexametaphosphate, commonly known as polyphosphate. Low levels of up to 2 mg/l can be remedied using phosphate compound treatment (Singer, 1988). Phosphate compounds are a family of chemicals that can surround minerals and keep them in solution. Phosphate compounds injected into the water system can stabilize and disperse dissolved manganese at this level. As a result, manganese compounds are not available to react with oxygen and separate from solution. The phosphate compounds must be introduced into the water at a point where the iron is still dissolved in order to maintain water clarity and prevent possible iron staining. This should be before the pressure tank and as close to the well discharge point as possible (Varner et al, 1994).

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

Phosphate compounds are not stable at high temperatures. If phosphate compound-treated water is heated (for example, in a water heater or boiled water), the phosphates will break down and release iron and manganese. The released iron and manganese will then react with oxygen and precipitate.

Adding phosphate compounds is not recommended where the use of phosphate in most cleaning products is banned. Phosphate, from any source, contributes to excess nutrient content in surface water (Seelig, 1992).

CHAPTER 4

MANGANESE REMOVAL FROM GROUNDWATER BY OXIDATION

4.1 INTRODUCTION

Besides arsenic, iron and salinity (in coastal areas), excessive concentration of manganese is also a significant groundwater quality problem in many areas of Bangladesh (DPHE/ BGS, 2001). Presence of manganese in potable water may cause problems related to aesthetics (e.g., development of color in clothes and plumbing fixtures) and may cause precipitation in the water distribution system. Evidence of manganese neuro-toxicity has been found in people following long-term exposure. The World Health Organization (WHO) has a provisional health-based guideline value of 0.5 mg/l for manganese in drinking water (WHO, 1993). The WHO guideline value from aesthetics consideration is 0.1 mg/l. Bangladesh Standard for manganese in drinking water is also 0.10 mg/l. In the nationwide groundwater-quality survey (DPHE/ BGS, 2001), it has been found that about 35% of sample wells exceeds WHO health-based guideline value (0.5 mg/l) and about 73% of samples exceed Bangladesh guideline value (0.1 mg/l). Manganese concentration as high as 10 mg/l has been detected in this survey. Therefore, development of appropriate manganese removal technology in the context of Bangladesh is of prime importance.

Broadly manganese removal technologies can be categorized in two groups: (i) ion exchange and (ii) oxidation followed by precipitation of manganese in insoluble form(s). As described in Chapter 2, chemical oxidation followed by filtration, is by far the most widely used manganese removal technique. Common chemical oxidants include potassium chlorine, ozone, and permanganate. Besides, simple aeration has also been used for oxidation and subsequent removal of manganese. Efficiency and effectiveness of manganese removal depend on a range of factors including type of oxidant used, initial manganese concentration, pH, alkalinity, and a range of other water quality parameters. Though considerable work has been done elsewhere in the world, very limited works (e.g., BAMWSP/ DFID/ Water Aid, 2001; Tahura et al, 2001) have so far been done on the effectiveness of different oxidizing agents in removing manganese from groundwater of Bangladesh.

In Bangladesh, bleaching powder and potassium permanganate are easily available and these chemicals are also widely used for oxidation of As(III) to As(V) in many arsenic removal systems (Tahura et al, 2001). It may be mentioned that aeration followed by filtration is often used for removal of dissolved iron from groundwater in Bangladesh. However, vary limited data are available on effectiveness of these chemicals and processes in removing manganese from water (e.g., Tahura et al, 2001).

In this study, removal of manganese from natural groundwater by the oxidation process has been assessed using two commonly available oxidizing agents, potassium permanganate and chlorine. Effectiveness of manganese removal by simple aeration has also been evaluated. Besides, removal of color produced during permanganate oxidation of manganese has been assessed by using sand filtration. This chapter presents results of manganese removal from natural groundwater by aeration and chemical oxidation using potassium permanganate and chlorine (bleaching powder).

4.2 MATERIALS AND METHODS

In this study, the effectiveness of two oxidizing agents, bleaching powder and potassium permanganate, in removing manganese from groundwater by the oxidation process has been evaluated. Laboratory batch experiments were carried out to assess removal of manganese from groundwater under various conditions. In this study groundwater collected from a deep tubewell pumping stations at BUET was used. The advantage of using this water is that the concentrations of both manganese and iron in this water are very low, and therefore concentrations of these two parameters could be varied by appropriate spiking. Table 4.1 shows the characteristics of groundwater used in this study.

All batch experiments were carried out in 1-L glass beakers. In a typical batch experimental set up, 500-mL groundwater sample was taken in each of a series of 1-L glass beakers. Initial manganese concentrations in the groundwater samples were varied by spiking with a stock solution of manganese (containing 500 mg/l of Mn), prepared by dissolving anhydrous manganous sulfate salt ($MnSO_4.H_2O$) in deionized water.

Required doses of the oxidizing agents (either potassium permanganate or bleaching power) were added to the beakers by from stock solutions of potassium permanganate and bleaching powder, respectively.

After addition of the oxidizing agent, the content of each beaker was mixed in a jar test apparatus at 100 rpm for 10 minutes (when KMnO4 was used as oxidant; Fig. 4.1) or 30 minutes (when bleaching powder was used as oxidizing agent). The samples were then kept at rest for 30 minutes to allow the manganese solids, formed as a result of oxidation, to precipitate. The pH and Eh of the water samples in each beaker were then measured. About 50 ml of water sample was then drawn from each beaker from a depth of about 1-cm below the surface of liquid. These samples were tested for total manganese, color (during chemical oxidation) and residual chlorine (when bleaching powder was used as an oxidizing agent). Part of the sample withdrawn from each beaker was filtered through a 0.45 μm filter, and the filtrate was analyzed for total manganese. Each experiment was carried out in duplicate. Similar experiments were carried out to assess the effect of pH on manganese removal by both the oxidizing agents. The pH of water sample was adjusted by addition of solution of either NaOH or HCl as required.

Figure 4.2 shows a flow diagram of the experimental procedure followed in this study. Besides, additional experiments were carried out to evaluate the removal of manganese from groundwater by aeration. Experimental evaluation was also done to determine the effectiveness sand filter to remove color produced from oxidation of manganese with potassium permanganate. Additional details of each type of experimental set up are briefly described below.

4.2.1 Manganese Removal by Oxidation with $KMnO_4$

Available information (e.g., Raveendran et al, 2001) suggest that oxidation of manganese by potassium permanganate occurs in less than 5 minutes where the manganese was not present in complexed form. In this study, a mixing time of 10 minutes was allowed for complete oxidation of manganese.

Effect of initial manganese concentration on it removal efficiency was evaluated by varying the initial concentration of manganese from about 1.0 to about 10.0 mg/L. Initial pH of the samples were measured to be within the range of 7.7 to 7.8. Required dose of permanganate was calculated from the stoichiometry of Eq. 4.1. According to Eq. 4.1, for each mg/l of dissolved manganese, the required dose of potassium permanganate for complete oxidation of manganese is 1.917 mg/l. For these experiments, concentration of permanganate was fixed at 1.2 times that required from stoichiometric consideration.

$$3\,Mn^{2+} + 2\,KMnO_4 + 2\,H_2O = 5\,MnO_2\,(s) + 2K^+ + 4H^+ \qquad (4.1)$$

To evaluate effect of pH on manganese removal, experiments were carried out with an initial manganese concentration of about 2.0 mg/l. For these experiments, permanganate dose was set at exactly that required from stoichiometric consideration (i.e., 2.84 mg/l of $KMnO_4$ for 2.0 mg/l of manganese). The pH of the water samples were varied from about 4.8 to 10.0, by either NaOH (N/44) or HCl (concentrated) solutions.

Experiments were carried out to evaluate the effect of the dose of potassium permanganate (which also contains manganese) on the removal of manganese and the presence of residual manganese. These experiments were carried out with and initial manganese concentration of 2.0 mg/l. The dose of potassium permanganate was fixed at six different factors of that required from stoichiometric ratio. The factors were 0.25, 0.5, 0.8, 1.0, 1.2, and 1.5. That is the permanganate dose was varied from 0.25 to 1.5 times that required from stoichiometric consideration.

The effect of settling time on manganese removal was determined, in similar experimental set up, in order to assess the settling of manganese solids by gravity. Initial manganese concentration was set at 1.0 mg/l, 2.0 mg/l, 5.0 mg/l, and 10.0 mg/l. Permanganate dose was fixed at 1.2 times that required from stoichiometric consideration). In these experiments, after the initial mixing of 10 minutes (at 100 rpm), the contents of the beaker were allowed to settle and water samples were collected (from a depth of about 1 cm below the water surface) at time intervals of 30, 90 and 180 minutes.

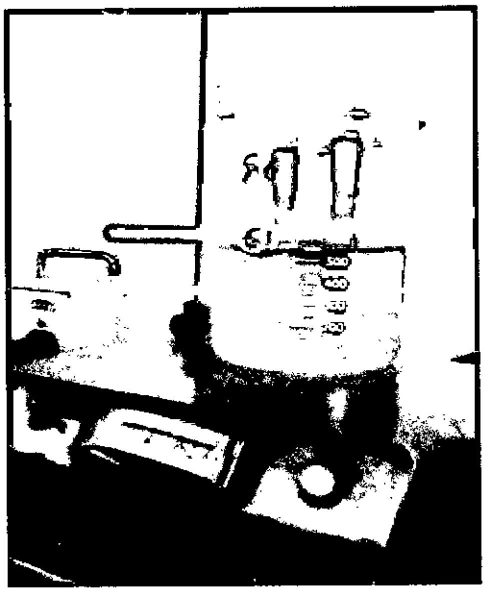


Figure 4.1: Mixing of $KMnO_4$ with groundwater containing Manganese

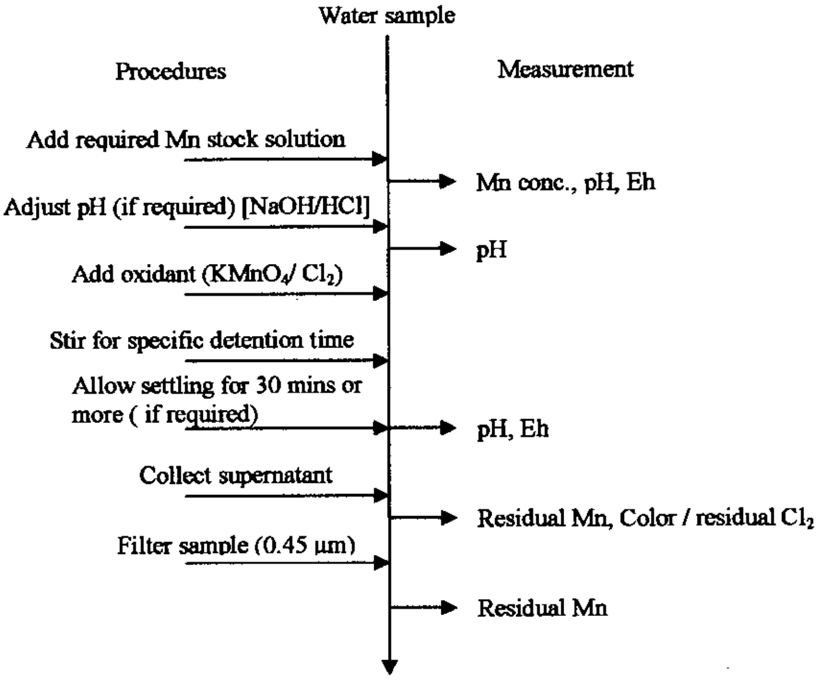


Figure 4.2: Flow diagram of experimental procedure followed for evaluating manganese removal by oxidation process

In manganese removal processes involving oxidation with potassium permanganate, it is customary to use some kind of filtration device to remove the manganese solids as well as the color produced due to addition of potassium permanganate. In Bangladesh sand filtration is common in many water treatment processes (e.g., arsenic and water treatment processes). Hence efficiency of sand filtration in removing manganese solids (formed as a result of oxidation with potassium permanganate) and color was evaluated in this study. The experimental set up is similar to that used by Ali et al. (2001). Sand filters were prepared in glass burettes having a cross-sectional area of 1 sq. cm. A pre-washed locally available sand sample was oven-dried at 105^0 C for 24 hrs.

The oven-dried sand was sieved and the portion of sand passing sieve # 30 and retained on sieve #40 was selected as filter media. This portion of the sand sample was then poured in to the burettes. Care was taken to ensure that no void space existed between the sand particles and the burette. Experiments on color removal were carried out for two different depths of sand filter, 10 cm and 20 cm.

For these experiments, water samples (3-litres) having initial manganese concentration of about 2.0 mg/l were treated with potassium permanganate at a dose 1.2 times that required from stoichiometric consideration. After the initial mixing for 10 minutes (at 100 rpm), the water sample was passed though the sand column. The flow rate was controlled to maintain a minimum contact time of 1 minute. The filtrate coming out of the bottom of the burette was collected at 30-minute interval and was analyzed for residual manganese and color. The experiments were carried out for a period of about 150 minutes.

4.2.2 Manganese Removal by Oxidation with Bleaching Powder

Available information (e.g., Seelig, 1992) suggest that oxidation of manganese by chlorine requires a contact time of about 20 minutes. In this study, a mixing time of 30 minutes was allowed for complete oxidation of manganese by chlorine (added in the form of bleaching powder).

Effect of initial manganese concentration on it removal efficiency was evaluated by varying the initial concentration of manganese from about 1.0 to about 10.0 mg/L. Required dose of chlorine (in the form of bleaching powder) was calculated from the stoichiometry of Eq. 4.2. According to Eq. 4.2, for each mg/l of dissolved manganese, the required dose of chlorine for complete oxidation of manganese is 1.29 mg/l. For these experiments, concentration of chlorine was fixed at 1.2 times that required from stoichiometric consideration. As oxidation by chlorine is known to be strongly dependent on pH (Benschoten et al, 1990), these experiments were carried out at three different pH values – 7.5, 8.5 and 10.0.

$$Mn^{2+} + Cl_2 + 2\,H_2O = MnO_2\,(s) + 2\,Cl^- + 4\,H^+ \tag{4.2}$$

To evaluate effect of pH on manganese removal, experiments were carried out with initial manganese concentration varying from about 1.0 mg/l. For these experiments, chlorine dose was set at exactly that required from stoichiometric consideration (i.e., 2.58 mg/l of Chlorine for 2.0 mg/l of manganese). The pH of the water samples were varied from about 5.2 to 10.0, by either NaOH (N/44) or HCl (concentrated) solutions.

A set of experiments was carried out to assess the effect of initial mixing time on manganese removal. For this purpose, initial contact time was fixed at 15, 25 and 35 minutes. For this set of experiments, initial manganese concentration varied from about 1.0 mg/L to 10.0 mg/l and pH was fixed at a value of about 10.0.

4.2.3 Manganese Removal by Aeration

Manganese removal by simple aeration was also evaluated in this study. The experimental set up for this purpose was similar to that used for manganese removal by an oxidizing agent, except that instead of adding an oxidizing agent, the water samples in the experimental beakers were aerated by vigorous mixing.

Available literature (e.g., Montgomery, 1986) suggest that for removal of manganese by simple oxidation, a contact time of several minutes to an hour may required for oxidation of manganese, depending on manganese concentration as well as some other parameter, e.g., pH. In this study, aeration (by vigorous mixing) was carried out for a period varying from 20 minutes to an hour. The mixing was done in a jar test apparatus, where mixing was carried out at 100 rpm. After completing the mixing, samples were filtered using 0.45 μm filter and analyzed for residual manganese.

For these experiments, initial manganese concentration was fixed at 2 mg/l and pH was varied from 7 to 11.

4.2.4 Chemicals, Preparation of Stock Solutions

All chemicals used in this study were of reagent grade. Stock solutions were prepared by dissolved appropriate salts to deionized water (Barnstead Fistreem III).

Manganese stock solution (containing about 500 mg/l of Mn) was prepared by dissolving anhydrous manganous sulfate salt ($MnSO_4.H_2O$; MW = 169.04) in deionized water. The stock solution was kept at a pH below 2.0 by acidifying with concentrated HCl. Stock solution of potassium permanganate (containing about 500 mg/l $KMnO_4$) was prepared by dissolving $KMnO_4$ crystals (MW = 158.07) in deionized water. The stock solution was kept in dark. A chlorine stock solution (having about 400 mg/l of Chlorine) was prepared by dissolving bleaching powder (with chlorine content of about 32%) in deionized water.

In this study, manganese concentration in water samples was measured by flame atomic absorption spectrophotometry, using an AAS (Shimadzu, 6800). A sample standard curve for manganese is shown in Fig. A1 in Appendix A. Measurement of pH was carried out with a digital pH meter (HACH, Sension 1) and Eh was measured with an Eh meter (WTW, Multiline P4). Color was measured with a spectrophotometer (HACH, DR2010). Residual chlorine in water samples was also measured with the spectrophotometer (by chlorine total DPD method). Other parameter was measured following standard methods (AWWA, 2002).

4.3 RESULTS AND DISCUSSIONS

4.3.1 Removal of Manganese by Oxidation with $KMnO_4$

This section describes the results of batch experiments designed to remove manganese from groundwater by oxidation with potassium permanganate. Batch experiments were conducted primarily to evaluate: (i) the effect of initial manganese concentration on manganese removal, (ii) effect of pH on manganese removal, (iii) effect of permanganate dose on manganese removal, and (iv) effect of settling time on manganese removal. Results from each set of experiment are described below.

Effect of Initial Manganese Concentration on Manganese Removal

Mechanisms involved in the removal of dissolved manganese from groundwater as a result of oxidation include: (i) oxidation (in solution) of dissolved Mn(II) into insoluble manganese solids [e.g., $MnO_2(s)$, $Mn_2O_3(s)$, $Mn_3O_4(s)$, and $Mn(OH)_2(s)$, MnOOH(s)]; (ii) surface mediated oxidation of Mn(II); and (iii) adsorption of dissolved Mn(II) onto oxide surfaces (e.g., on the insoluble manganese oxide surfaces). Permanganate being a highly reactive oxidant, oxidation (in solution) of Mn(II) into insoluble manganese solids is the primary removal mechanism (Benschoten et al., 1992).

Figure 4.3 shows percentage of removal of manganese for different initial manganese concentrations, varying from about 1.0 mg/l (0.0182 mM) to about 10.0 mg/l (0.182 mM). The permanganate dose for these experiments was fixed at 1.2 times that required from stoichiometric consideration. Figure 4.3 shows very good removal of manganese (expressed as "% removed") for all different initial manganese concentrations. In fact, for initial manganese concentration of up to about 2.0 mg/l, almost complete removal was achieved (i.e., residual manganese concentration below the MDL of 0.001 mg/l). For initial concentration ranging from about 4 to 10 mg/l, % removal approached about 98%.

Figure 4.4 shows residual manganese concentration (after filtration) for different initial manganese concentration. It shows that although manganese removal, when expressed "% Mn removed", does not appear to depend significantly on initial manganese concentration (Fig. 4.3), in terms of residual manganese the effect is not insignificant. For example, for an initial manganese concentration of about 10.0 mg/l, 98% removal means a residual concentration of 0.20 mg/l, which does not satisfy the Bangladesh drinking water standard as well as the WHO guideline value (from aesthetics consideration). However, the maximum residual concentration of manganese (0.22 mg/l for initial manganese concentration of about 10.0 mg/l) was much below the WHO health-based guideline value.

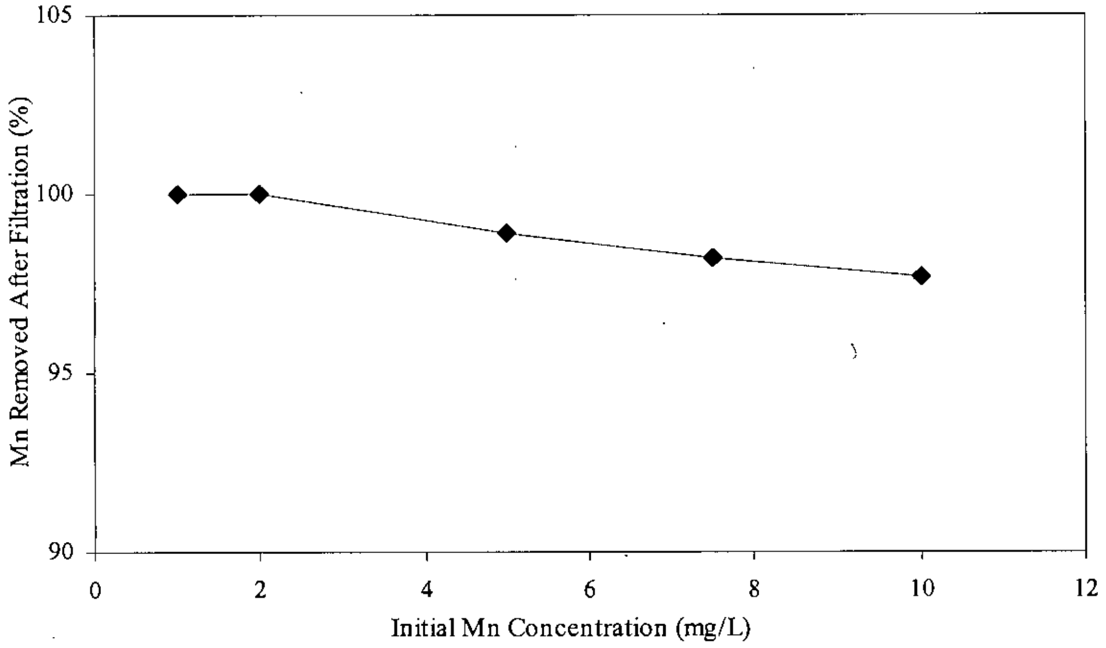


Figure 4.3: Removal of manganese by oxidation with $KMnO_4$ for different initial manganese concentrations (stoichiometry ratio = 1.2; Initial pH =7.7)

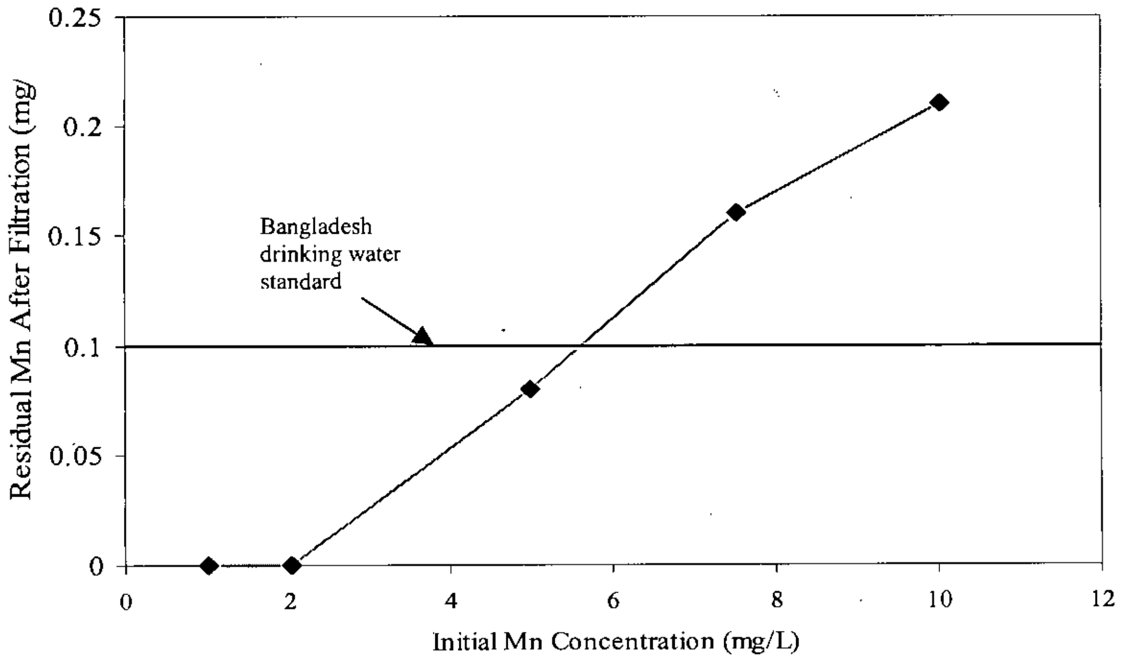


Figure 4.4: Residual manganese remaining in solution after filtration for different initial manganese concentration after oxidation with $KMnO_4$.(Stoichiometry ratio = 1.2)

In previous studies (e.g., Marble et al., 1999), it has been found that it is more difficult to remove Mn when the initial concentration is low, regardless of the oxidant used. However, for the lowest initial manganese concentration (about 1.0 mg/l) used in this study, this effect was not apparent. In comparison with the study conducted by Raveendran et al (2001), better removal is achieved in this study. In the study of Ravvendran et al (2001), for an initial manganese concentration of about 0.3 mg/L only 50% removal of manganese was achieved for $KMnO_4$ dose of 1.2 times of that obtained from stoichiometric consideration. Since pH of water sample for the different experiments varied over a relatively narrow range of 7.44 to 7.90, pH does not appear to have a significant effect on removal of manganese among the different experiments.

Results presented in Figs. 4.3 and 4.4 suggest that although oxidation by potassium permanganate (followed by filtration) could remove significant manganese from groundwater, for higher initial concentrations exceeding about 5.0 mg/l manganese, the residual manganese achievable may not satisfy the Bangladesh drinking water standard of 0.10 mg/l.

Measured Eh values for these experiments varied from a low of 230 mV for a permanganate dose of 2.3 mg/l (for 1 mg/l of manganese) to a high of 556 mV for a permanganate dose of about 23 mg/l (for 10 mg/l of manganese). As noted earlier pH for these experiments varied from 7.44 to 7.90. For these ranges of pH and Eh, the Eh-pH diagram of manganese (Fig. 3.3 of Chapter 3) suggest that the precipitated solids would be either $Mn_2O_3(s)$ (dark brown to black) or $Mn_3O_4(s)$ (reddish brown). The precipitated form would change from $Mn_3O_4(s)$ to $Mn_2O_3(s)$ as Eh value increases.

The observed color of the precipitates for different experimental conditions matched well with the color of the expected precipitate for that particular condition. For example, figures 4.5(a) shows photographs of precipitates of manganese solids (reddish brown) for an initial manganese concentration of 4.98 mg/l, for which measured pH and Eh were 7.74 and 225 mV, respectively. According to Fig. 3.3 of Chapter 3, for this condition the most likely precipitate is $Mn_3O_4(s)$, having a reddish brown color, which matched well with the observed color. Similarly, Fig. 4.5(b) shows dark brown colored precipitates of manganese solids for an initial manganese concentration of 10.02 mg/l, for which measured pH and Eh were 7.44 and 556 mV, respectively. According to Fig 3.3 of

Figure 4.5 (a) Color of precipitation for water with initial manganese concentration 5 mg/L (pH = 7.4; Eh = 230 mV)

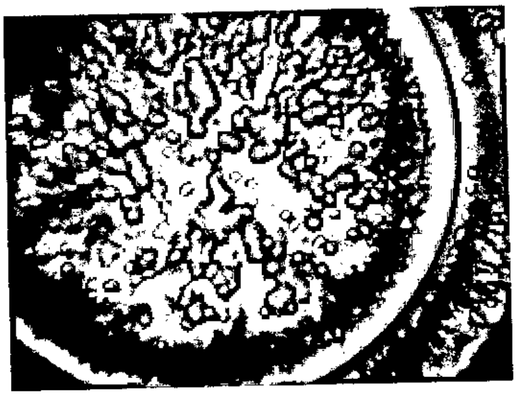


Figure 4.5 (b) Color of precipitation for water with initial manganese concentration 10 mg/L (pH = 7.9; Eh = 560 mV)

Chapter 3, for this condition the most likely precipitate is Mn_2O_3(s), having a dark brown to black color.

Effect of pH on Manganese Removal

In this study, effect of pH manganese removal was evaluated in batch experiments with an initial manganese concentration of about 2.0 mg/l, with a permanganate dose set at exactly that required from stoichiometric consideration (i.e., 2.84 mg/l of $KMnO_4$ for 2.0 mg/l of manganese). The pH of the water samples were varied from about 4.8 to 10.0. Figure 4.6 shows removal of manganese as a function of pH. Thus pH appears to have a major influence on the removal of manganese. In general, removal increased as pH increased. Beyond pH of about 8, removal is almost independent of pH.

It should be noted that oxygenation kinetics equation for manganese clearly shows that rate of reaction of Mn (II) has a second order relationship with hydroxyl ion concentration, which indicate that an increase in one pH unit, cause 100 fold increase in rate of reaction (Stumm and Morgan, 1984).

The pH of water also affects manganese removal by influencing the adsorption of dissolved Mn(II) on the MnO_2(s) formed as a result of oxidation. According to Marble et al (1998) overall mass transfer of Mn(II) from solution to active sites at the surface decreases as pH decreases because of competition with H^+. The capacity of oxide surface at pH 9 is about 2 mole of Mn(II) adsorbed per mole of MnO_2 (s). However, permanganate being a very strong oxidizing agent, it is capable to oxidize manganese over a wide pH range of 5-10 (Samblebe, 2003), though for rapid oxidation it is preferable to raise pH above 7.0 (Benschoten et al., 1992).

Thus, results from this study appear to agree well with those observed by other researchers (e.g., Raveendran,et al, 2001). Since pH of natural groundwater in Bangladesh usually falls around the neutral range, manganese from such groundwater could be effectively removed by potassium permanganate without any pH adjustment.

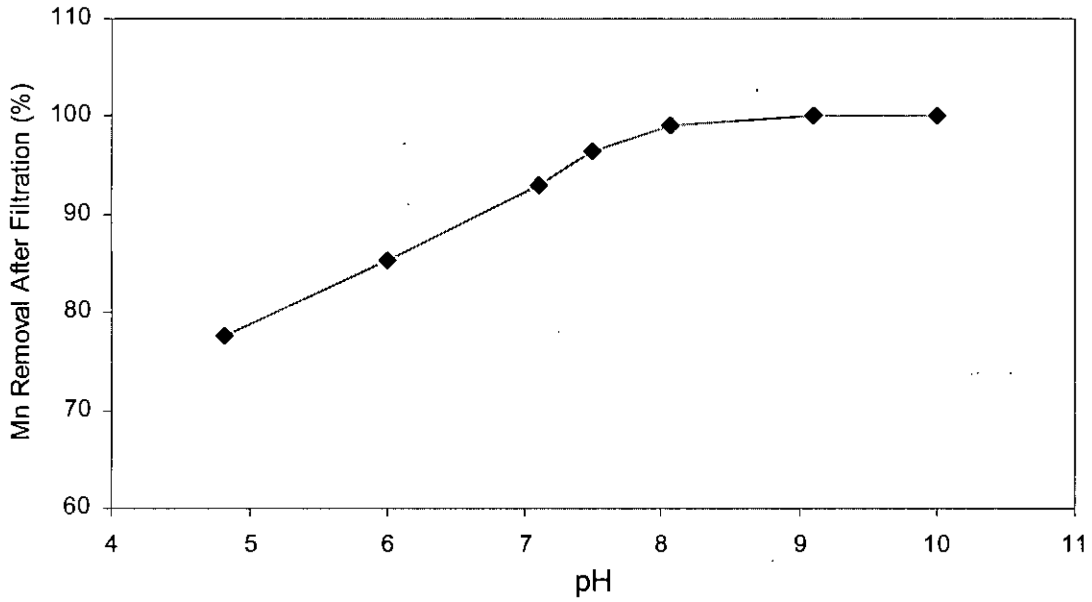


Figure 4.6: Removal of manganese by oxidation with $KMnO_4$ for different pH value (Initial Mn concentration= 2.0 mg/L; $KMnO_4$ stoichiometry ratio = 1.2)

Effect of Permanganate Dose on Manganese Removal

According to the stoichiometric equation for manganese oxidation by potassium permanganate (Eq. 4.1), it would require 1.92 mg of potassium permanganate to oxidize 1 mg of manganese ion. In practice, the actual amount of potassium permanganate used has been found to be less than that indicated by stoichiometry. It is thought that this is because of the catalytic influence of MnO_2 on the reactions (O'Connell, 1978). Unused permanganate, if any, would contribute to be increased residual manganese concentration.

In this study, effect of permanganate dose on manganese removal was evaluated in batch experiments with an initial manganese concentration of about 2.0 mg/l, where permanganate dose was varied from 0.25 times to 1.5 times that required from stoichiometric consideration. For 12 sets of experiments carried out for this purpose, pH varied from 7.56 to 8.10.

Figure 4.7 shows removal of manganese for different doses of potassium permanganate (expressed as multiple of stoichiometric ratio). It shows that manganese removal was low (about 50%) for a stoichiometric ratio of 0.25, and has increased as permanganate dose increases from 0.25 up to a stoichiometric ratio of 1.0. At a stoichiometric ratio of 1.0, manganese removal approaches 100%. At a stoichiometric ratio of 1.2, manganese removal decreased slightly and was about 97%, with residual manganese concentration of about 0.05 mg/l, below the Bangladesh drinking water standard of 0.10 mg/l. At even higher stoichiometric ratio (1.5), manganese removal decreased significantly. This was because of the presence of unused potassium permanganate that contributes to the residual manganese. At a stoichiometric ratio of 1.5, manganese removal drops to about 85% with residual manganese concentration of about 0.30 mg/l.

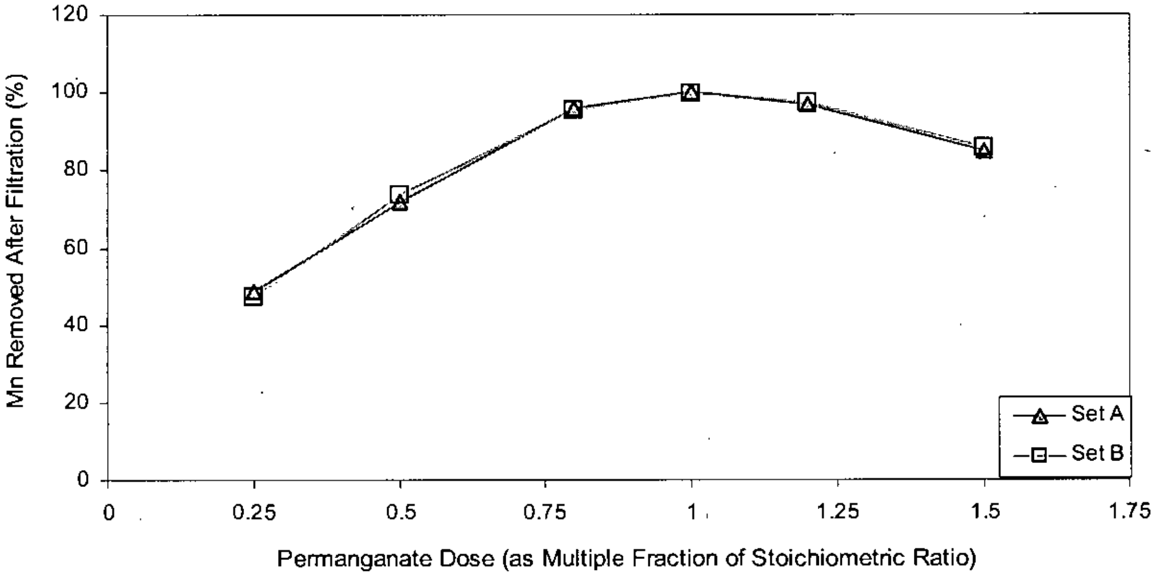


Figure 4.7: Removal of manganese by oxidation with $KMnO_4$ for different doses of $KMnO_4$ expressed as multiple of stoichiometric ratio (Initial Mn concentration= 2.0 mg/L)

Thus, results from this study show maximum manganese removal at a permanganate dose equal to that required from stoichiometric consideration. However, a slight overdose of permanganate (e.g., for ensuring a factor of safety) would not affect residual manganese concentration significantly when initial manganese concentration is below 5.0 mg/L. However, for higher values of initial Mn concentration (> 5.0 mg/L) is a concern.

As noted earlier, pH value of these experiments varied from 7.56 to 8.1, which is a favorable range for manganese oxidation. Permanganate dose may have a higher influence on manganese removal below neutral pH range.

Eh values measured for these experiments varied from 174 mV to 230 mV; generally increasing with increasing permanganate dose. For this range of Eh and pH values (varying from 7.56 to 8.1), the precipitated solid would most likely be Mn_3O_4(s), according to the Eh-pH diagram shown in Fig 3.3 in Chapter 3. As before, the precipitates were found to be reddish to dark brown.

Effect of Settling Time on Manganese Removal and Color

In order to evaluate effect of settling time (detention time) on removal of manganese (by gravity settling of manganese solids) and color, experiments were carried out with initial manganese concentration varying from about 1.0 to about 10.0 mg/l. Potassium permanganate dose was set at 1.2 times that required from stoichiometric consideration. These experiments are the same as those carried out to assess the effect of initial manganese concentration on manganese removal.

Figure 4.8 shows removal of manganese from solution as a function of time for different initial manganese concentrations. It shows that for a particular initial manganese concentration, manganese removal (by gravity settling of manganese flocs) increases with increasing settling/ detention time. For example, for an initial manganese concentration of about 2.0 mg/l, manganese removal (for a sample taken from 1-cm below the surface of water) after 30 minutes was about 86%, after 90 minutes about 96%, and after 3 hours about 100%. Figure 4.8 shows that after about 3 hours of detention time, manganese removal by gravity settling approaches that achievable by filtration (with a 0.45 m filter).

Figure 4.9 shows residual manganese concentration (for water sample collected form 1-cm below water surface) in water as a function of settlement/ detention time for different initial manganese concentrations. It shows the with prolonged detention time (3 hours), residual manganese concentration could be brought down to levels satisfying the WHO standard (health-based). But however, for initial manganese concentration equal to or greater than 5.0 mg/L, residual manganese concentration was above Bangladesh standard (WHO aesthetic-based standard) even after allowing 3 hrs settlement/detention time.

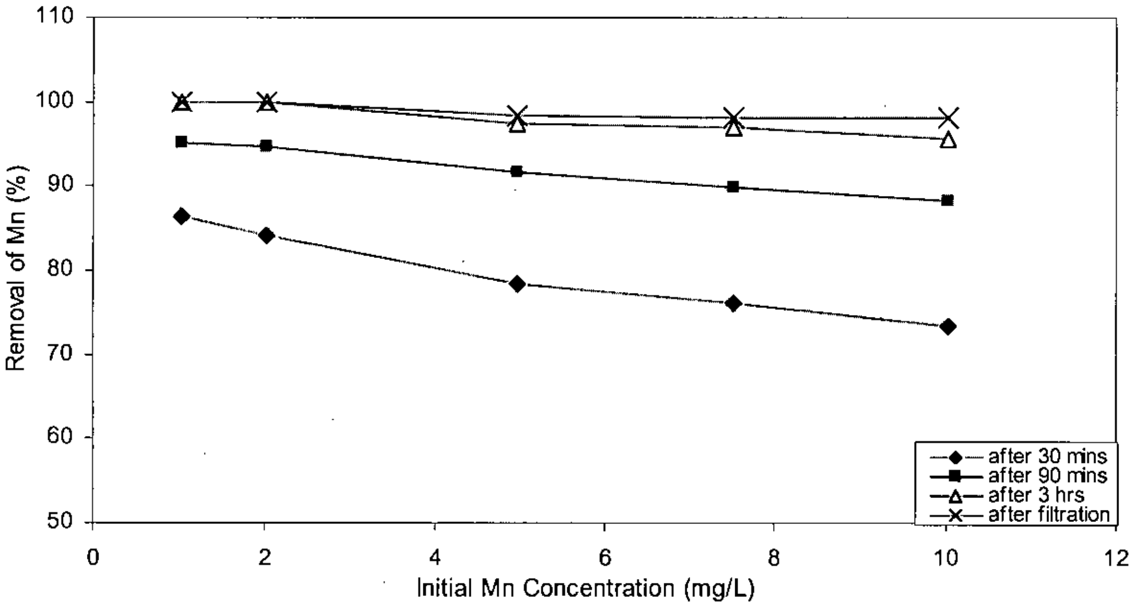


Figure 4.8: Removal of manganese by oxidation with $KMnO_4$ as a function of initial manganese concentration for different settling times. ($KMnO_4$ stoichiometric ratio =1.2; Initial pH = 7.7)

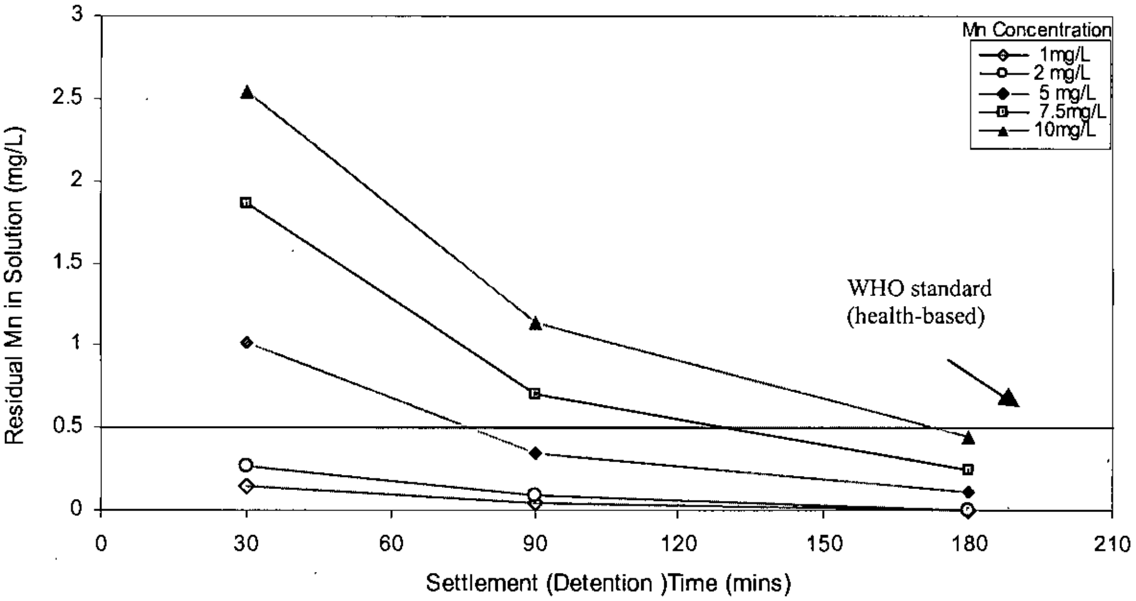


Figure 4.9: Residual manganese concentrations as a function of settling time after oxidation with $KMnO_4$ for different initial manganese concentrations. (stoichiometric ratio = 1.2; Initial pH 7.7).

Figure 4.10 shows concentration of color (in Pt.-Co. Unit) in water at different times after addition of potassium permanganate. It shows that for a particular time interval, color increases as initial manganese concentration (and hence corresponding potassium permanganate dose) increases. For example, for an initial manganese concentration of about 1.0 mg/l, the potassium permanganate dose was 2.3 mg/l and the corresponding color, after 30 minutes, varied from 78 to 82. For initial manganese concentration of about 10.0 mg/l, the potassium permanganate dose was 23.0 mg/l and the corresponding color, after 30 minutes, varied from 549 to 556. Thus, color concentration appears to be proportional to the dose of potassium permanganate added.

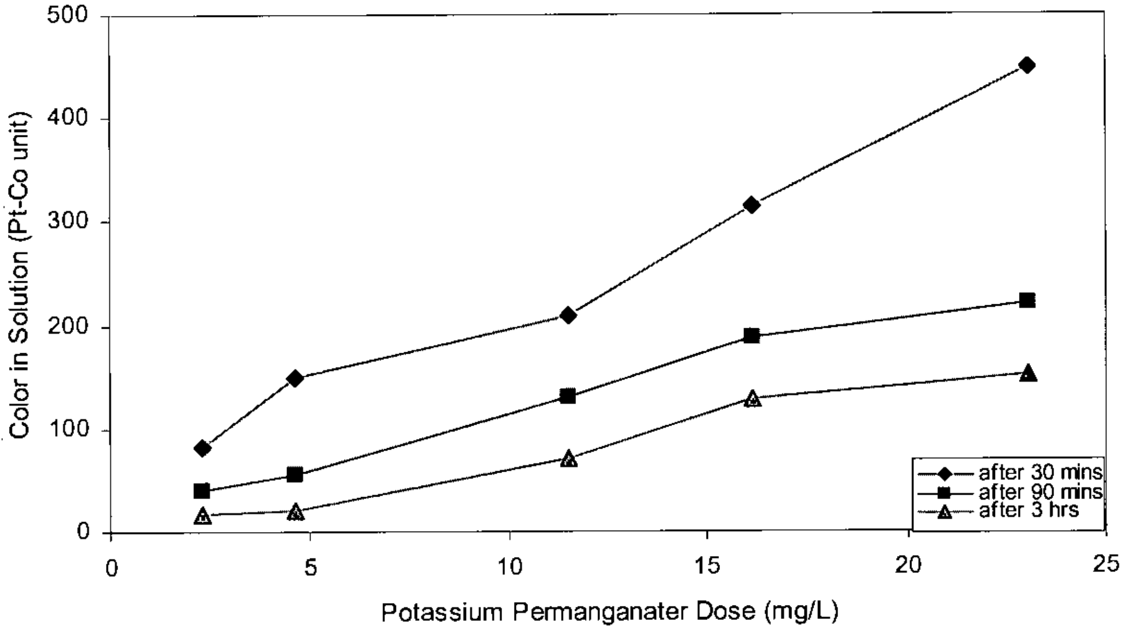


Figure 4.10: Color remaining in solution as a function $KMnO_4$ doses for different settling times. (Stoichiometry ratio= 1.2; Initial pH 7.7)

Figure 4.10 also shows that for a particular initial manganese concentration (and hence for a particular permanganate dose), color decreases with time as a result of settling. For example, for an initial manganese concentration of about 2.0 mg/l, the potassium permanganate dose was 4.6 mg/l and the corresponding color (average value) after 30 minutes was 140 Pt.-Co. unit, after 90 minutes 54 Pt.-Co. unit, and after 3 hours 24 Pt.-Co. unit.

Figure 4.11 shows color of water samples as a function of settling/ detention time for different initial manganese concentration. It shows that except for the lowest initial manganese concentration (i.e., 1.0 mg/l), all color concentrations were above the Bangladesh drinking water standard, even after 3 hours of settling/ detention time. Thus, it is clear that settling/ detention alone would not remove color from water treated with potassium permanganate. Hence, appropriate filtration would be required to remove color, although it appears that manganese solids (produced as a result of oxidation with potassium permanganate) could be removal by prolonged gravity settling.

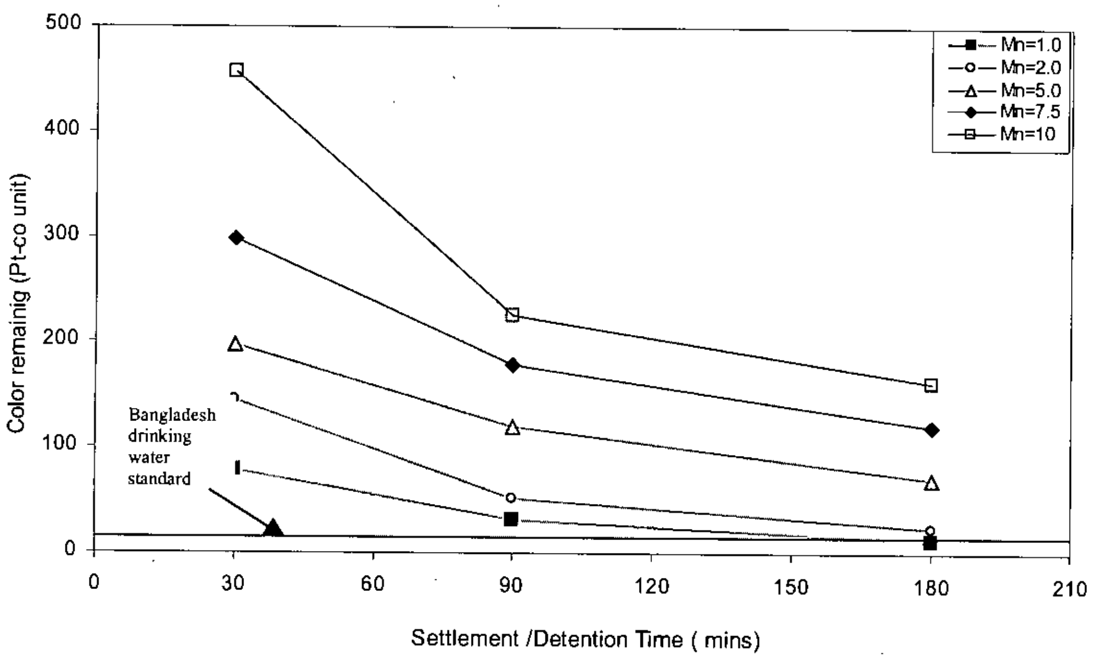


Figure 4.11: Color remained in solution as a function of settlement time for different amount of initial manganese concentration (Stoichiometry ratio= 1.2)

Removal of Color and Manganese by Sand Filtration after Oxidation with Potassium Permanganate

Figures 4.12 shows removal of color as a function of bed volume of liquid passed through the 10-cm and 20-cm deep sand filter column. Initial concentration of color of the water samples, having an initial manganese concentration of about 2.0 mg/l and treated with potassium permanganate, were 244 and 225 Pt.-Co. unit, respectively. Significant color removal was achieved with both the filters. However, for the 10-cm filter, measured color slightly exceeded the Bangladesh drinking water standard (15 Pt.-Co.) for bed volume of up to about 80.

Figures 4.13 shows removal of manganese as a function of pore volume of liquid passed through the 10-cm and 20-cm deep sand filter column. Manganese concentration in the filtrate varied from 0.01 to 0.04 mg/l for both the sand filters. In similar experiments performed earlier in this study, residual manganese concentration after filtration with a 0.45 μm filter paper was < 0.001 mg/l. Though such low levels of manganese could not be achieved by sand filtration, all residual manganese concentrations (after sand filtration) were well below the Bangladesh drinking water standard of 0.10 mg/l.

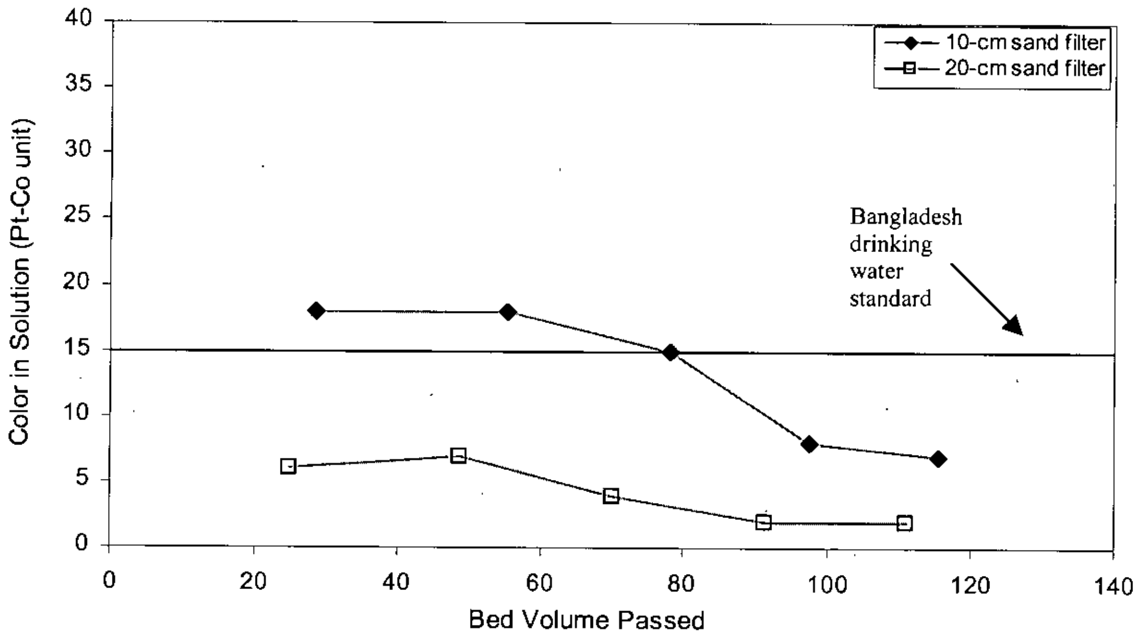


Figure 4.12: Color remaining in solution after passage through sand filter column as a function of pore volume of liquid passed. (Initial Mn concentration = 2.0 mg/L; Stoichiometry ratio for $KMnO_4$ = 1.2)

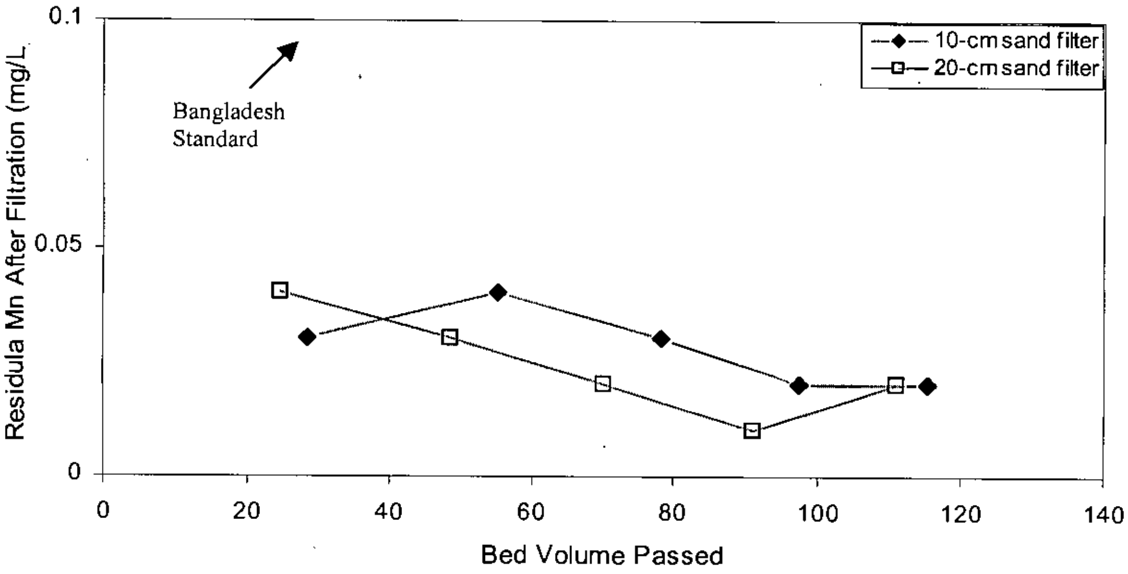


Figure 4.13: Residual manganese remaining in solution after passage through sand filter column, as a function of pore volume of liquid passed. (Initial Mn concentration 2.0mg/L; Stoichiometry ratio for $KMnO_4$ = 1.2)

4.3.2 Removal of Manganese by Oxidation with Bleaching Powder

Effect of Initial Manganese Concentration and pH on Manganese Removal

Figure 4.14 shows manganese removal by oxidation with chlorine (added in the form of bleaching powder) at different pH values for different initial manganese concentrations (varying from about 1.0 mg/l to about 10.0 mg/l). The chlorine dose was fixed at 1.2 times that required from stoichiometric consideration. As explained earlier, experiments were carried out at three different pH values: 7.5, 8.5 and 10.0. pH was adjusted with NaOH (N/44) solution. After the equilibration period, the final pH was also recorded. For the 10 sets of experiments run at pH ≈ 7.5, the final measured pH varied from 7.24 to 7.42; for experiments run at pH ≈ 8.5, the final measured pH varied from 8.21 to 8.42; and for experiments at pH ≈ 10.0, the measured pH varied from 9.68 to 9.75.

Figure 4.14 shows for all three pH values, manganese removal (expressed as % removal) decreased as initial manganese concentration increased. At pH ≈ 7.5, manganese removal is relatively poor, varying from about 50% for an initial manganese concentration of 1 mg/l to about 23% for an initial concentration of 10 mg/l. At pH ≈ 8.5, manganese removal improved significantly, varying from about 83% for an initial manganese concentration of 1 mg/l to about 73% for an initial concentration of 10 mg/l. At pH close to 10, complete manganese removal was achieved (i.e., residual manganese below the MDL of 0.001 mg/l).

Figure 4.15 shows chlorine dose added and residual chlorine remaining in solution at three different pH values. It is clear that utilization of added chlorine becomes much better as pH increases. At pH ≈ 7.5, measured Eh values varied from – 77 to – 54 mV; for pH ≈ 8.5, Eh varied from – 176 to – 70 mV; and for pH ≈ 10, measured Eh varied from – 88 to – 70 mV. For these ranges of pH and Eh, the Eh-pH diagram of manganese (Fig.3.3 of Chapter 3) suggest that the precipitated solids would be either $Mn(OH)_2(s)$ (cream colored) or $Mn_3O_4(s)$ (reddish brown). The precipitated form would change from $Mn(OH)_2(s)$ to $Mn_3O_4(s)$ as Eh value increases. Observed color of precipitates is shown in Fig. 4.16(a), (b), and (c). It indicates that the color of the precipitate was off-white, when pH was relatively low and cream-brown to light reddish-brown, when pH was relatively high.

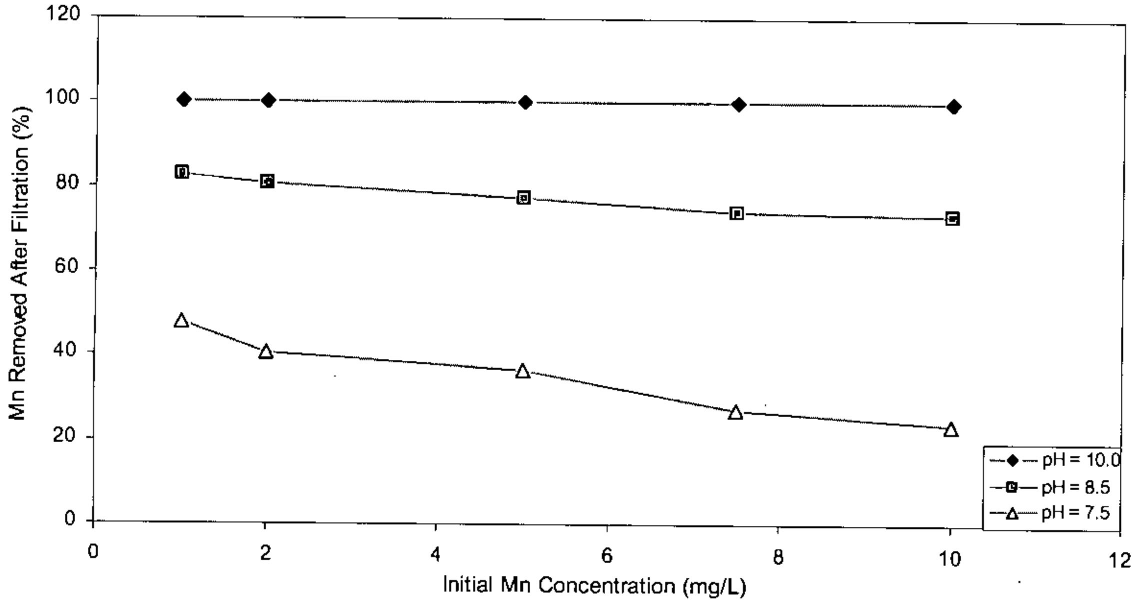


Figure 4.14: Removal of manganese by oxidation with bleaching powder, as a function of initial manganese concentration at different pH values (Chlorine stoichiometry ratio = 1.2)

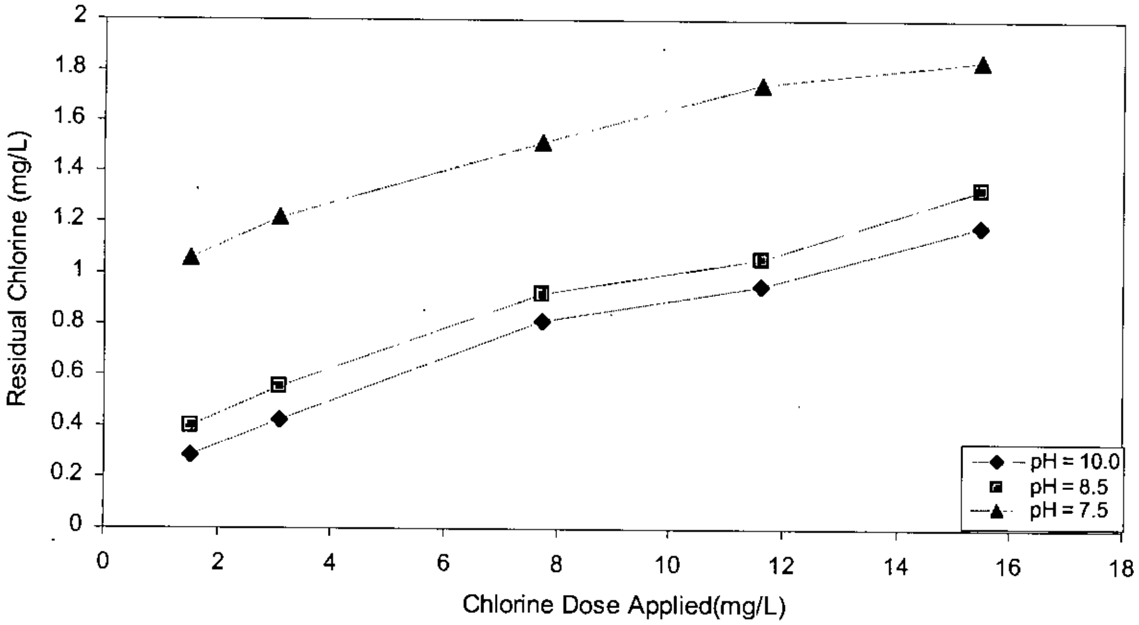


Figure 4.15: Residual chlorine remained in solution after oxidation with chlorine of groundwater containing different amount of initial manganese for amount of chlorine dose applied (Initial Mn Concentration = 2.0 mg/L; Chlorine stoichiometry ratio = 1.2)

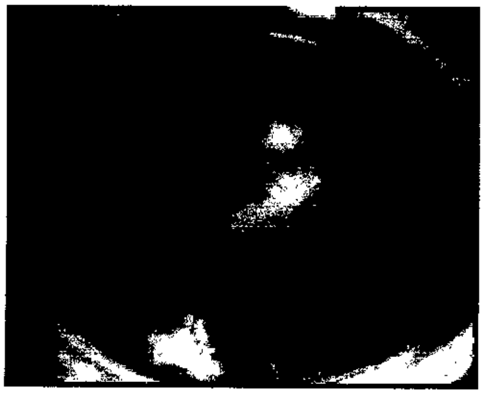


Figure 4.16(a) Color of precipitation for water with initial manganese concentration 1.0 mg/L (pH ≈7.4; Eh ≈ -70 mV)

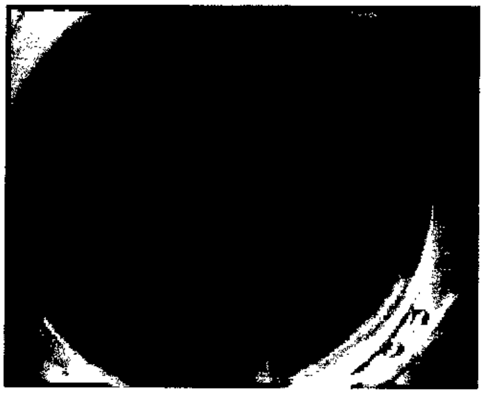


Figure 4.16(b) Color of precipitation for water with initial manganese concentration 5.0 mg/L (pH ≈8.4; Eh ≈ -176 mV)

Figure 4.16(c) Color of precipitation for water with initial manganese concentration 10.0 mg/L (pH ≈9.7; Eh ≈ -80 mV)

Figure 4.17 shows results of another set of experiments carried out to evaluate the effect of pH on manganese removal by bleaching powder. This experiment was carried out with an initial manganese concentration of about 2.0 mg/l; chlorine dose was set at exactly that required from stoichiometric consideration and pH was varied from 5.2 to 10. As shown in Fig. 4.15, manganese removal was found to be strongly dependent on pH. Removal of manganese varied from a very low of about 8.5% at pH 5.2 to about 100% at pH 10.

These results are not surprising as chlorine is a weak oxidant, and manganese removal by chlorination is usually not very effective until pH is raised above 8.5; and for high level of manganese it is often needed to raise pH above 9.5 (Benschoten et al, 1990). Samblebe (2003) also reported that for slow oxidizing agents like molecular oxygen or chlorine it is necessary to raise the pH above 8.5 for effective oxidation reaction of manganese. Besides higher pH also promotes rate of oxidation of manganese by oxygen. In treatment systems, soda ash is often injected with the chlorine to raise pH to optimum levels. Adjusting the pH to alkaline levels also reduces the corrosivity of the water to pipes and plumbing (Seelig, 1992).

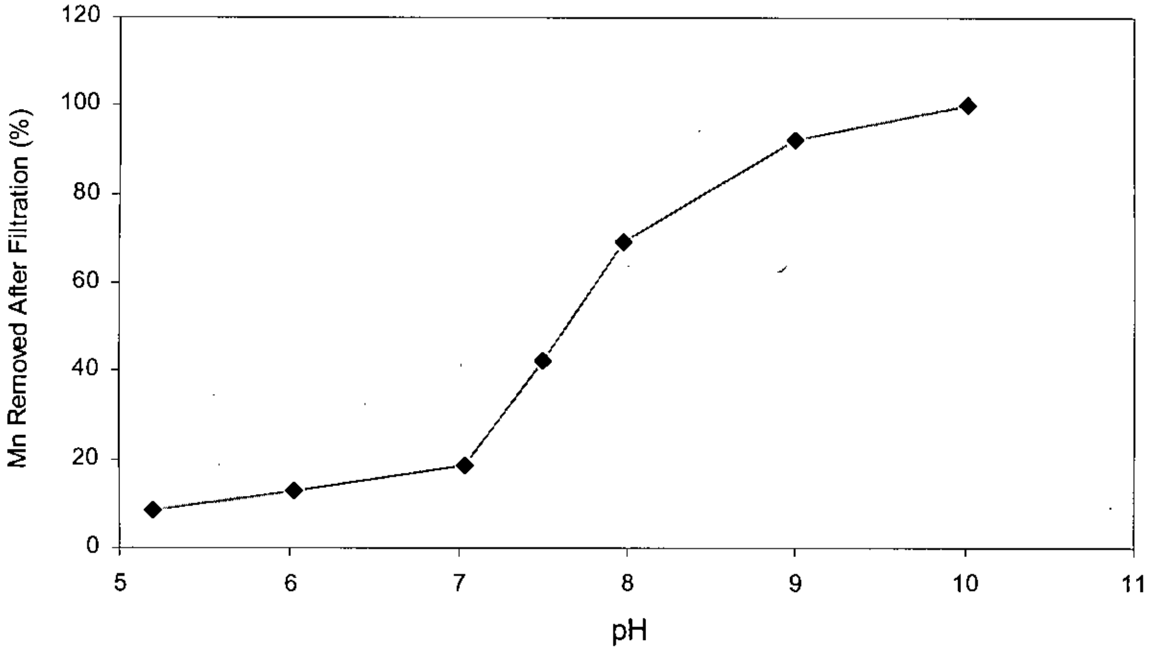


Figure 4.17: Removal of manganese by oxidation with chlorine at different pH values (Initial Mn concentration =2.0 mg/L; Chlorine dose added = 2.58 mg/L)

Effect of Contact Time on Manganese Removal by Bleaching Powder

Since chlorine (bleaching powder) is a slow oxidizing agent, effect of contact time on manganese removal was evaluated in this study. For this purpose, experiments were carried out with initial manganese concentrations varying from about 1.0 to 10.0 mg/l; chlorine dose was set at 1.2 times that required from stoichiometric consideration and pH was fixed at close to 10.0. The contact time of the oxidant (bleaching powder) was fixed at 15 minutes, 25 minutes and 35 minutes. Figure 4.18 shows manganese removal as a function of initial manganese concentration for the three different contact times. It shows that for any particular initial manganese concentration, removal increases as contact time increases. For example, for an initial manganese concentration of about 2.0 mg/l, average manganese removal for 15, 25 and 35 minute contact times are about 65, 89 and 99 percent, respectively. Thus, it appears that efficiency of manganese removal by bleaching powder could be improved by increasing the contact time with the oxidant.

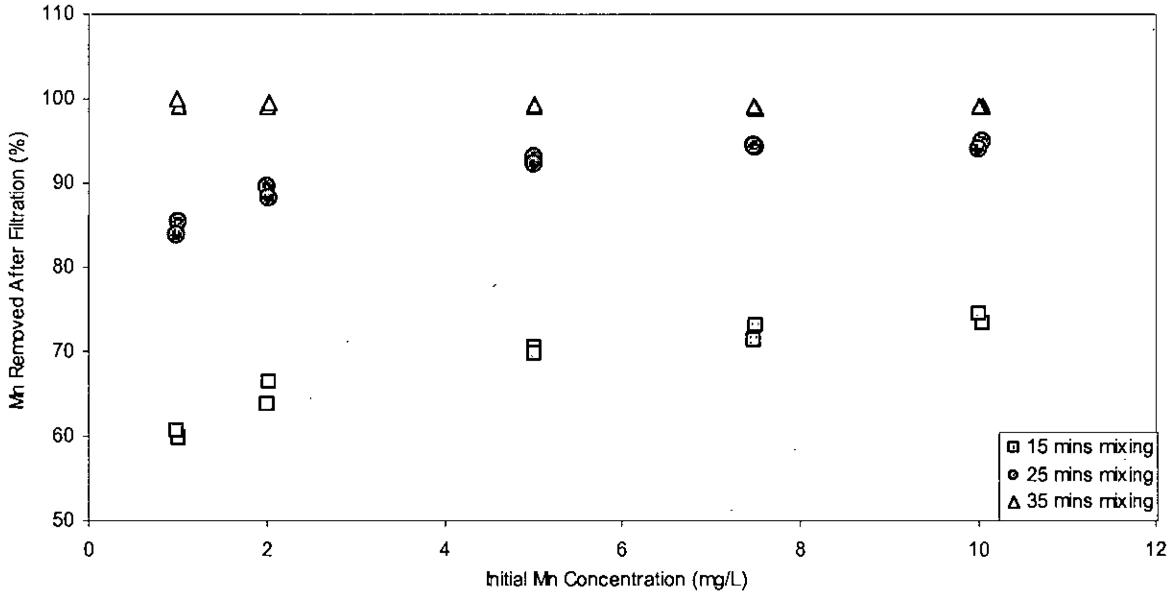


Figure 4.18: Removal of manganese by oxidation with chlorine as a function of initial manganese concentration for different contact times (Initial Mn conc. = 2.0 mg/L; Initial pH = 10; chlorine stoichiometry ratio=1.2)

4.3.3Manganese Removal by Aeration

Figure 4.19 shows removal of manganese (present at an initial concentration of about 2.0 mg/l) by simple aeration as a function of pH for different period of mixing (aeration). It shows that for a particular pH manganese removal increased as aeration period increased; and for a particular aeration period removal increased as pH increased. However, these results show that pH has a much more pronounced effect on manganese removal than aeration time. For example for a 30 minute contact time, removal of manganese increased from about 10% to about 93% as pH increased from 7.04 to about 10.

These results are not surprising because the rate of oxidation of Mn (II) has a second order relationship with hydroxyl ion concentration, which indicate that an increase in one pH unit would cause about 100 fold increase in rate of the oxidation reaction (Stumm and Morgan, 1984). On the other hand, manganese oxidation is not strongly dependent on the concentration of dissolved oxygen. It has been observed that above about 30% saturation value of dissolve oxygen, there is no significant dependence of the manganese oxidation reaction on the concentration of dissolve oxygen. Many other researchers [e.g., Graveland and Heertjes, 1975; Tebo and Emerson, 1985; Tebo and others, 1991] reported no dependence of the rate of Mn(II) removal on DO above concentrations of about 1 mg/l (i.e.about 12% air saturation, or 0.03 mM) and an approximate linear dependence at lower DO values (Marble et al, 1999).

A comparison of manganese removal (after filtration) by bleaching powder and simple aeration at different pH values (pH 7 to 10) is shown in Figure 4.20. The figure shows that at pH 7 removal of manganese by both methods was almost same. But at pH values in between 7 to 9, manganese removal by bleaching powder oxidation was slightly higher than that from aeration. At higher pH (at 10), removal was almost same. It should be noted that for bleaching powder a contact time of 30 mins was maintained and in case of aeration, removal (after filtration) for a contact time of 60 mins was plotted. Therefore, it appears that oxidation by mixing with bleaching powder is slightly more effective within the pH range of 7 to 9 compared to oxidation by aeration (by mixing). However, it should be noted that, during bleaching powder oxidation, aeration also occurred during mixing. Therefore, manganese removal by bleaching powder oxidation may also include effect of oxidation by aeration during mixing.

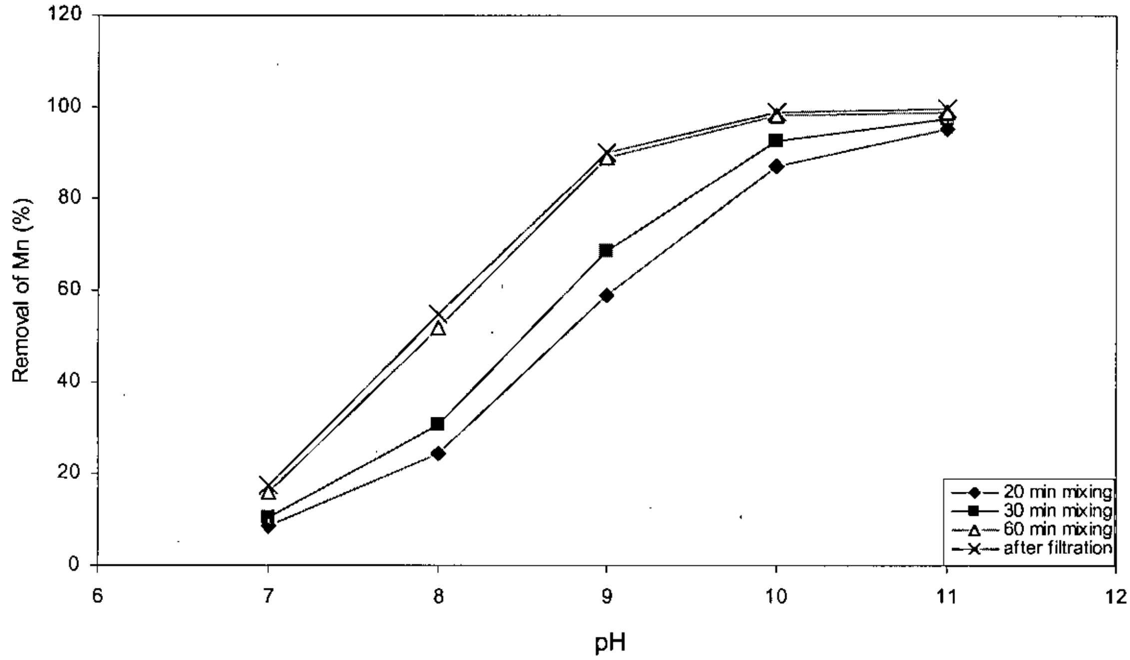


Figure 4.19: Removal of manganese by aeration for different initial manganese concentration at different pH values (Initial Mn = 2.0 mg/L)

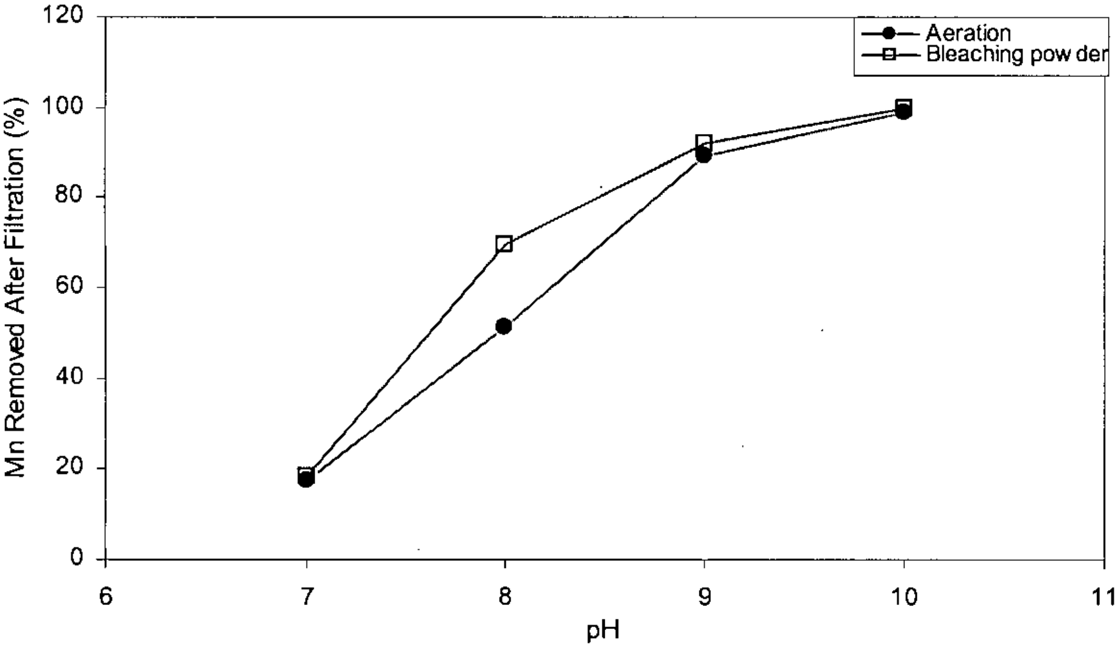


Figure 4.20: Comparison of removal of manganese (after filtration) by aeration and by bleaching powder oxidation at different pH values (Initial Mn = 2.0 mg/L; for aeration contact time= 60 mins; for bleaching powder oxidation contact time = 30 mins)

4.4 SUMMARY

Potassium permanganate is found to be very effective oxidizing manganese. Very good removal of manganese for different initial manganese concentrations varying from 1.0 to 10.0 mg/L was achieved. For initial manganese concentration of up to about 2.0 mg/l, almost 100% removal was achieved. Although oxidation by potassium permanganate (followed by filtration) could remove significant manganese from groundwater, for higher initial concentrations exceeding about 5.0 mg/l manganese, the residual manganese achievable may not satisfy the Bangladesh drinking water standard of 0.10 mg/l.

Manganese oxidation with $KMnO_4$ increases rapidly above pH 7.5 (greater than 95%). Complete removal can be achieved around pH 9. Since pH of natural groundwater in Bangladesh usually falls around the neutral range, it appears, manganese from such groundwater could be effectively removed by potassium permanganate without any pH adjustment.

Optimum manganese removal (100%) has been found at a permanganate dose equal to that required from stoichiometric consideration. However, a slight overdose of permanganate (1.2 times of stoichiometry ratio) did not affect residual manganese concentration significantly. A dose about 0.8 times of stoichiometry ratio removed about 95% manganese for an initial manganese concentration of 2.0 mg/L.

Sand filter has been proved very effective (for both 10-cm and 20-cm depth) in removal of the color developed in water due to addition of $KMnO_4$. Sand filtration has also been found to be very effective in removing solid manganese oxides efficiently (>99%, for initial Mn concentration of 2.0 mg/L).

For an initial manganese concentration of 2.0 mg/L, complete removal was possible for a settlement time of 3hrs. For initial Mn concentration varying from 5.0 to 10.0 mg/L, removal by a 3-hrs settlement was greater than 95%.

Manganese oxidation using Bleaching powder has been found to be less effective than permanganate in the natural pH range of groundwater. At pH 7.5, removal by chlorine oxidation varied from about 23% to 49% for initial Mn concentration of 10.0 to 1.0 mg/L, respectively. At pH 8.5, corresponding removal was 83% and 73%, respectively. At pH 10, complete removal occurred regardless of initial concentration.

Manganese oxidation by aeration is possible at high pH value. At pH 7, removal after aeration, followed by filtration has been found to be only 15% for an initial Mn concentration of 2.0 mg/L. At pH 9, removal increased to 89% (for a contact time of 60 mins) Complete removal was achieved at pH 11, regardless of contact time.

CHAPTER 5

MANGANESE OXIDATION IN PRESENCE OF IRON

5.1 INTRODUCTION

Occurrence of iron in groundwater is one of the most wide spread and significant water quality problems in Bangladesh. In most of the areas of Bangladesh significantly high amount of iron is present in groundwater. As described in chapter two, more than 65% tubewells surveyed during National Hydrochemical Survey (NHS), exceeded WHO guideline value (0.3 mg/L) for iron (DPHE/BGS, 2001). Presence of iron in water is not a health concern but cause the water to be unsightly, taste bad, sticky hair and stain plumbing fixtures and laundry (Cameron and Bourgin, 1995). In literature reviews in chapter two, it is described that manganese can cause similar problems even existing at very low concentration (less than 0.02). From NHS it is found that only about 47% of tubewells of Bangladesh have both iron and manganese concentration below the acceptable limit from aesthetic view point (0.3 mg/L and 0.10 mg/L respectively). Therefore, in many areas of Bangladesh it may be necessary to remove both of these elements from groundwater to increase the effective use of the groundwater.

Considerable works have been carried out in Bangladesh over the last three decades for removal of iron from groundwater. In recent years substantial amount of work has been done on removal of arsenic and iron-arsenic. Consideration of possible presence and removal of manganese has given less emphasis. Only a few studies (e.g., Tahura et al, 2001; Ali et al, 2001; BAMWSP/DFID/Water Aid, 2001) on iron and arsenic removal have provided data on manganese removal by those treatment options of iron and arsenic removal. Moreover in those studies, manganese concentration was below 1.0 mg/L. Only two tubewells had concentration above 1.0 mg/L (BAMWSP/DFID/Water Aid, 2001) but it was found that removal of manganese was poor for that tubewells. As both iron and manganese are present at considerable level in many groundwater sources, it is necessary to develop any treatment option for simultaneous removal of these two elements.

Processes in which oxidation is followed by filtration are found to effectively remove soluble iron from water. Usually oxidation of iron is accomplished by simple aeration or chlorination or potassium permanganate application (Shahid, 1998). These oxidizing agents are also used for manganese oxidation. Iron is oxidized at relatively lower pH value than manganese. Soluble ferrous iron is oxidized very rapidly to insoluble ferric at pH range 7 to 11(Shahid, 1998). Whereas, manganese oxidation is more effective at relatively higher pH range (above 7.5 in case of permanganate oxidation). So in natural pH range, for a water source where both iron and manganese are present at elevated level, a portion of oxidation dose provided for manganese removal may be consumed by dissolved iron. These may lead to inefficient removal of both iron and manganese by oxidation.

Again during oxidation processes insoluble iron flocs are formed. Manganese solids produced from oxidation gradually settle down with time. As evaluated in chapter four, considerable amount of settlement time is required for removal of oxidized manganese solids from solution. Presence of iron may influence settlement of solid manganese particles.

In chapter four, it is found that during permanganate oxidation and as well as chlorine oxidation of high manganese concentration, significant amount of color is produced. Therefore it was necessary to provide father treatment option for this color removal. Presence of soluble iron in water may have some effect on color removal produced during oxidation.

In many iron treatment plants, iron is removed by simple aeration at elevated pH (7.5 to 8) followed by suitable filtration option (Shahid, 1998). From assessment of manganese removal by simple aeration (chapter four), it is found that at pH below 10 manganese removal by aeration is not very effective. However, if soluble iron is present in such water, that can be precipitated easily at this pH value. This precipitation of insoluble iron may enhance the removal of manganese by simple aeration.

In this study, oxidation of manganese present in groundwater has been evaluated in presence of dissolved iron using potassium permanganate as oxidizing agent. Permanganate oxidation has been done on both natural groundwater and artificially prepared samples. Besides, effectiveness of simple aeration in manganese removal in presence of iron has also been assessed. This chapter presents results of laboratory investigations on manganese removal from water by permanganate oxidation and aeration in presence of dissolved iron.

5.2 MATERIALS AND METHODS

In this study, laboratory batch experiments were carried out in a way similar to that described in chapter four. Natural groundwater collected from BUET pumping station was used in these experiments. In order to assess effect of alkalinity on manganese removal, additional experiments were carried out in synthetic water samples prepared with deionized water, having low alkalinity.

All batch experiments were carried out in 1-L glass beakers using in 500-ml samples. Initial manganese concentration of the water samples were varied by spiking with manganese stock solution (500mg/L) prepared according to the description given in chapter four.

Required concentration of iron in groundwater was added by spiking the samples in beakers with iron stock solution (having 500 mg/L Fe), prepared by dissolving anhydrous ferrous sulfate salt ($FeSO_4. 7H_2O$).

All batch studies were carried out according to the procedure described in chapter four. Additional details of different experimental set up are briefly described in the next section.

5.2.1 Manganese Oxidation with $KMnO_4$ in Presence of Dissolved Iron

This study was carried following the procedure described in article 4.2.1 for manganese removal by oxidation with $KMnO_4$.

Effect of presence of dissolved iron on manganese removal from natural groundwater (alkalinity = 240 mg/L as $CaCO_3$) by oxidation with $KMnO_4$ was studied by varying the initial iron concentration from about 1.0 to 10.0 mg/L. Initial manganese concentration was fixed at 2.0 and 5.0 mg/L. Dose of $KMnO_4$ was set at 1.0 and1.2 times to that required from stoichiometric relation for manganese oxidation (Eq. 4.1). Groundwater was first spiked with manganese, and then iron stock solution was added to achieve a range of iron concentrations (e.g., 1, 3, 5 and 10 mg/L). After adding the oxidant, mixing was done for 10 mins and samples were allowed to settle for 30 mins before filtration in similar way described in chapter four.

Experiments were carried out to assess the effect dissolved iron on manganese oxidation at low alkalinity and low pH. Instead of using natural groundwater, in this study, deionized water was used. Alkalinity of the artificial water was varied from 89 to 102 mg/L as $CaCO_3$ using a $NaHCO_3$ solution (20 g/L). pH was varied between 5.98 to 6.1 by adding concentrated HCl solution. The experiments were carried out with initial manganese concentration of about 2mg/L. Dissolved iron concentration was varied from 1.0 mg/L to 10.0 mg/L. Permanganate dose was set at exactly that required from stoichiometric requirement for manganese oxidation (Eq. 4.1).

Effect of dose of potassium permanganate on simultaneous removal of iron and manganese in natural groundwater was determined. Permanganate dose was calculated from stoichiometric relation for manganese and as well as for iron. According to Eq. 5.1, for complete oxidation of iron by $KMnO_4$, about 0.94 mg of $KMnO_4$ dose is required for 1 ml of dissolved iron.

$$3Fe^{2+} + KMnO_4 + 7H_2O = 3Fe(OH)_3\,(s) + MnO_2\,(s) + K^+ + 5H^+ \qquad (5.1)$$

Therefore for simultaneous oxidation of 1.0 mg/L iron and 1.0 mg/L manganese in groundwater, the total amount of $KMnO_4$ dose required is 2.86 mg/L. For these experiments, $KMnO_4$ dose was varied by different factors this requirement. The factors were 0.25, 0.5, 0.75 and 1.0. Manganese concentration was fixed at 2.0 mg/L and iron at 5.0 mg/L. Therefore, permanganate dose was varied from 0.25 to 1.0 times of that required to oxidize 2 mg/L manganese and 5.0 mg/L iron simultaneously according to stoichiometry of Eq. 4.1 and Eq. 5.1. For example, stoichiometry fraction 0.25 means that of 25% of $KMnO_4$ dose required for 2.0 mg/L manganese and 5.0 mg/L iron has been used. Alkalinity of natural groundwater was found to be 238 mg/L as $CaCO_3$

Dissolved iron is known to get oxidized in contact with air under suitable alkalinity and pH condition. Hence, removal of manganese from water (having dissolved iron) that has been aerated (for iron oxidation) was investigated. In this experiment pH of water samples were raised to about 8.0 (In between 8 to 8.1). pH was increased using NaOH solution (N/44). Water was spiked with an initial manganese concentration of about 2.0 mg/L Iron concentration was varied from 1.0 to 10. 0 mg/L. After spiking water with iron, samples were stirred for 15 mins in order to oxidize iron in water by aeration before adding manganese to water. After that manganese stock solution was added to water samples to provide an initial concentration of 2.0 mg/L. Permanganate dose required to oxidize manganese only was added to water. Dose was set to exactly that required from stoichiometric consideration for manganese oxidation.

5.2.2 Manganese Removal by Aeration in Presence of Iron

Manganese oxidation by simple aeration in presence of dissolved iron was also evaluated in this study. Experiments similar to that described in article 4.2.4 were carried out. Initial manganese concentration of manganese was fixed to about 2.0 mg/L. Initial iron concentration was varied from 1.0 to 10.0 mg/L. After spiking water with required dose of manganese and iron, water samples were aerated by vigorous mixing at 100 rpm. Mixing was carried out for about 30 mins. Samples were then allowed to settle for 30 mins and then filtered and analyzed for iron and manganese. Initial pH varied from 7.65 to 7.72.

5.2.3 Chemicals and Measurement of Parameters

As described in chapter four, all chemicals used in this study were of reagent grade. Iron stock solution (containing about 500 mg of iron/L of solution) was prepared by dissolving anhydrous ferrous sulfate ($FeSO_4 . 7H_2O$; MW = 278.0) in deionized water. The stock solution was kept at a pH below 2.0 by acidifying with concentrated HCl solution. Manganese and permanganate stock solutions were prepared according to the procedure described in chapter four in article 4.2.6.

In this study both iron and manganese concentration in water was measured by flame atomic absorption spectrophotometry, using an AAS (Shimadzu, 6800). A sample standard curve for iron is shown in Fig. A2 in Appendix A. Measurement of other parameters (e.g., pH) was carried out following procedures described in article 4.2.6.

5.3 RESULTS AND DISCUSSIONS

5.3.1 Removal of Manganese by $KMnO_4$ Oxidation in Presence of Iron

This section describes the results of batch experiments carried out to assess manganese removal from groundwater when iron is also present in water. Oxidation was performed either by using potassium permanganate or by aeration. Batch experiments were conducted to assess: (i) the effect of iron present in varying concentration in natural groundwater on removal of manganese by permanganate oxidation, (ii) Effect of iron on manganese removal from synthetic water having low alkalinity and pH, (iii) removal of both iron and manganese present in groundwater by oxidation with $KMnO_4$, and (iv) removal of manganese by chemical oxidation from groundwater which has been aerated at elevated pH for removal of iron.

Effect of Dissolved Iron Concentration on Manganese Removal

Figure 5.1(a) and 5.1(b) show the percentage of manganese and iron removal respectively as a function of initial iron concentration, varying from 1.0 mg/L (0.0178 mM) to about 10.0 mg/L (0.178 mM). The figure is plotted for initial manganese concentrations of 2.0 mg/L (0.036 mM) and 5.0 mg/L (0.091 mM). The permanganate dose for these experiments was fixed at 1.2 times that required from stoichiometric consideration for manganese oxidation. pH of water samples for these experiments varied from 7.77 to 7.62.

The figure shows that for higher initial manganese concentration (5.0 mg/L) removal of both iron and manganese was good. About 90% of manganese removal was achieved even when initial iron concentration was as high as 10.0 mg/L, while removal was over 98% for an initial iron concentration of 1.0 mg/L. But for lower initial manganese concentration (2.0 mg/L), percentage of manganese removal decreased significantly with increasing iron concentration. For initial iron content of 10.0 mg/l, manganese removal was about 78%. For both cases iron removal was very good. For initial Mn concentration of 2 mg/L, removal of iron was more than 99% even when iron concentration was about 10.0 mg/L. This is clear from the figure that as iron is capable to be oxidized to its undissolved form under the experimental conditions. Part of the oxidizing agent added for manganese oxidation may have been utilized for oxidation of iron, resulting in lower removal of Mn.

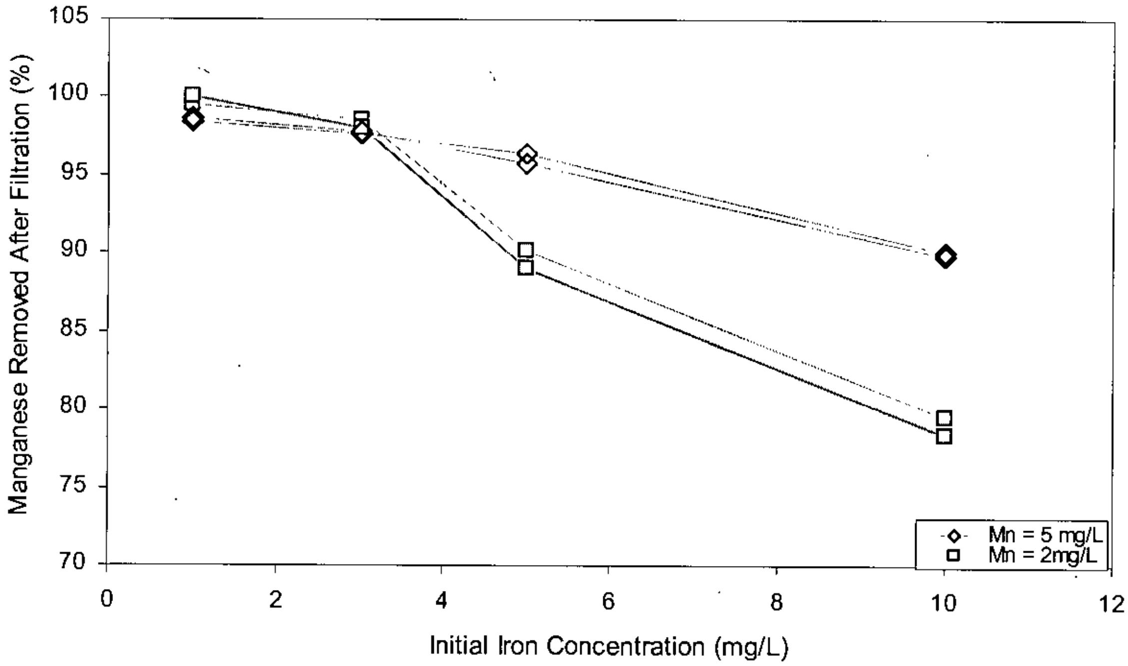


Figure 5.1 (a): Percentage removal of manganese as a function of different initial iron concentration present in groundwater ($KMnO_4$ stoichiometry ratio = 1.2)

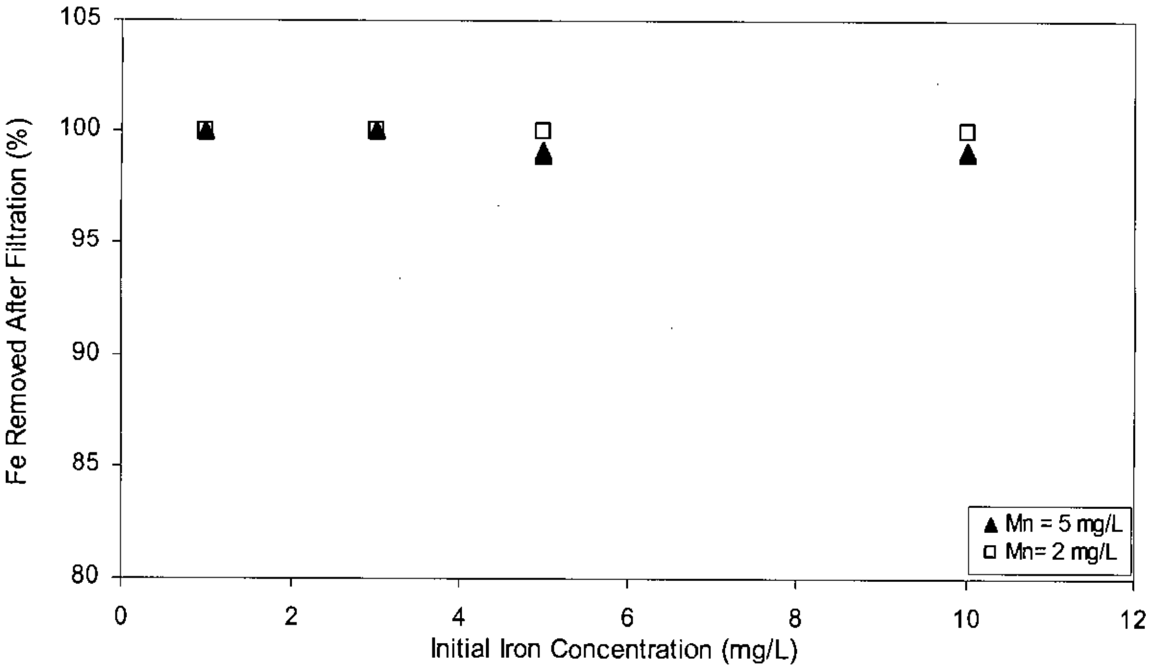


Figure 5.1 (b): Percentage removal of iron as a function of initial iron concentration present in groundwater ($KMnO_4$ stoichiometry ratio for Mn = 1.2)

Figure 5.2 shows the amount of residual manganese remaining in solution after filtration for different initial iron concentration in water. The permanganate dose was 1.2 times of that required from stoichiometric consideration. It shows that although the removal was good when expressed as percentage (fig. 5.1), but the residual concentrations of manganese were high, especially in presence of higher iron contents. For an initial manganese concentration of 5.0 mg/L, residual manganese after filtration exceeded Bangladesh drinking water standard value for manganese (0.10 mg/L) as well as WHO Health-based guideline value (0.50 mg/L), for initial iron concentrations of 3 mg/L or higher. And in case of manganese concentration 2mg/L, residual concentration was above allowable limit for initial iron content of 5.0 mg/L or higher.

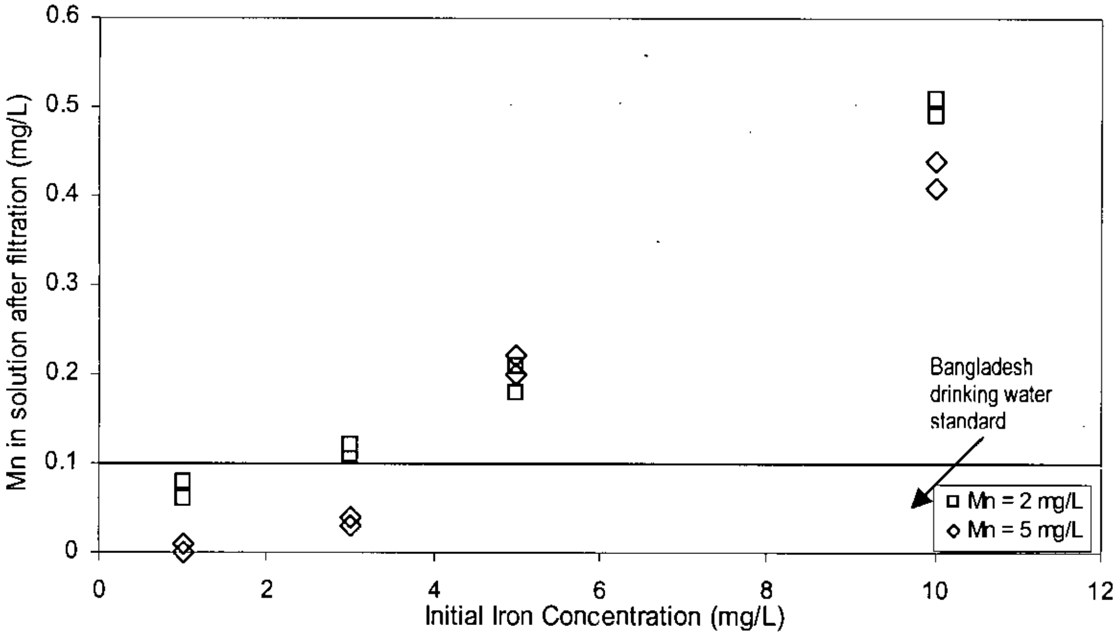


Figure 5.2: Residual manganese in solution after filtration for different initial iron concentration in water

If these results are compared with experiments described in chapter four article 4..3.1, where manganese was oxidized with $KMnO_4$ in the absence of iron, residual concentration was much less than allowable limit for initial manganese concentrations of 2 and 5mg/L. This indicates that the presence of iron, decreased manganese removal efficiency significantly and increased residual concentration of manganese in solution.

Figure 5.3 shows comparison of manganese removal (initial Mn concentration = 2.0 mg/L) in presence of iron (varied from 1.0 to 10.0 mg/L) for two different dose of $KMnO_4$ (1.0 and 1.2 times that required for Mn oxidation). Quantitatively, for an initial manganese concentration of 2 mg/L, amount of $KMnO_4$ dose added was 3.84 and 4.61 mg/L for stoichiometric fraction of 1.0 and 1.2 respectively. The figure shows that in case of stoichiometric ratio 1.2, manganese removal was relatively good (as % removal) even when iron was as high as 10.0 mg/L. But in case of stoichiometric ratio 1.0 for $KMnO_4$, removal gradually decreased with increase in iron concentration. This probably indicates that when less oxidant is available, iron consumes a part of the oxidant before manganese could get oxidized.

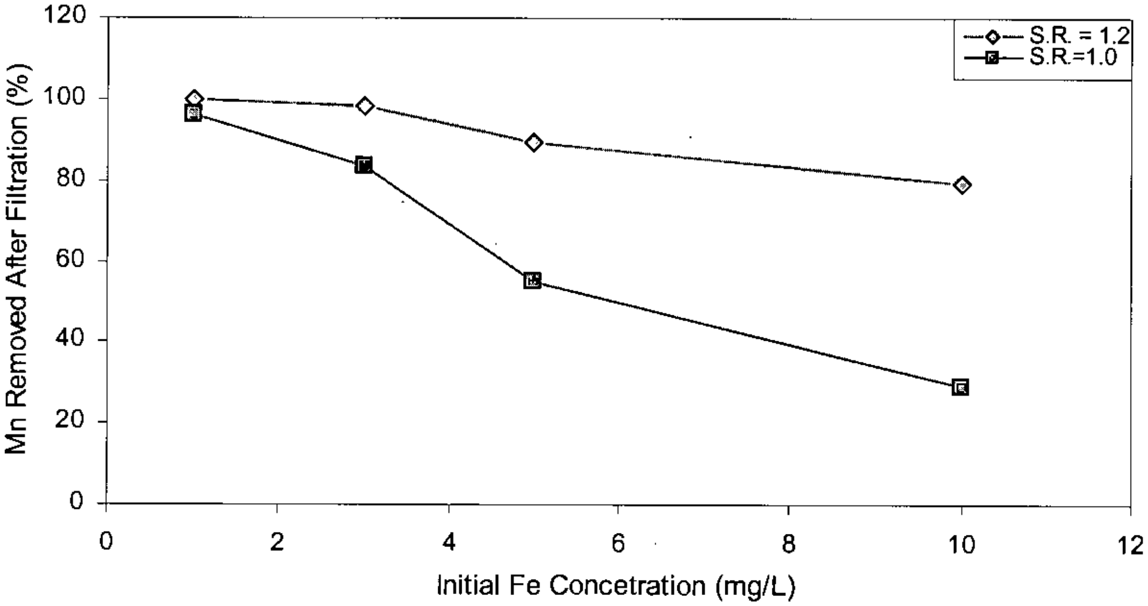


Figure 5.3: Manganese removal as a function of initial iron concentration by oxidation with $KMnO_4$ at two different stoichiometry ratio (S. R.) of $KMnO_4$ (initial manganese concentration = 2.0 mg/L)

Results presented in Fig. 5.1 and 5.2 suggests that complete manganese oxidation in presence of high iron content in water is not possible with an oxidant dose required just for manganese oxidation. In pH range (7.5 to 7.8) at which the experiments were conducted was more favorable for iron oxidation than for manganese.

Manganese Removal from Low Alkalinity-Low pH Water in Presence of Iron

Previous studies on iron removal (e.g. Shahid, 1998) suggest that at low pH (less than 7) and at low alkalinity, iron removal efficiency is also reduced. Therefore an attempt was made to assess manganese oxidation in presence of iron in water at low pH and low alkalinity, where iron may not get oxidized before manganese.

Figure 5.4(a) and 5.4(b) show the comparison between manganese and iron removal respectively under normal pH (7.6 to 7.8) and alkalinity (240 mg/L as $CaCO_3$) conditions with that at low pH (6 to 6.1) and low alkalinity (<100 mg/L as $CaCO_3$) value. From Fig. 5.4 (a) and (b), it is clear that manganese removal follows the same trend under both experimental conditions. That is in both cases, manganese removal decreased with increase in initial iron concentrations. However the removal was a little less for low pH and low alkaline condition than that in case of normal pH range. For example, at initial Fe concentration of 3 mg/L, % of manganese removal after filtration was about 83% and 80% at normal pH and at low pH condition, respectively. Figure 5.4 also indicates that iron removal was also high even at low pH and low alkalinity, even for initial iron concentration as high as 10.0 mg/L.

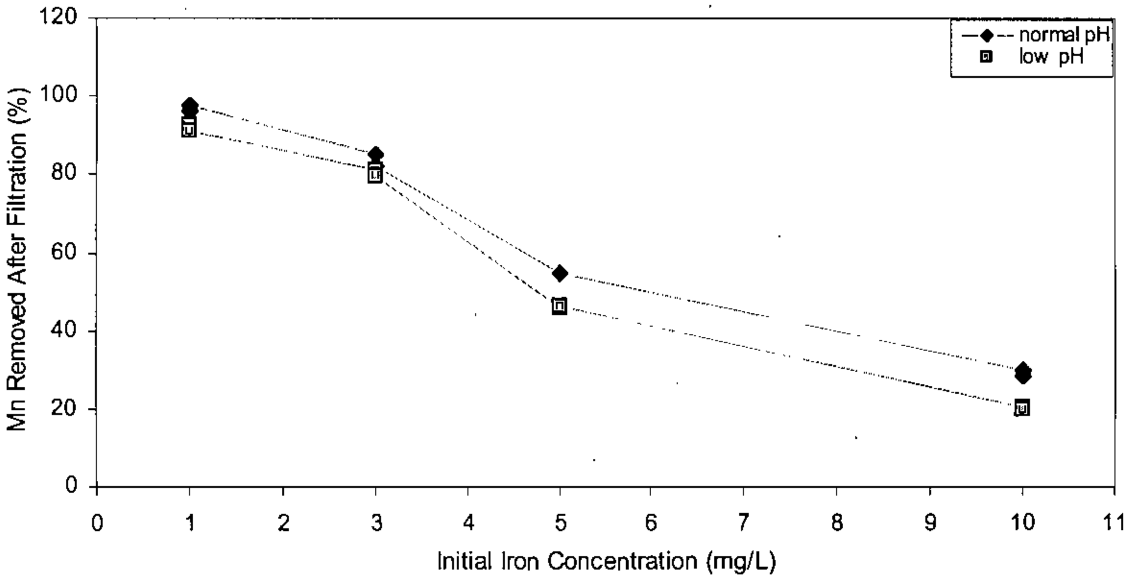


Figure 5.4 (a): Comparison of manganese removal with $KMnO_4$ as a function of different initial iron concentration in low pH -low alkalinity water and in normal pH - normal alkalinity condition.

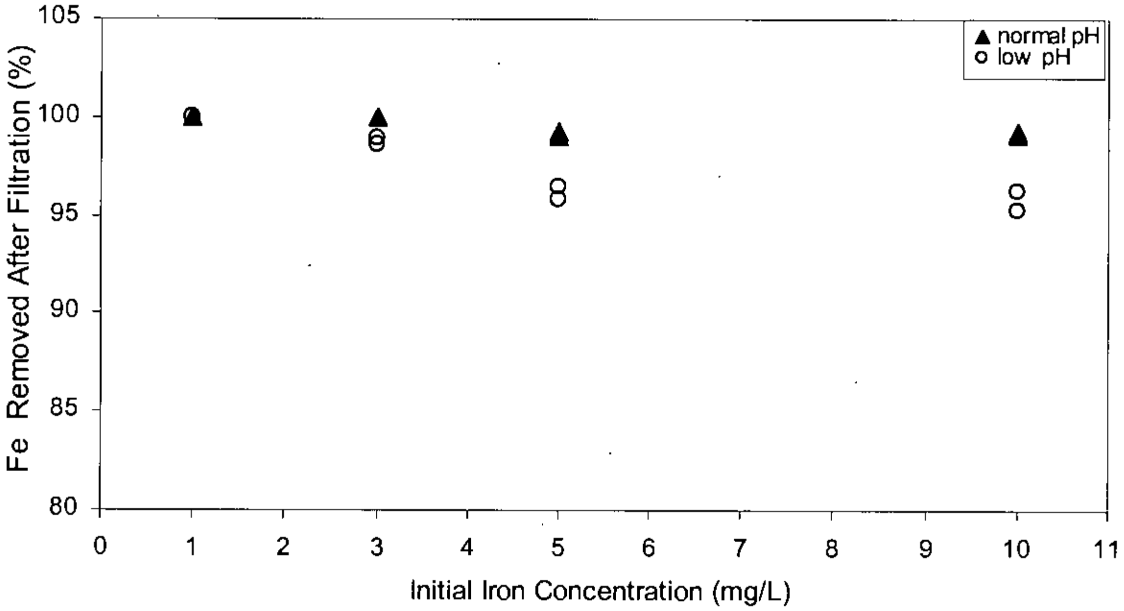


Figure 5.4(b): Comparison of % iron removal as a function of different initial iron concentration in low pH -low alkalinity water and that in normal pH - normal alkalinity condition.(Initial Mn concentration = 2.0 mg/L; Stoichiometry ratio for $KMnO_4$ = 1.0)

This is probably due to the fact that permanganate being a very strong oxidizing agent capable to oxidize both iron and manganese even at low pH (for pH range of 5 to 10; Samblebe,2003).Though alkaline environment enhance oxidizing power of permanganate, its effect was not significant for the experimental condition used in the study.

Figure 5.4 suggests that even at low pH and low alkaline environment, manganese removal by $KMnO_4$ is poor in presence of iron. As $KMnO_4$ is a strong oxidant agent, it is capable to oxidize iron at low pH and low alkaline condition.

Figure 5.5 shows the residual manganese remaining in solution after $KMnO_4$ oxidation in presence of iron at low pH and low alkalinity condition. It shows that residual manganese was always above the Bangladesh standard (0.10 mg/L) for manganese. However for initial iron concentration less or equal to 3.0 mg/L, concentration of residual manganese was below WHO health-based guideline value (0.50 mg/L) for manganese. Fig. 5.5 shows that although the removal of iron (expressed as "% removed") was high, for higher initial iron concentration residual iron was greater than who guideline value for iron (0.30 mg/L).

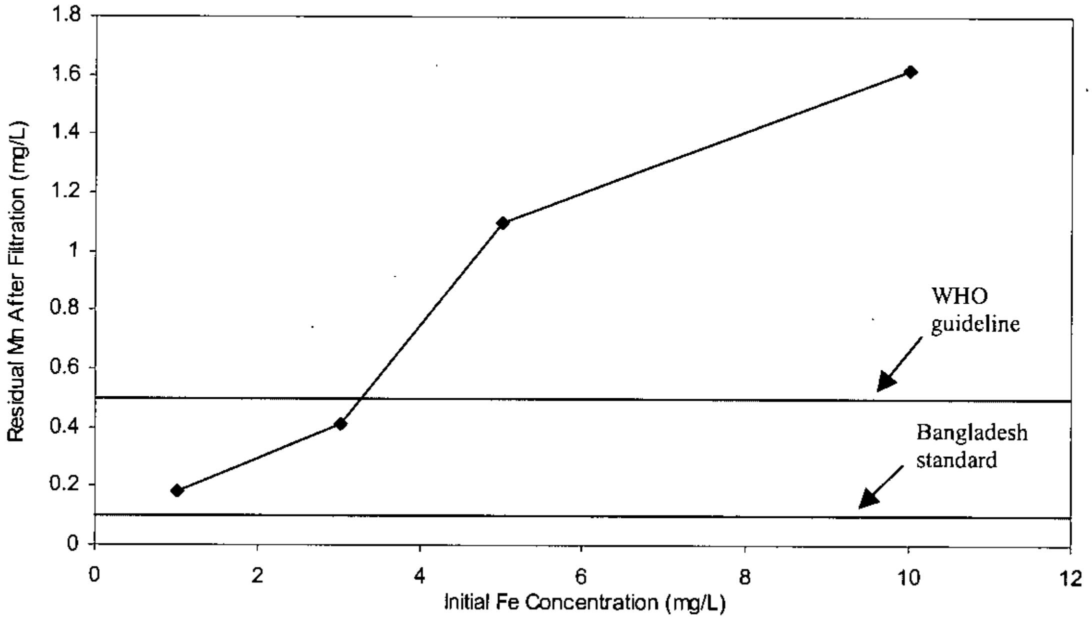


Figure 5.5: Residual manganese remain in solution after oxidizing with $KMnO_4$ at low pH low-alkaline water for presence of dissolved iron at different concentrations. (Initial Mn concentration = 2.0 mg/L; $KMnO_4$ stoichiometric ratio = 1.0)

Removal of Both Iron and Manganese by Oxidation with $KMnO_4$ Dose

Results presented earlier shows that manganese removal in the presence of iron, decreased with increase in iron concentration. This shows that, when both iron and manganese are present in water, it is necessary to provide sufficient oxidant dose to oxidize and remove both of these two elements. For oxidation $KMnO_4$ dose required may be less than that indicated by stoichiometry because of possible oxidation of iron by air. Therefore experiments were conducted to assess the amount of $KMnO_4$ dose required to remove iron and manganese simultaneously.

Figure 5.6 shows % of manganese removal (after filtration) for different combined stoichiometry fraction. The figure indicates that regardless of the amount of $KMnO_4$ dose applied, complete removal of iron occurred after filtration. But for manganese, removal increased with increase of dose fraction up to the fraction 0.75, then again it decreased. Removal of manganese was greater than 93% in case of stoichiometric fraction of 0.75; whereas it was 84% when the dose was exactly that indicated by stoichiometry of iron and manganese oxidation.

Quantitatively, to oxidize 5.0 mg/L of Fe, about 4.7 mg/L of $KMnO_4$ dose is needed according to Eq. 5.1. For removal of both 2.0 mg/L manganese and 5.0 mg/L of iron, about 8.54 mg/L of $KMnO_4$ is required. Fig. 5.6 indicates that almost 100% Fe removal was achieved after filtration irrespective of $KMnO_4$ dose. Therefore, if the oxidation of iron is carried out by $KMnO_4$, then for combined $KMnO_4$ fraction of 0.25 (i.e., 2.14 mg/L $KMnO_4$) and 0.5 (i.e., 4.27 mg/L $KMnO_4$), no $KMnO_4$ was available to oxidize manganese. However, for these $KMnO_4$ fractions, removal of manganese about 8% and 60 %, respectively was achieved. For $KMnO_4$ fraction 0.75, (i.e., 6.41 mg/L $KMnO_4$), about 1.71 mg/L $KMnO_4$ in excess of that required for complete Fe oxidation was available to oxidize Mn, which is capable to oxidize 44.5% Mn. Whereas at this dose, removal of Mn was about 94%. Therefore, oxidation of Fe did not occurred by $KMnO_4$ alone, aeration (during mixing) and autocatalytic oxidation of manganese may play significant role in removing both Mn and Fe.

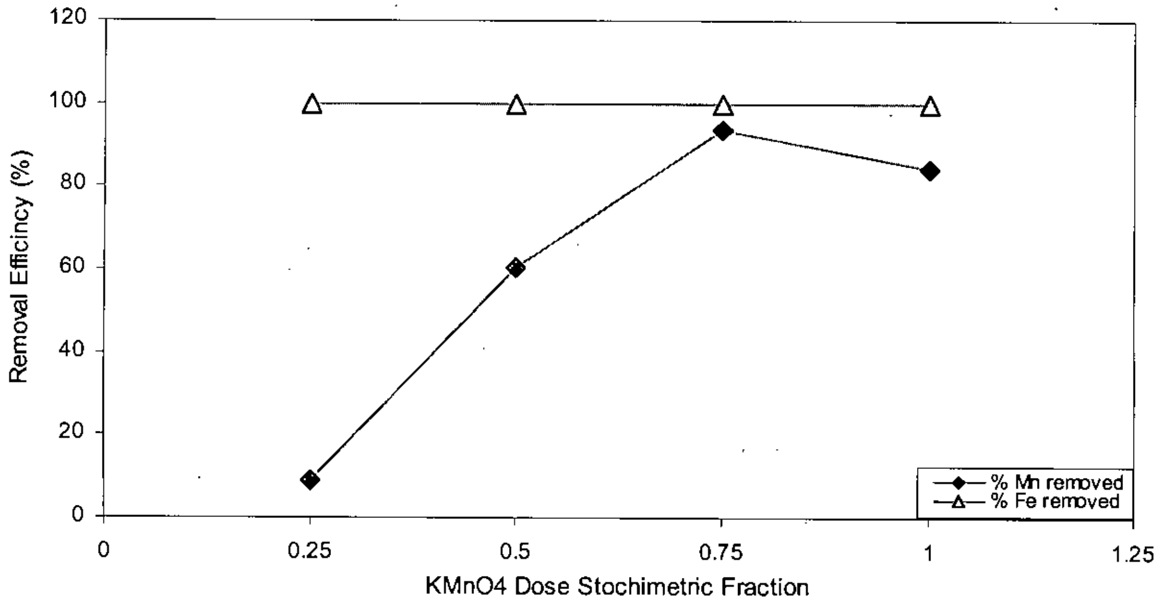


Figure 5.6: Simultaneous removal of manganese and iron for different $KMnO_4$ dose expressed as a fraction of that required for complete oxidation of both iron and manganese. (Initial Mn concentration = 2.0 mg/L; initial iron concentration = 5.0 mg/L)

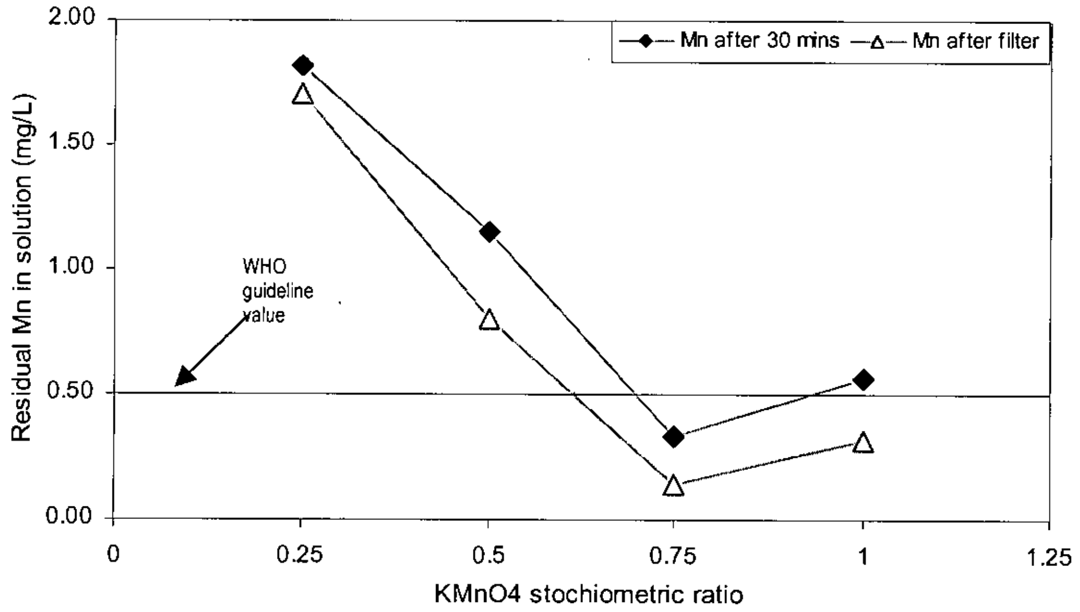


Figure 5.7: Manganese concentration remaining in solution after simultaneous removal of manganese and iron at different $KMnO_4$ dose expressed as a fraction of that required for complete oxidation of both iron and manganese. (Initial Mn concentration = 2.0 mg/L; initial iron concentration = 5.0 mg/L)

Figure 5.7 shows residual manganese concentration for different dose of $KMnO_4$. It shows that although the removal of manganese was high in case of stoichiometric fraction 0.75 (as % removed), residual concentrations were well above Bangladesh drinking water standard and WHO aesthetics based guideline, though lower than WHO health based guideline.

Manganese Oxidation by $KMnO_4$ with Pre-Oxidation of Iron by Aeration

Previous results from this study indicate that when iron is present in groundwater, it is difficult to remove manganese completely, even with addition of required amount of oxidant dose for removal of both iron and manganese. On the other hand, almost complete removal of manganese was achieved in the absence of iron, under similar experimental conditions. Therefore, removal of iron by aeration prior to addition of $KMnO_4$ may improve manganese removal in the presence of iron.

Experiments were carried out to evaluate the removal efficiency of manganese with $KMnO_4$ oxidation with pre-oxidation of iron by aeration. For these experiments, initial manganese concentration was fixed at 2.0 mg/L and initial pH was adjusted to about 8.0

(to enhance iron removal by aeration). Iron concentration was varied from 1.0 to 10.0 mg/L. $KMnO_4$ dose was set at exactly that required for complete oxidation of manganese only.

Figure 5.8 shows removal of both manganese and iron from these experiments. It shows that pre-oxidation removes about 30% to 47% of initial iron in water varied from 1.0 to 10.0 mg/L respectively. After addition of permanganate dose, complete removal of iron was achieved regardless of initial concentration. The figure also indicates that with pre-oxidation of iron by aeration, greatly increase the removal of manganese, and complete removal of manganese was also achieved after oxidation with $KMnO_4$. This indicates that prior aeration for removal of iron can enhance simultaneous removal of both manganese and iron.

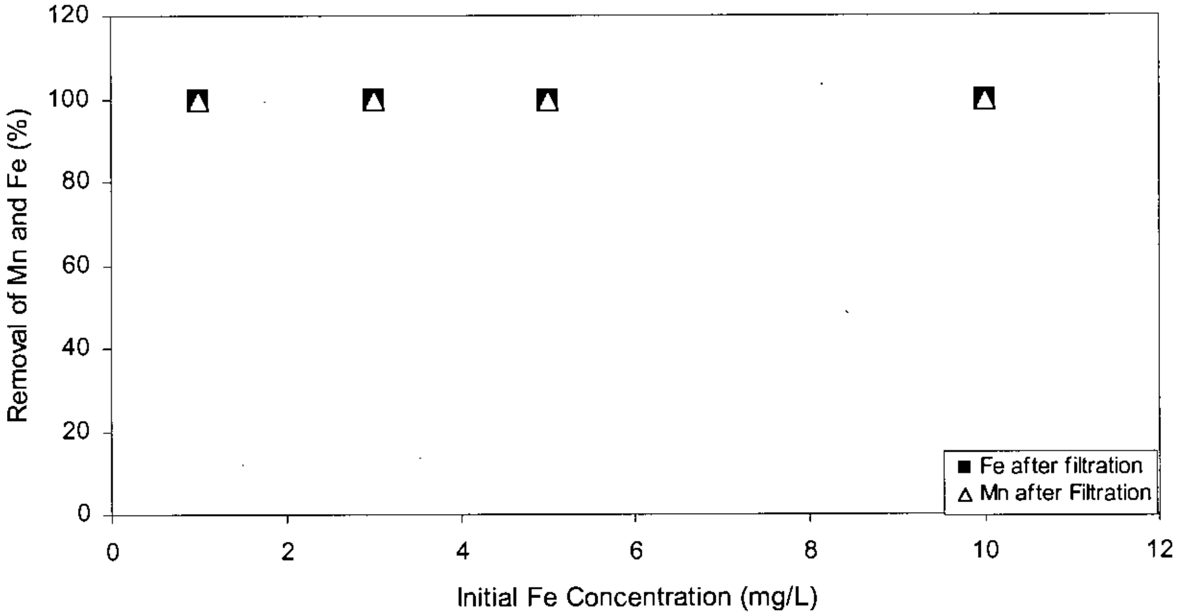


Figure 5.8: Removal of manganese with $KMnO_4$ oxidation in presence of iron with pre-oxidation of iron by aeration ($KMnO_4$ stoichiometry ratio for Mn= 1.0).

5.3.2 Removal of Manganese and Iron from Water by Aeration

From previous experimental result it has been found that aeration enhances the removal of iron from water. An attempt was made to evaluate the removal of both manganese and iron from water by simple aeration.

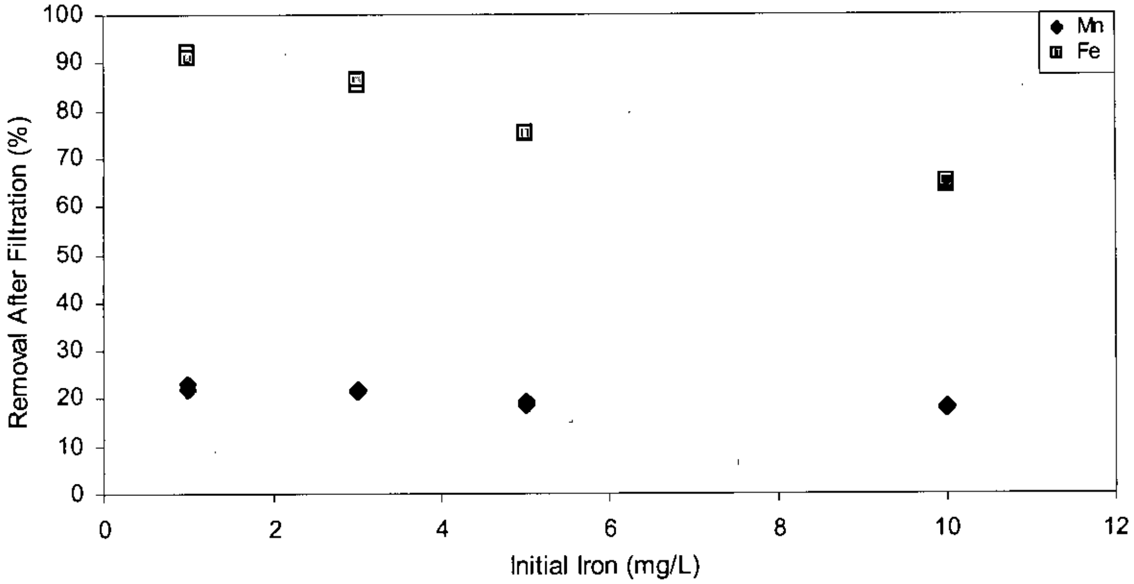


Figure 5.9: Simultaneous removal of manganese and iron by simple aeration for different initial iron concentration (Initial Mn concentration= 2.0 mg/L).

Figure 5.9 shows the % of removal of manganese and iron by simple aeration. The figure shows that both iron and manganese removal decreased with increase of initial iron concentration in water. However if Fig.5.8 is compared with the Fig. 4.19 in chapter four showing manganese removal by aeration, it would indicate that in presence of iron removal of was slightly less than manganese removed by aeration in absence of iron. This implies that presence of iron may not enhance manganese removal by simple aeration.

CHAPTER 6

MANGANESE REMOVAL BY COAGULATION-ADSORPTION-COPRECIPITATION

6.1 INTRODUCTION

In many water treatment facilities chemical coagulation process is used to enhance the removal of colloidal and dissolved substances from water. Especially in Bangladesh chemical coagulation (e.g. iron coagulation, alum coagulation etc.) processes are extensively used to remove arsenic as well iron from groundwater. When both iron and arsenic is present in water, iron coagulation enhances removal of both of these substances. In addition to iron and arsenic, manganese is another very common element found in water in almost allover the world. Many researches suggest (Benschoten and Lin, 1992; Raveendran et al, 2001; Samblebe, 2003; Seeling, 1992; Sharma et al, 2001 etc.) chemical oxidation, especially with $KMnO_4$, ClO_2, as the most effective treatment option for manganese removal. One of the common difficulties with chemical oxidation is the removal of color, for which it is necessary to filter water through a suitable filter media after chemical oxidation. Where as color produced from water treatment can effectively reduced through flocculation and coagulation.

The subject of controlled coagulation for the removal of the objectionable manganese dioxide resulting from manganese oxidation has received little attention (Passelt et al, 1967). According to Morgan and Stumm (1981) oxygenation of manganese (II) show various average degree of oxidation (MnO_x). Variations in x often can be attribute to sorption of manganese (II) by the oxide, thus increasing the apparent ratio Mn:O and decreasing the magnitude of x. Despite the variable nature of x, the formula for manganese dioxide is commonly given, as the name implies, as MnO_2 (Gabono et al, 1965).

According to Passelt et al (1967), for the pH range of practical interest for water treatment (5 to 11), colloidal MnO_2 is characterized by a net negative particle charge.

Hence, for normal conditions, colloidal hydrous MnO_2 is should behave in a fashion similar to many other negatively charged colloids (such as SiO_2), respond accordingly to treatment with common coagulants such as ferric sulfate and alum.

An important characteristic of hydrous manganese dioxide in aqueous solution is its ability to exchange surface-bound H^+ and OH^- ions in response to changes in the relative concentrations or activities of these ions in solution phase; i.e., in response to changes in pH. If the negatively charged OH^- ion is present in excess at the hydrated surface, the colloid will exhibit a net negative charge, while a net positive surface charge will be exhibited in the presence of an excess of H^+ ions (Passelt et al, 1967).

The hydrolyzing metal ions Fe (III) and Al (III) are the most common coagulants for water treatment. The behavior of these metals with respect to coagulation of colloidal hydrous MnO_2 produced from dissolved manganese oxidation is thus direct interest. According to Passelt (1967), both Fe(III) and Al(III) undergo relatively extensive hydrolysis and polymerization in aqueous solution to yield a broad spectrum of charged species of different "molecular" size and charge density. The nature of predominant hydrolysis and polymerization species formed is strongly dependent upon pH, other factor being constant. At low pH these species are positively charged, but increases in pH lead eventually to formation of negatively charged metal-hydroxo polymeric forms.

Coagulant aids often promote settling, when the sedimentation characteristics of flocs formed by normal coagulation procedures are poor. There are two categories of coagulant aids. The first includes those for which a substantial increase in floc size occurs as a result of sorption and enmeshment of particles by long-chain polymeric molecules. The second includes clay-type minerals that affect an increase in the density of floc particles. MnO_2, because of its high specific gravity, might well act as a coagulant aid in water treatment operations and thus be included in the second category (Black, 1985). Therefore, removal of manganese by coagulation, insoluble manganese itself may act as coagulant aid and thus may enhance further removal.

All the studies discussed above highlights the possibility of removal of oxidized manganese (MnO_2) by coagulation. Therefore, for this option it is necessary to oxidize manganese first and then Mn solids would be removed by coagulation.

In context of Bangladesh, coagulation using $FeCl_3$ and alum is widely used to remove arsenic from groundwater (e.g., Ali et al, 2001; Tahura et al, 2001; BAPWSP/DFID/Water Aid, 2001). In these studies it has been found that some of the methods also removed manganese, but in those cases manganese concentration was below 1.0 mg/L. Moreover in many methods of arsenic removal by coagulation utilized some permanganate to oxidize As(III) to As(V) (e.g. Ali et al, 2001). And coagulation was followed by filtration to enhance surface adsorption of arsenic.

No reliable data has been found on effective removal of dissolved manganese in water by coagulation-adsorption process alone. By addition of coagulant under favorable environment it may be possible that dissolved manganese get adsorbed onto coagulant flocs and thus get settled by gravity. Therefore, it is necessary to assess the possibility of removing dissolved manganese by coagulation adsorption and coprecitation.

Iron coagulation is being widely used in removal of arsenic from groundwater of Bangladesh. In this study, experiments have been carried out to assess manganese removal by Fe(III) coagulation, adsorption and coprecipitation processes. Moreover, study was also made to evaluate the possibility of manganese removal by utilizing dissolved ferrous iron as adsorbent in coagulation process.

6.2 MATERIALS AND METHODS

In this study, effectiveness of manganese removal by coagulation with two common iron salts [ferric chloride and ferrous sulfate) was evaluated. Moreover, effect of pH on manganese removal by Fe(III) coagulation was also assessed. As in previous studies described in chapter four and five, groundwater collected from BUET pumping station was used for this study. Alkalinity of groundwater was 242 mg/L as $CaCO_3$. Stock solutions for manganese, potassium permanganate, and iron (II) were prepared following the procedures in chapter four and five. Stock solution of Fe(III) salt (i.e., ferric chloride) was prepared by dissolving anhydrous ferric chloride salt ($FeCl_3.6H_2O$; MW = 270.30) in deionized water. A stock solution having 500 mg Fe(III) per liter of solution was prepared. The pH of the stock solution was kept below 2.0 by adding concentrated HCl in order to keep ferric iron in dissolved form.

For a particular initial manganese concentration and coagulant dose, one set of experiments was conducted without the addition of any oxidizing agent, while another set was conducted with the addition of oxidizing agent (potassium permanganate). This was be done for differentiating the mechanisms (oxidation versus adsorption) of manganese removal from water. In each set of experiment, water samples (500 ml) in 1-L glass beakers were coagulated in a digital paddle-type coagulation apparatus. The coagulant dose was varied from 2 mg/l (as iron) to 25 mg/l (as iron).

After addition of potassium permanganate (if needed), coagulant dose was added to the beaker from stock solution of either Fe(II) or Fe(III). Then the contents of the beakers were mixed rapidly for 1 minute at a speed 100 rpm. Then a slow mixing was done for 15 minutes at a speed of 45 rpm. Samples were then allowed to settle for 30 minutes. Then clear supernatant was collected from the beaker from about 1-cm below the water surface and analyzed for manganese, color, and iron concentrations. Collected samples were then filtered through 0.45-μm filter in order to determine total dissolved manganese present in water. In order to determine the effect of pH on manganese removal by coagulation with ferric solution as coagulant, pH was varied from 7 to 11 by adding NaOH (N/44) solution. Figure 6.1 shows the experimental set up for manganese removal by coagulation with the addition of $KMnO_4$ as oxidizing agent. Additional details of each type of experimental set up are briefly described below.

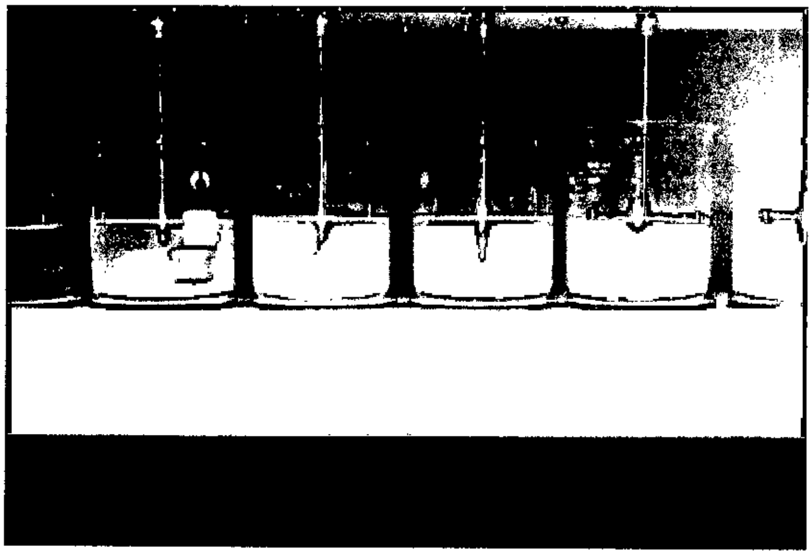


Figure 6.1: Experimental Set-up for manganese removal by Coagulation

6.2.1 Manganese removal by Coagulation-Adsorption-Coprecipitation

Experiments were conducted for initial manganese concentration of 2 mg/L. Ferrous sulfate concentration was varied from 2 to 25 mg/L (as Fe). Two sets of experiments were carried out. In one set $KMnO_4$ was added at a concentration (2.84 mg/l) exactly equal to that required from stoichiometric consideration for manganese oxidation. After 1 minute of rapid mixing (100 rpm), 15 minutes of slow mixing (45 rpm) followed by 30 minutes of settlement, supernatant samples were collected. The pH values of the samples were within the range of 7.5 to 7.7. Similar experiments were conducted with ferric chloride added as coagulant. Coagulant dose in this case was varied from 10.0 mg/l to 25.0 mg/L (as Fe). The pH values for these experiments varied from 7.59 to 7.72.

6.2.2 Effect of pH on Coagulation of Manganese with Fe (III) Coagulation

In order to evaluate the influence of pH on removal of manganese from groundwater by coagulation with $FeCl_3$, experiments similar to those described above were carried out where pH of the samples was varied from 7 to 11 by adding NaOH (N/44). Experiments were carried out without addition of the chemical oxidant (e.g., $KMnO_4$.) Manganese concentration was fixed at about 2 mg/L. Coagulant dose (ferric chloride) was fixed to 15 mg/L (as Fe).

6.3 RESULTS AND DISCUSSIONS

6.3.1 Manganese removal by Iron Coagulation

In this study, batch experiments were carried out to evaluate the effectiveness of coagulation-adsorption process in removing dissolved manganese from groundwater. Experiments were carried to determine: (i) the effectiveness of Fe(II) as coagulant in removing manganese with or without pre-oxidation of manganese by $KMnO_4$ dose, (ii) the effectiveness of Fe(III) as coagulant in removing manganese with or without pre-oxidation of manganese by $KMnO_4$ dose, and (iii) effect of pH on removal of manganese with iron (III) coagulation. Experimental results are briefly described below.

Manganese Removal by Iron (II) (Ferrous Sulfate) Coagulation

The primary mechanism involved in the removal of metal ions by coagulation with iron (II) (ferrous sulfate) involves adsorption of dissolved metal ions onto the surface of iron flocs and subsequent precipitation of the flocs. In case of manganese, in addition to adsorption, some manganese could be removed by oxidation of dissolved Mn(II) to insoluble manganese solids, either by oxygen (from air) or potassium permanganate (if added).

Figure 6.2 shows the % removal of manganese after coagulation. The figure gives a comparison between removal efficiency with and without $KMnO_4$ oxidation. Fig. 6.2 shows that manganese removal by coagulation was relatively good (as % removed) when manganese was oxidized with $KMnO_4$.

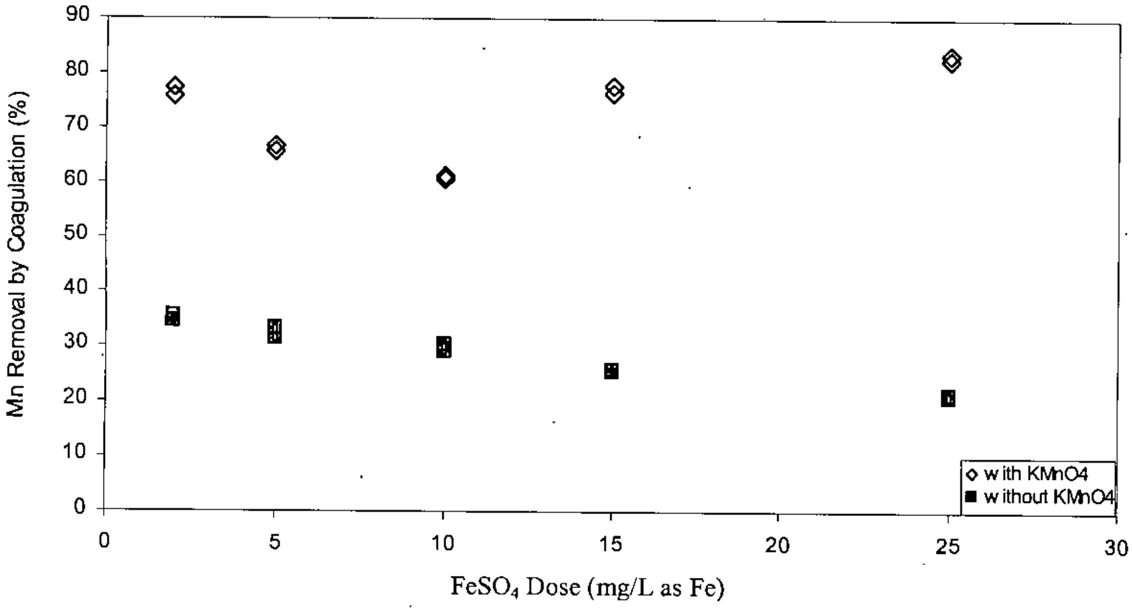


Figure 6.2: Removal of manganese by iron coagulation-adsorption process by using dissolved $FeSO_4$ as coagulant with and without addition of $KMnO_4$ (Initial Mn concentration =2.0 mg/L; $KMnO_4$ stoichiometry ratio =1; pH =7.6)

Poor removal (about 20% to 34%) was achieved in case of coagulation without the chemical oxidation. Part of this removal may be due to oxidation of dissolved manganese into insoluble manganese by oxygen (from air) and its subsequent precipitation.

In case of coagulation without chemical oxidation, % removal decreased with increase in coagulant dose, though the reason for this apparent trend is not clear. In case of coagulation with chemical oxidation of manganese, removal decreased with increase in coagulant dose up to 10 mg/L of iron (II), and then increased with increase in coagulant dose.

For coagulant $FeSO_4$dose of 3, 5 and 10 mg/L, manganese removal has been found to be about 78%, 66% and 60%, respectively. In chapter 5 it has been found that for similar Mn and Fe (II) contents, removal of Mn was 82%, 54% and 29%, respectively for dissolved Fe (II) concentration of 3, 5 and 10.0 mg/L respectively (Fig. 5.3). This probably implies that controlled mixing for the purpose of coagulation enhanced Mn removal in presence of Fe(II).

From results obtained in this study, it appears that when the oxidizing agent is added, oxidation of dissolved manganese to insoluble forms and their subsequent precipitation is the primary mechanism for manganese removal. Very little dissolved manganese could be removed in the coagulation experiments through adsorption of dissolved manganese onto iron flocs.

Figure 6.3 illustrates the amount of residual manganese remaining in solution after coagulation. It shows that although the removal of manganese was good (when expressed "as % removed"), in case of coagulation with chemical oxidation, the residual concentrations were well above the allowable national standard (0.10 mg/l) and the limit set by WHO (aesthetics). For coagulant dose of 5.0 and 10.0 mg/L, residual manganese was greater than WHO health-based limit (0.5 mg/l).

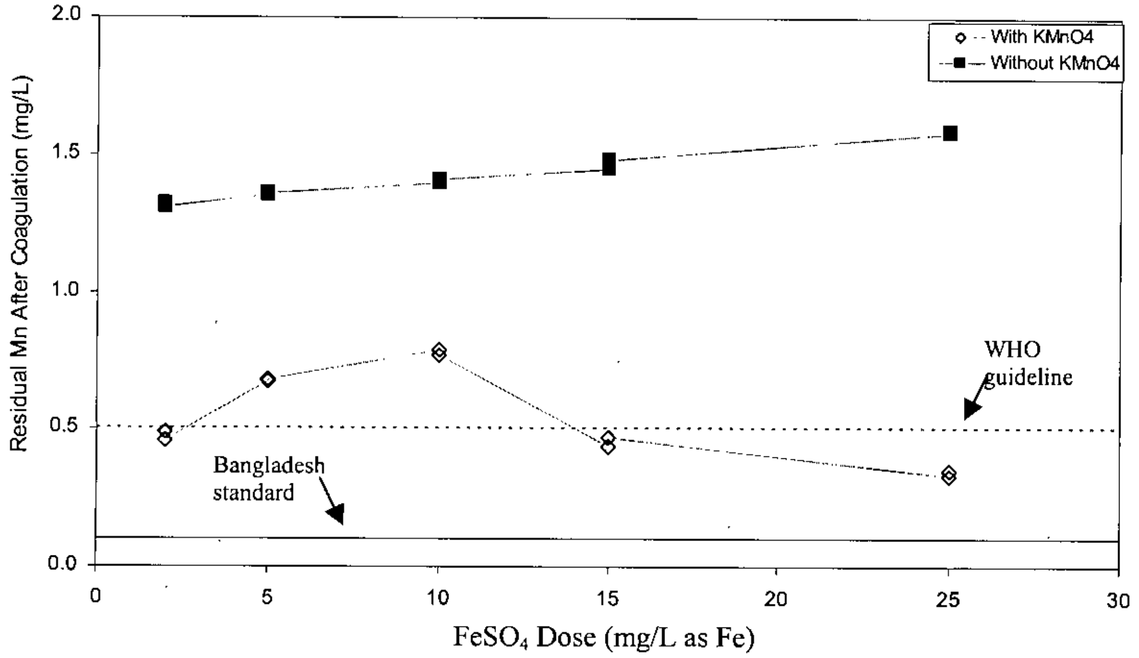


Figure 6.3 : Residual manganese concentration in solution after coagulation with $FeSO_4$, with and without pre-oxidation of dissolved manganese using $KMnO_4$. (Initial Mn concentration =2.0 mg/L; $KMnO_4$ stoichiometry ratio =1; pH =7.6)

Manganese Removal by Iron (III) (Ferric Chloride) Coagulation

Iron (III) salts, such as ferric chloride, are widely used as coagulant for removal of arsenic from groundwater. In this study, effectiveness of ferric chloride coagulation in removing dissolved manganese from groundwater was evaluated.

Figure 6.4 illustrates the removal of manganese by coagulation with ferric chloride, with and without chemical oxidation of manganese. It shows that regardless of amount of coagulant, removal of manganese in case of coagulation with chemical oxidation was greater than 90%. In contrast, removal of manganese by coagulation without chemical oxidation was much less, varying from about 25% (at a coagulant dose of 10 mg/l) to about 37% (at a coagulant dose of 25 mg/l). Results presented in Fig. 6.4 also suggest that chemical oxidation of manganese (and not adsorption of dissolved manganese) is the primary mechanism of manganese removal in the coagulation experiments where $KMnO_4$ was used.

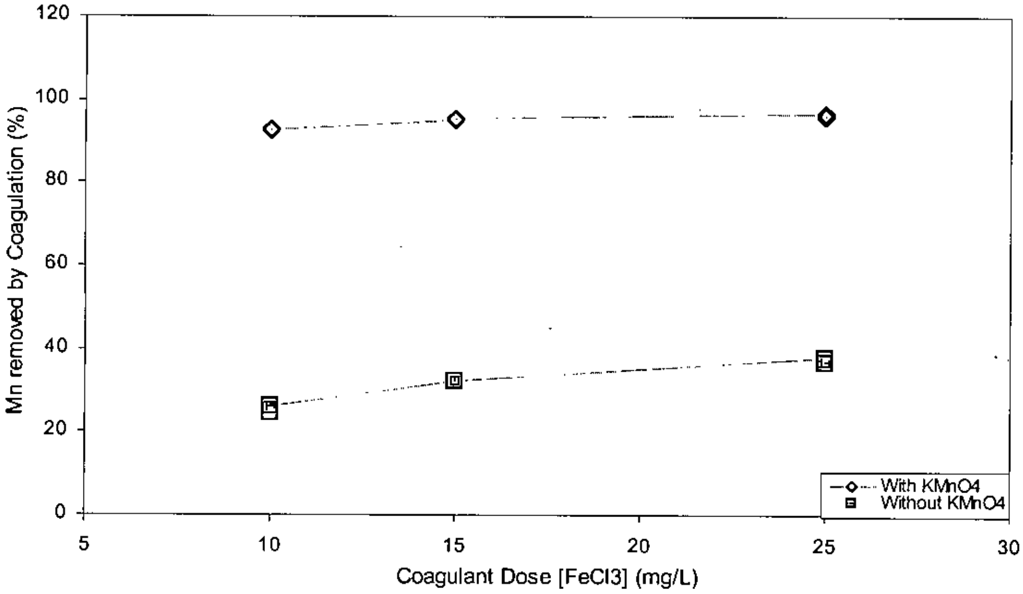


Figure 6.4 : Removal of manganese by iron coagulation-adsorption process using Fe(III) as coagulant, with and without pre-oxidation of dissolved manganese using $KMnO_4$. (Initial Mn concentration = 2.0 mg/L; $KMnO_4$ stoichiometry ratio =1)

However, if these results are compared with results obtained from coagulation with ferrous sulfate (Fig 6.5), it becomes clear that ferric chloride coagulation was more effective in removing manganese from groundwater that ferrous sulfate. The difference was more significant for coagulation with chemical oxidation by potassium permanganate. This may be due to the fact that in case of coagulation by ferrous sulfate, part of the oxidant added ($KMnO_4$) was used up for conversion of ferrous iron to ferric iron; and this portion of the oxidant was no longer available for oxidation of dissolved manganese. It may be noted that as described by Black (1985), solid oxide form of manganese (MnO_2), because of its high specific gravity, might well act as a coagulant aid in water treatment operations.

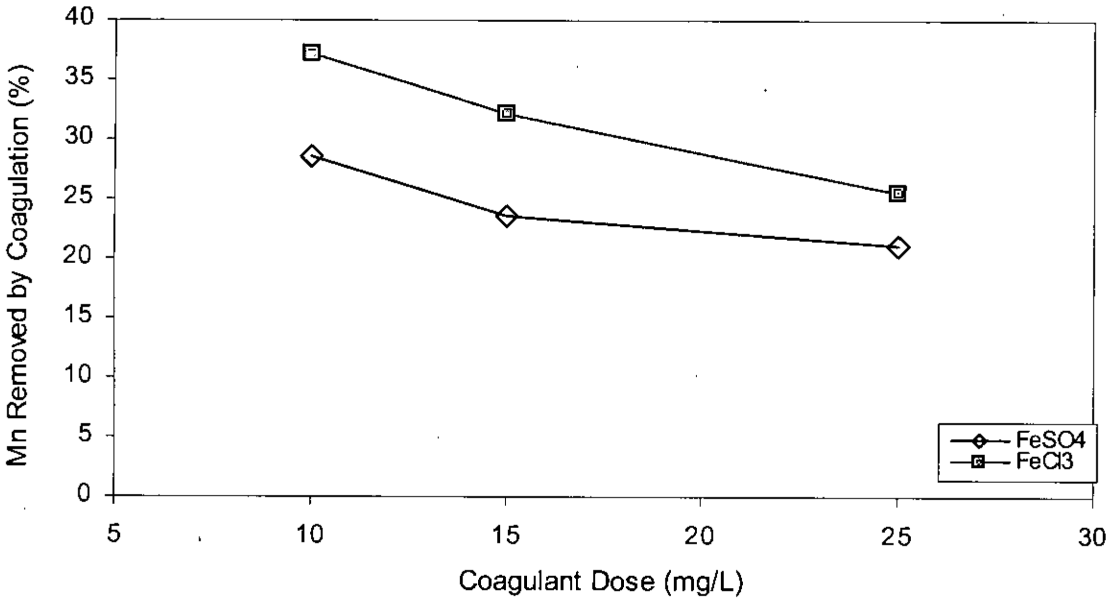


Figure 6.5 : Comparison of Fe(III) and Fe(II) as coagulant in removing manganese from water. (Initial Mn concentration = 2.0 mg/L; $KMnO_4$ stoichiometry ratio =1)

Effect of pH on Manganese Removal by Iron (III) Coagulation

Since adsorption of dissolved manganese on to metal hydroxides is likely to be favored at higher pH values, experiments were carried out to assess if greater manganese removal could be achieved by coagulation at higher pH values. Results from this study presented earlier suggest that Fe(III) is better coagulant than Fe(II) for manganese removal. Effect of pH on manganese removal by coagulation was therefore carried out with ferric chloride.

Figure 6.6 shows the removal of manganese by Fe(III) coagulation as a function of pH. It shows that removal of manganese was low (less than 40%) for pH less than 9. However, at higher pH values manganese removal increased sharply and almost complete removal was achieved at pH 11.

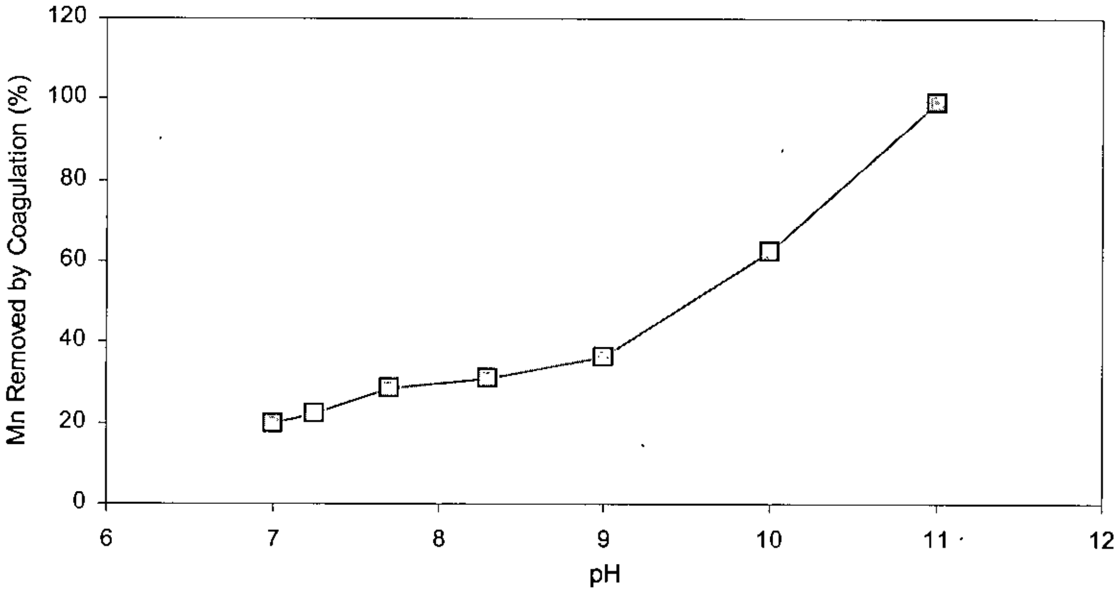


Figure 6.6 : Effect of pH on removal of manganese by Fe (III) coagulation-adsorption process using Fe(III) as coagulant without pre-oxidation of dissolved manganese using $KMnO_4$.(Initial Mn concentration = 2.0 mg/L; $KMnO_4$ stoichiometry ratio =1)

In previous experiment on manganese removal by simple aeration (Chapter Four), it has been found that high manganese removal (greater than 90%) could be achieved by simple aeration pH value 10 and 11 (regardless of contact time). Thus, the apparent higher removal of manganese in coagulation experiments (shown in Fig. 6.5) appears to be the result of oxidation of manganese by air. The coagulant (ferric chloride) does not appear to be responsible for this high removal of manganese at higher pH values. These results once again demonstrated that very little manganese removal could be achieved by coagulation alone. Thus, very little manganese removal could be expected in traditional arsenic removal systems based on coagulation.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

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

- Potassium permanganate is very effective oxidant for removal of manganese from groundwater. Manganese removal by permanganate oxidation was maximum at permanganate dose equal to that required from stoichiometric consideration. However for very high initial manganese concentration, although the removal was significantly high with slight over dose of permanganate, residual manganese concentration was well above the allowable limit set by Bangladesh drinking water standard (0.1 mg/L)

- Potassium permanganate, being a very strong oxidizing agent, is capable to oxidize manganese over a wide pH range of 5-10. However, removal rate above pH 7.0 was significantly high and above pH 8.0, manganese removal with $KMnO_4$ oxidation becomes independent of pH. This implies that natural groundwater containing dissolved manganese can be effectively removal with permanganate without any adjustment to natural pH.

- One drawback of permanganate oxidation is the formation of color due to the oxidation of dissolved manganese. It has been found that even for the lowest concentration of manganese used in this study (1.0 mg/L), all color concentrations were above the Bangladesh drinking water standard, even after 3 hours of settling/ detention time. Thus, it is clear that settling/ detention alone would not remove color from water treated with potassium permanganate. Hence, appropriate filtration option would be required to remove color.

- Significant color (produced from potassium permanganate oxidation of manganese) removal would be possible using of sand filters having 10 to 20 cm depth. However, sand filter with greater depth found to be more effective in removing color. Sand filter is also capable to remove solid manganese formed by oxidation. Although residual concentrations after sand filtration were not be as low as that obtained by 0.45μm filter paper (<0.001 mg/L), all residual manganese concentrations (after sand filtration) were well below the Bangladesh drinking water standard of 0.10 mg/l.

- Manganese removal by chlorination in natural pH range (7. to 8.5) would be very poor. Manganese oxidation with chlorine would not be very effective until pH is raised above 8.5; and for complete oxidation of manganese, it is necessary to raise pH near 10.

- Manganese oxidation with chlorine is also dependent on contact time. Insufficient contact time may lead to poor removal of manganese by chlorine oxidation even at an elevated pH.

- Manganese removal by simple aeration is also possible. Similar to chlorine oxidation, manganese removal by aeration requires sufficient contact time (often may need 30 to 60 minutes contact). pH has a very pronounced effect on manganese removal by aeration. For effective removal of manganese by aeration, pH is needs to be raised above 10.

- Within pH range of 7 to 9, manganese oxidation with bleaching powder is more effective than aeration. However, at higher pH values (≅ 10), both of these options are capable to remove manganese completely.

- Presence of dissolved iron in groundwater may significantly influence manganese oxidation with potassium permanganate. In natural pH range a part of the oxidant added for manganese oxidation could be consumed by iron and could result in ineffective removal of manganese.

- When both iron and manganese is present in water, providing oxidation dose for removal of both iron and manganese may lead to sufficient removal of manganese. However dose requirement would be less than that required from stoichiometric consideration for iron and manganese. This is due to the fact that some manganese as well as iron would be removed from water by the aeration during mixing.

- When dissolved iron is present in water, removal of manganese by chemical oxidation may become effective, if water is aerated for a suitable time before adding the oxidant. By aeration a significant portion of iron would get oxidized and therefore would not influence manganese oxidation and thus complete removal of both iron and manganese could be possible.

- Ferric chloride coagulation is found to be more effective in removing manganese from groundwater that ferrous sulfate. However, without pre-oxidation of manganese (e.g., using $KMnO_4$) coagulation would not be capable to remove dissolved manganese significantly.

- Coagulation (with $FeCl_3$) at higher ph values increased manganese removal. But at higher pH values (>10) manganese removal is dominant by oxidation with air rather than by adsorption onto iron flocs. These results demonstrated that very little manganese removal could be achieved by coagulation alone.

7.2 RECOMMENDATIONS FOR FUTURE STUDIES

- To conduct study on manganese removal using groundwater having naturally occurring high manganese concentrations
- To investigate removal options for reducing residual manganese levels below the Bangladesh standard (0.1 mg/L) for higher initial manganese concentration.
- To investigate effect of parameters such as organic matter on manganese removal efficiency.
- To investigate the effectiveness of sand filtration alone or coagulation followed by conventional sand filtration as used in iron and arsenic removal plants in removing manganese from groundwater.

REFERENCES

Ali, M. A., Badruzzaman, A.B.M., Jalil,M.A., Hossain, M. D., Hussainuzzaman, M. M., Badruzzaman, M., Mohammad, O.I. and Akter, N., (2001), "Development of Low-cost Technologies for Arsenic Removal from Groundwater", BUET-UNU International Workshop on Technologies for arsenic Removal from Drinking Water, May 2001

ANSI/NSF,(2000), "American National Standards Institute, NSF International. Drinking water treatment chemicals-Health effects", ANSI/NSF 60-2000. Ann Arbor, MI

ASTDR, (2000), "Toxicological Profile for Manganese", US Department of Health ond Human Services, Public Health Service, Agency for Toxic Substances and Desiese Registry, Atlanta, GA.

BAMWSP/ DFID/ Water Aid, (2001), "Rapid Assessment of Household Level Arsenic Removal Technologies", Phase II report, March 2001.

Banta,R.G. and W.R.mARKESBERY,(1977), "Elevated manganese levels associated with dementia and extrapyramidal signs". Neurology 27:213-216.

Barceloux, D. G., (1999), " Manganese Isuues", Clin. Toxicol. 37:293-307

Benschoten, J. B., and Lin, W., (1992), " Kinetic Modeling of Manganese (II) Oxidation by Chlorine Dioxide and Potassium Permanganate", Environmental Science and Technology, Vol. 26 No. 7. Journal of the American Water Works Association 83[6], 80-87. 1992.

BGS/WaterAid (2001), "Groundwater Quality: Bangladesh", Department of Public Health Engineering, British Geological Survey, January 2001.

Black, A. P., (1985), "Determination of Mobility of Colloidal Particles", Jour. AWWA 54:926, August

Boman, B. J., Wilson, P. C., and Ontermaa E. A., (1999), "Understanding Water Quality Parameters for Citrus Irrigation and Drainage Systems", Env. Sci. & Tech., 18(5), 781

Cameron, I.R. (1995) "Biological Iron and Manganese Removal: An Untapped Potential", Water 23, 2 pp 25-28, AWWA Regional Conference, Coolangatta.

Cameron, I. R., and Bourgin, F. (1995), "New Frontier - Biological Iron and Manganese Removal from Drinking Water", AWWA Queensland Regional Conference.

Canavan, M,M., Cobb, S. and C.Srinker, (1934), "Chronic manganese poisoning". Arch. Neurol. Psych. 32:501-12

Cao, R. Y., Gu G. W., Huang, Z. M. and Ye H., (2001), " The Generation, Oxidation and Disinfection of Chlorine Dioxide", Tongji Quality Supervision and Examination Center of Environment Protective product NEPA

Casale, R. J., LeChevallier, M.W., and Pontius, F.W., (2001), "Review of Manganese Control and Related Manganese Issues", Denver: American Water Works Association (AWWA) Research Foundation and AWWA

Collipp, P. J., S. Y. Chen, and S.Maitinsky, (1983), "Manganese in infant formulas and learning disability". Annals Nutr. Metabol. 27:488-494.

COMA (1998).Nutrition and Bone Health:with particular reference to calcium and vitamin D.Report of the Subgroup on Bone Health,Working Group on the Nutritional Status of the Population,Committee on Medical Aspects of Food and Nutrition Policy.The Stationery Office,London

Cook,D.G.,S.Fahn, and K.A.Brait,(1974),Chronic manganese intoxication". Archives of Neurology 30:59-64.

Davidson, L.,A., Cederblad, B. Lonnerdal., and B. Sandstorm., (1989), "Manganese absorption from human milk, cow's milk, and infant formulas in humans". Amer.J.Dis. Children 43(7):823-827

Devenyi, A. G., T. F. Barron, and Mamourian, A. C., (1994), "Dystonia, hyperintense basal ganglia, and high whole blood manganese levels in Algille's syndrome". Gastroenterol. 106(4):1068-1071.

Douglas, B., McDaniel, D., and Alexander, J., (1994), "Concepts and Models of Inorganic Chemistry", 3rd ed.; Wiley & Sons:New York

DPHE/BGS (2001), "Arsenic Contamination of Groundwater in Bangladesh", Department of Public Health Engineering, DFID, British Geological Survey, 2001.

Ehrlich, P.R. Dobkin, D.S., (1996), "Manganese clinical Nutrition in Health and Disease", (Handbook of Nutrtionally Essential Mineral elments.

Elias, Z.,J.M.Mur, F.Pierre, et al,(1989), "Chromosome aberrations in peripheral blood lynphocytes of welders and characterisation of their exposure by biological samples analysis". J.Occup. Med.31:477-483.

Evans, F.L., (1972), "Ozone in water and wastewater treatment", Ann Arber Science Publishers, London.

Fechter, L.D, (1999), Distribution of manganese". Neuro Toxicol. 20:197-201.

Ficek, K. J. (1985), "Manganese Removal Using Potassium Permanganate in Low pH, Low Hardness Waters", AWWA Annual Conference, Washington D.C.

Gabono, J. P., Etienne, P., and Lavrent, J. F., (1965), "Study of the Surface Properties of Manganese Dioxide", Electrochim. Acta, 10:947.

Gage, B., O'Dowd, Dr. D. H., Williams P., (2001), "Biological Iron and Manganese Removal: Pilot and Full Scale Applications", Ontario Water Works Association conference, May 3rd, 2001

Graveland, A., Heertjes, P.M., (1975), "Removal of manganese from ground water by heterogeneous autocatalytic oxidation", Transactions of the Institution of Chemical Engineers, 53, 154-164.

Gregory, D., Carlson, K. (1996), "Oxidation of Dissolved Manganese in Natural Waters, 1996 Annual Conference Proceedings"; American Water Works Association

Hauser, R.A., T.A.Zesiewicz, C.Martinez, A.S.Rosemurgy, and C.W.Olanow, (1996),Blood manganese correlates with brain magnetic resonance imaging changes in patients with liver disease". Can.J. Neurol.Sci. 23:95-98.

HSDB,(2001), "Manganese compounds".Hazardous Sabstances Data Bank. Last revised:May 23, 2001.

Hurley,L.S., C.L.Keen and D.L. Baly,(1984), "Manganese deficiency and toxicity: effects on carbohydrate metabolism in the rat". Neuro Toxicol. 5:97-104.

IOM,(2002), Institute of Medicine. Directary Reference intakes: Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nikel, Silicon, Vanadium and Zinc". Food and Nutrition Board, Institute of Medicine. Washington DC: National Academy Press.pp.10-1-10-22.

IPCS,(1999), "Manganese and its Compounds. Concise International Chemical Assessment Document 12, International Programme on Chemical Safety, World Health Organisation.

Jimbo, Y. and Goto, K., (2001), "Iron and manganese removal by a membrane filtration system ", IWA Publishing, Water Supply Vol 1 No 5-6 pp 357–364

Kassim, Dr. M. A.(1994), "Biological Iron and Manganese Removal", 20th WEDC Conference Colombo, Srilanka, p-281-283.

Kwamura, C.L., H. Ikuta, S. Fukuzimi, R. Yamada, S. Tsubaki, T. Kodama, and S. kurata,(1941), “Intoxication by manganese in well water”. Kitasato Arch. Exp. Med. 18:145-169.

Keen, C.L., J.G. Bell and B.Lonnerdal,(1986), “ The effect of age on manganese uptake and retention from milk and infant formulas in rats”. J.Nutr. 116:395-402.

Kondakis,X.G., N.Makris, M. Prinou and T.Papapetropoulos,(1989), “Possible Health effects of high manganese concentration in drinking water”. Arch. Environ. Health 44:175-178.

Lemley, A., Schwartz, J. J., and Wagenet, L. (1999), “Iron and Manganese in Household Drinking Water”, Fact Sheet 6, Cornell Cooperative Extension, New York State College of Human Ecology.

Lynam, D.R., J.W. Roos, G.D. Pfeifer, B.F.Fort and T.G. Pullin,(1999), “Environmental effects and exposures to manganese from use metyllcyclopentadienyl manganese tricarbonyl(MMT) in gasoline”. Neuro Toxicol. 20:145-150.

Marble, J. C., Corley, T. L., Conklin, M. H., and Fuller, C. C., (1999), “Environmental Factors Affecting Oxidation of Manganese in Pinal Creek, Arizona”, U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting Charleston South Carolina March 8-12,1999--Volume 1 of 3--Contamination From Hard-Rock Mining, Water-Resources Investigation Report 99-4018A

Martin, S. T., (2003), “Precipitation and Dissolution of Iron and Manganese Oxides”, Washington, D.C.: American Chemical Society, 1986, pp 487-502.

Masschelein, W.J., (1979), “Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds”, Ann Arbor Sci. Publ., Ann Arbor, MI.

Minear, R. A.; Keith, and Lawrence H., (1982), " Water analysis", Academic Press, Orlando

Montgomery, J. M., (1985), "Water Treatment Principles and Design", Wiley-Intuscical Publication, New York.

Moss, A.J., A.S.Levy, I.Kim, Y.K.Park,()1989), " Use of vitamin and mineral supplements in the United States: current uses, types of products, and nutrients. Advance Data, Vital and Health Statistics of National Center for Health Statistics. Hyattsville, MD: National Center for Health Statistics. No174. Hyattsville, MD:National Center for Health Statistics(as cited in IOM, 2002)

NGO FORUM (1997), "Annual Report on Drinking Water and Sanitation"

NTP,(1993), " Toxicology and carcinogenesis studies of manganese(II)Sulfate Monohydrate (CAS No. 10034-96-5)in F344/N Rats and B6C3F_1 Mice (Feed Studies). NTP Tech. Rep.Ser.428. National Toxicology Program, Research Triangle Park, NC.

National Rural Water Association (NRWA), (2004) Regulatory Policy Development Project: Manganese.

O'Connell, R.T., (1978), "Suspended Solids Removal." Water Treatment Plant Design, Ann Arbor Science Publishers, Inc, Ann Arbor, MI.

Posselt, H.S., F. J. Anderson, and W.J. Webber., (1967), "The Surface Chemistry of Hydrous Manganese Dioxide," Presented at meeting of Water, Air, and Waste Chemistry Division, American Chemical Society, Bar Harbor, FL, April.

Raveebdran, R., Asgworth, B., Chatelier, B., and (2001) "Manganese Removal in Drinking Water Systems", 64th Annual Water Industries Engineers and Operators Conference, Bendigo, Bendigo, 5-6 September 2001.

Rayner-Canham, G.(1996), "Descriptive Inorganic Chemistry", Freeman:New York, USA

Roles, H.A., M.I. Ortega Eslava, E. Ceulemans, A.Robert, and D.Lison,(1999), " Prospective study on the reversibility of neurobehavioral effects in workers exposed to manganese dioxide"" NeuroToxicol. 20:255-271.

Royal Academy of Engineering International Travel Grant Report, (2003), 8 th International Congress on Mine Water and the Environment,19 th -22 nd October 2003.

Hasan, S., "Manganese removal from Groundwater of Bangladesh", Unpublished undergraduate thesis work.

Samblebe, M. (2003), "Manganese Removal Using Chlorine Oxidation and Powdered Activated Carbon", 66 th Annual Water Industry Engineers and Operators' Conference, Eastbank Centre – Shepparton, 3- 4 September 2003, p 86-95

Seelig, B., Derickson, R., and Bergsrud, F., (1992) "Iron and Manganese Removal: Treatment Systems for Household Water Supplies", NDSU Extension Service, North Dakota State University, USA.

Singer, P.C. (1991), "Research Needs for Alternative Oxidants and Disinfectants", Annual AWWA Conference, Philadelphia, June 23-27.

Shacklette, H.T., and J.G. Boerngen, (1984), " Element concentrations in soils and other surficial materials of the coterminous United States". USGS Paper 1270. Washington, DC: US Govern. Printing Office,p.6.

Shahid, S., (1998), "Removal of Iron from Groundwater by Coagulation and Sedimentation", M.Sc. Thesis, Department of Civil Engineering, Bangladesh University of Engineering & Technology, Dhaka, Bangladesh.

Sharma, S.K., Petrusevski, B., J.C. Schippers, (2001), "Advance Groundwater Treatment Iron, Manganese, Fluoride and Boron removal" published by IDE-Delft, International Institute for Infrastructure, Hydraulic and Environmental Engineering, Netherlands.

Standard Methods (2002), "Standard Methods for the Examination of Water and Wastewater", American Public Health Association, AWWA, and Water Pollution Control Fed., Washington, D.C.

Stevens, A.A., (1982), "Reaction of Chlorine Dioxide", Environ. Health Perspect. 46; 101

Stumm, W. and Morgan, J.J., (1981), "Aquatic Chemistry", Willey & Sons Inc. New York.

Tahura, S., Shahidullah,S. M., Rahman, T. and Hasnat, A., (2001), Evaluation of an Arsenic Removal Household Device: Bucket Treatment Unit", BUET-UNU International Workshop on Technologies for arsenic Removal from Drinking Water, May 2001.

Tebo, B.M., Emerson, S., (1985), "Effect of oxygen tension, Mn(II) concentration, and temperature on the microbially catalyzed Mn(II) oxidation rate in a marine fjord", Applied and Environmental Microbiology, 50(5), 1268-1273.

Tebo, B.M., Ghiorse, W.C., Waasbergen V., L.G., Siering, P.L., Caspi, R., (1997), "Bacterially-mediated mineral formation: Insights into manganese (II) oxidation from molecular genetic and biochemical studies", Reviews in Mineralogy,. 35, 225-266.

Ter, H, G.M.Griffing, M.Brandt, D.Oberding and M.Kapron, (1975), "Methylcyclopentadienyl manganese trycarbonyl as an antiknock: Composition and fate of manganese exhaust products. J Air Pollut. Control assoc. 25:585-860(as cited in ATSDR, 2000).

Thomson,A.B., D.Olatunbosun, L.S.Valverg,(1971), " Interrelation of intestinal transport system for manganese and iron ". J.Lab. Clin. Med. 78:642-655.

US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (1997), ".Draft toxicological profile for manganese update".

USEPA, (1984) , "Health Assessment Document for manganese. Environmental Critaria and Assessment Office, U.S. Environmental Protection Agency, Cincinati, OH (EPA-600//83/13F)

USEPA. (1986a), "Reference Values for Risk Assessment", Environmental Criteria and Assessment Office. Cincinati, OH.

USEPA (1986b), "Guidance for Carcinogenic risk Assessment", US Environmental Protection Agency, Fed. reg. 51(185):33992-34003.

USEPA (1990), "Comments on the Use of Methylcyclopentadienyl Manganese Tricarbonyl in Unleaded Gasoline", U.S. Environmental Protection Agency, Office of Research and Department, Research Triangle Park, NC.

USEPA (1996a), "Exposure factors handbook", Vol-I-General factors, U.S. Environmental Protection Agency, Washington, DC.

USEPA (1996b), "Proposed Guidelines Carcinogenic Risk Assessment", Environmental Protection Agency, Office of Research and Department, Washington, DC.

USEPA, (2001), "Contaminant Candidate List Preliminary Regulatory Determination Support Document for Manganese", EPA #815-R-01-013. (November) Washington DC

USEPA (2002), "Announcement of Preliminary Regulatory Determinations for Priority Contaminants on the Drinking Water Contaminant Candidate List", Federal Register 67:106:38222-38244.

USEPA, (2002), "Health Effects Support Document for Manganese" (External Review Draft--April) EPA #R-02-029. Washington DC

USEPA, (2004), " Drinking Water Health Advisory for Manganese" U.S. Environmental Protection Agency, Washington, DC.

Varner, D., Skipton, S., Hay, D., and Jasa P. (1994), " Drinking Water: Iron and Manganese", NHDES Technical Bulletin, WD-WS-3-7.

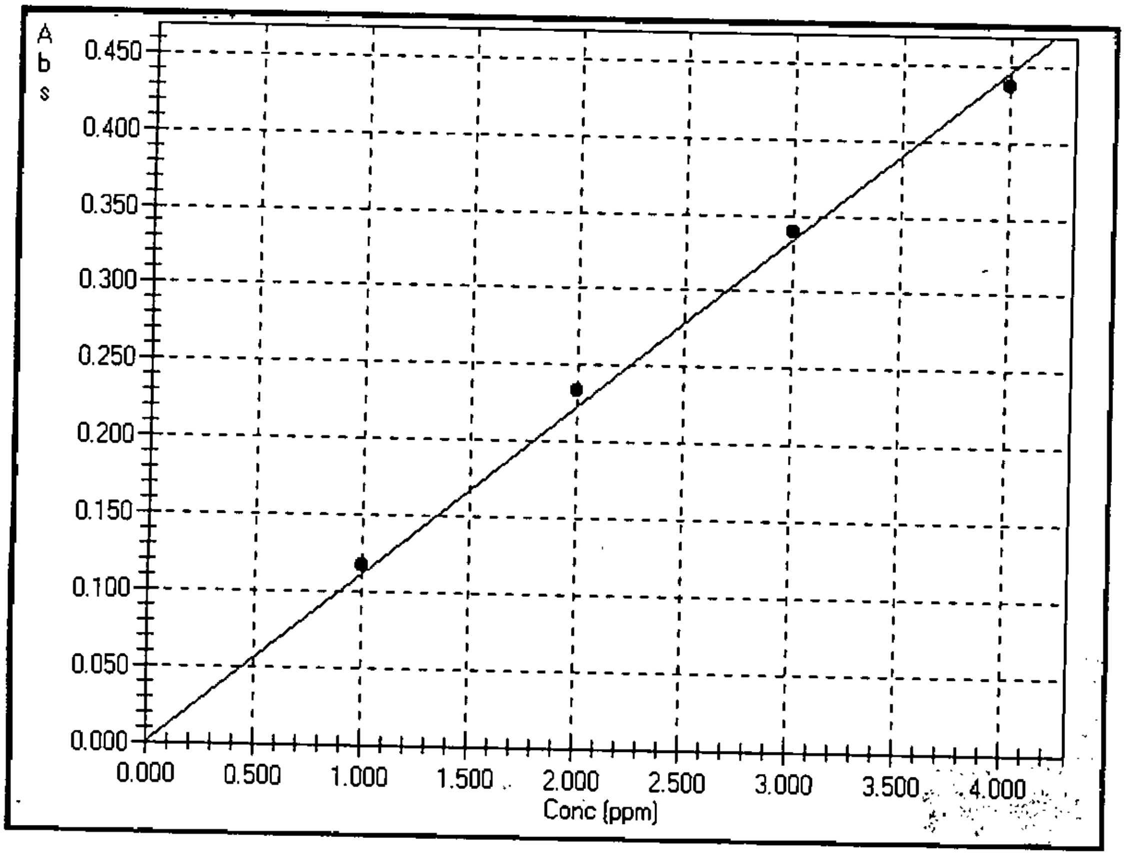
Vieregge,P.,Heinzow,B.Korf,G.,Teichert,H.F.,Schleifenbaum,P.,Mosinger,H.U.(1995), "Long term exposure to manganese in rural well water has no neurological effects",Canadian Journal ofNeurological Sciences 22 ,286-289

Wang, J.D., C.C.Chuang, Y.H.Hwang, J.M.Lin and J.S.Chen,(1989), "Mnganese induced parkinsonism: An outbreak due to unrepaired ventilation control system in a ferromanganese smelter". Br.J.Ind. Med.46:856-859.

Woolf, A.,R.Wright, C.Amarasiriwardena. and D.bellinger,(2002), "Achild with chronic manganese exposure from drinking water. Environ. Health Persp. 110:613-616.

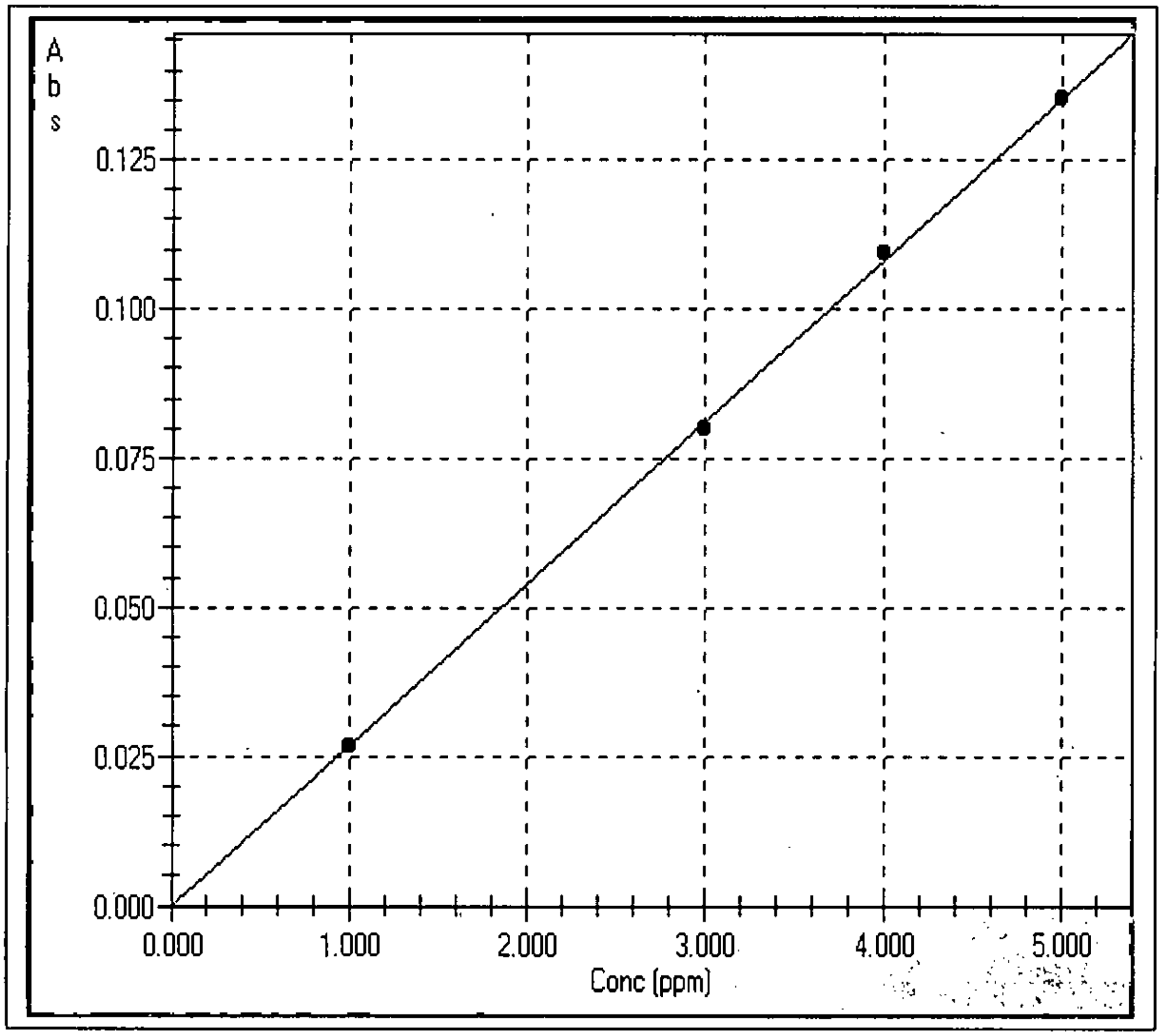
Zayed, J., C.Thibault, L. Gareau, et al, (1999), "Airborne manganese particulates and methylcyclopentadienyl manganese tricarbonyl (MMT) at selected outdoor sites in Montreal". Neuro Toxicol. 20(2-3):151-158

APPENDIX- "A"



Abs = 0.1116 Conc. + 0
Regression, r = 0.9993

Figure A1: A sample standard curve for manganese standards plotted in AAS (Shimadzu, 6800) for determination of manganese in groundwater



Abs = 0.0271 Conc. + 0
Regression, r = 0.9998

Figure A2: A sample standard curve for iron standards plotted in AAS (Shimadzu, 6800) for determination of manganese in groundwater

APPENDIX- "B"

Study on Manganese Removal from Groundwater by Oxidation

Table B1: Water quality parameters for groundwater collected from BUET pumping station.

Sl. no.	Water Quality Parameters	Unit	Concentration Present	Bangladesh Standard for Drinking Water (ECR'97)
1	pH	--	7.78	6.5-8.5
2	Color	Pt. Co. unit	2.00	15
3	Turbidity	NTU	0.35	10
4	Carbon-dioxide, CO_2	mg/L	41.0	-
5	Total Alkalinity as $CaCO_3$	mg/L	238.0	-
6	Total Hardness as $CaCO_3$	mg/L	236.0	200-500
7	Iron, Fe	mg/L	0.02	0.3-1.0
8	Manganese, Mn	mg/L	0.004	0.1
9	Arsenic, As	g/L	<1.0	50
10	Chloride, Cl	mg/L	130.0	150-600
11	Fluoride, F	mg/L	0.29	1
12	Nitrate-Nitrogen, NO_3-N as N	mg/L	0.2	10 as N
13	Total Dissolved Solids (TDS)	mg/L	504.0	1000

Table B-2 : Effect of settling time on removal of manganese present in different concentration in groundwater with $KMnO_4$ oxidation (Stoichiometry ratio = 1.2)

	Unit	1A	1B	2A	2B	3A	3B
Initial Mn Concentration	mg/L	1.03	1.01	2.03	2.02	4.95	4.98
KMnO4 Dose Added	mg/L	2.304	2.304	4.608	4.608	11.52	11.52
Residual Mn After 30 mins Settlement	mg/L	0.15	0.17	0.27	0.3	1.02	1.08
Residual Mn After 90 mins Settlement	mg/L	0.05	0.04	0.09	0.11	0.35	0.41
Residual Mn After 3 hrs settlement (mg/l)	mg/L	0	0	0	0	0.11	0.13
Residual Mn After Filtration	mg/L	0	0	0	0	0.06	0.08
Manganese Removal After 30 Mins Settlement	%	85.4	83.2	86.7	85.1	79.4	78.3
Manganese Removal After 90 Mins Settlement	%	95.1	96.0	95.6	94.6	92.9	91.8
Manganese Removal After 3 hrs Settlement	%	100.0	100.0	100.0	100.0	97.8	97.4
Manganese Removal After Filtration	%	100.0	100.0	100.0	100.0	98.8	98.4
pH After Removal		7.88	7.9	7.84	7.86	7.74	7.7
Eh After Removal	mV	230	228	236	248	338	325
Color after 30 mins settlement	Pt-Co unit	78	82	145	150	197	208
Color after 90 mins settlement	Pt-Co unit	32	40	52	55	121	130
Color after 3 hrs settlement	Pt-Co unit	12	18	24	22	71	70
Color after Filtration	Pt-Co unit	0	0	0	0	4	0

Table B-2 (continued) : Effect of settling time on removal of manganese present in different concentration in groundwater with $KMnO_4$ oxidation (Stoichiometry ratio = 1.2)

	Unit	4A	4B	5A	5B
Initial Mn Concentration	mg/L	7.48	7.52	9.98	10.02
KMnO4 Dose Added	mg/L	16.128	16.128	23.04	23.04
Residual Mn After 30 mins Settlement	mg/L	1.86	1.79	2.54	2.66
Mn Concentration After 90 mins Settlement	mg/L	0.7	0.77	1.14	1.18
Residual Mn After 3 hrs settlement (mg/l)	mg/L	0.24	0.23	0.35	0.38
Residual Mn After Filtration	mg/L	0.16	0.15	0.22	0.21
Manganese Removal After 30 mins Settlement	%	75.1	76.2	74.5	73.5
Manganese Removal After 90 mins Settlement	%	90.6	89.8	88.6	88.2
Manganese Removal After 3 hrs Settlement	%	96.8	96.9	96.5	96.2
Manganese Removal After Filtration	%	97.9	98.0	97.8	97.9
pH After Removal		7.6	7.58	7.5	7.44
Eh After Removal	mV	469	480	549	556
Color after 30 mins settlement	Pt-Co unit	298	315	456	448
Color after 90 mins settlement	Pt-Co unit	179	188	225	220
Color after 3 hrs settlement	Pt-Co unit	120	128	162	151
Color after Filtration	Pt-Co unit	8	8	12	15

Table B-3: Effect of pH on manganese removal from groundwater by oxidation with $KMnO_4$ (Stoichiometry ratio =1.0)

	Unit	1	2	3	4	5	6	7
Initial Mn Concentration	mg/L	2.01	2.03	1.99	2.02	1.99	2.01	1.98
Adjusted pH		4.82	6	7.1	7.5	8.07	9.1	10
Mn conc after 30 mins settling	mg/L	0.96	0.78	0.33	0.28	0.16	0.18	0.21
Mn Concentration After Filtration	mg/L	0.45	0.3	0.14	0.07	0.02	0	0
Mn Removal After 30 mins Settling	%	52.24	61.58	83.42	86.14	91.96	91.04	89.39
Mn Removal After Filtration	%	77.61	85.22	92.96	96.53	98.99	100.00	100.00
pH After Removal		7.54	7.68	7.78	7.86	8.20	8.34	8.78
Eh After Removal	mV	182	205	228	230	239	235	232
Color After Removal	Pt-Co unit	92	85	81	75	68	75	71

Table B-4: Effect of $KMnO_4$ dose on oxidation of manganese in groundwater by varying the stoichiometric fraction

	Unit	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b	6a	6b
Initial Mn Concentration	mg/L	2.01	2.02	1.99	2.02	1.98	1.98	2.01	2.03	1.98	2.01	2.01	1.98
KMnO4 Fraction of Stoichiometric Ratio		0.25	0.25	0.5	0.5	0.8	0.8	1	1	1.2	1.2	1.5	1.5
Mn Concentration After 30 mins Settlement	mg/L	1.46	1.51	0.78	0.69	0.36	0.33	0.28	0.29	0.42	0.39	0.95	0.93
Mn Concentration After Filtration	mg/L	1.03	1.07	0.56	0.53	0.08	0.09	0	0.01	0.06	0.05	0.31	0.28
Color After 30 mins Settlement	Pt-Co unit	224	236	110	119	78	74	85	91	130	141	359	385
pH After Removal		7.57	7.56	7.84	7.84	7.95	7.98	8.1	8.05	8.01	8.02	8.02	8.04
Eh After Removal	mV	174	177	196	192	210	215	224	230	218	222	212	202
% Mn Removal After Filtration	%	48.76	47.03	71.86	73.76	95.96	95.45	100.00	99.51	96.97	97.51	84.58	85.86
% Mn Removal After 30 Mins Settlement	%	27.36	25.25	60.80	65.84	81.82	83.33	86.07	85.71	78.79	80.60	52.74	53.03

Table B-5: Removal of color produced during oxidation of manganese present in groundwater by potassium permanganate using 10 cm depth sand filter. ($KMnO_4$ Stoichiometry ratio = 1.2)

	Unit	**1**	**2**	**3**	**4**	**5**
Initial Mn Concentration	mg/L	2.01	2.01	2.01	2.01	2.01
Initial Color After Mixing	Pt-Co unit	244	244	244	244	244
Time Interval for Measurement	Mins	30	30	30	30	30
Volume of Filtrate Water	ml	285	268	230	192	178
Rate of Filtration	ml/min	9.50	8.93	7.67	6.40	5.93
Contact Time	Mins	1.05	1.12	1.30	1.56	1.69
Color After Filtration	Pt-Co unit	18	18	15	8	7
Residual Mn after Filtration	mg/L	0.03	0.04	0.03	0.02	0.02
Color Removed by Filtration	%	92.62	92.62	93.85	96.72	97.13
Mn Removal by Filtration	%	98.51	98.01	98.51	99.00	99.00

Table B-6: Removal of color produced during oxidation of manganese present in groundwater by potassium permanganate using 20 cm depth sand filter. ($KMnO_4$ Stoichiometry ratio = 1.2)

	Unit	1	2	3	4	5
Initial Mn Concentration	mg/L	2.03	2.03	2.03	2.03	2.03
Initial Color After Mixing	Pt-Co unit	225	225	225	225	225
Time Interval for Measurement	Mins	30	30	30	30	30
Volume of Filtrate Water	ml	495	475	435	420	395
Rate of Filtration	ml/min	16.50	15.83	14.50	14.00	13.17
Contact Time	Mins	1.21	1.26	1.38	1.43	1.52
Color After Filtration	Pt-Co unit	6	7	4	2	2
Residual Mn after Filtration	mg/L	0.04	0.03	0.02	0.01	0.02
Color Removed by Filtration	%	97.33	96.89	98.22	99.11	99.11
Mn Removal by Filtration	%	98.03	98.52	99.01	99.51	99.01

Table B-7: Oxidation of groundwater containing different amount of manganese by chlorination at pH 7.5. (Stoichiometry ratio = 1.2)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
Initial Mn Concentration	mg/L	1.01	1.02	2.01	2.02	4.98	5.02	7.5	7.48	9.97	10.01
Chlorine Dose Added	mg/L	1.548	1.548	3.096	3.096	7.74	7.74	11.61	11.61	15.48	15.48
Mn Concentration after 30 min settling	mg/L	0.56	0.61	1.29	1.35	3.21	3.31	5.62	5.64	7.79	7.81
Mn Concentration After Filtration	mg/L	0.51	0.54	1.18	1.21	3.16	3.21	5.49	5.4	7.58	7.7
Mn Removal After 30 mins Settlement	%	44.55	40.20	35.82	33.17	35.54	34.06	25.07	24.60	21.87	21.98
Mn Removal After Filtration	%	49.50	47.06	41.29	40.10	36.55	36.06	26.80	27.81	23.97	23.08
pH after removal		7.24	7.28	7.37	7.35	7.36	7.37	7.38	7.41	7.42	7.4
Eh After Removal	mV	-58	-65	-77	-74	-68	-70	-60	-58	-54	-60
Residual Cl_2	mg/L	1.06	1.04	1.21	1.24	1.56	1.51	1.72	1.79	1.82	1.88
Color After 30 mins Settlement	Pt-Co unit	0	4	0	0	5	4	0	4	8	9

Table B-8: Oxidation of groundwater containing different amount of manganese by chlorination at pH 8.5. (Stoichiometry ratio = 1.2)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
Initial Mn Concentration	mg/L	1.01	1.03	2.01	2.01	4.98	4.99	7.49	7.51	9.98	10.02
Chlorine Dose Added	mg/L	1.548	1.548	4.64	4.64	7.74	7.74	11.61	11.61	15.48	15.48
Mn Concentration after 30 min settling	mg/L	0.25	0.27	0.61	0.62	1.69	1.6	3.01	2.95	4.39	4.45
Mn Concentration After Filtration	mg/L	0.17	0.18	0.4	0.39	1.12	1.15	1.97	1.92	2.72	2.66
Mn Removal After 30 mins Settlement	%	75.25	73.79	69.65	69.15	66.06	67.94	59.81	60.72	56.01	55.59
Mn Removal After Filtration	%	83.17	82.52	80.10	80.60	77.51	76.95	73.70	74.43	72.75	73.45
pH after removal		8.25	8.21	8.29	8.31	8.42	8.4	8.37	8.35	8.39	8.41
Eh After Removal	mV	-72	-70	-80	-82	-105	-104	-155	-154	-174	-176
Residual Cl_2	mg/L	0.41	0.38	0.52	0.55	0.99	0.87	1.04	1.09	1.3	1.35
Color After 30 mins Settlement	Pt-Co unit	0	4	0	0	5	8	12	17	18	22

Table B-9 Oxidation of groundwater containing different amount of manganese by chlorination at pH 10.0 with variation in contact time. (Stoichiometry ratio = 1.2)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
Initial Mn Concentration	mg/L	1.02	0.99	2.01	2.02	5.01	5.02	7.51	7.48	10.04	10.01
Chlorine Dose Added	mg/L	1.548	1.548	4.64	4.64	7.74	7.74	11.61	11.61	15.48	15.48
Mn Concentration After 15 min contact	mg/L	0.41	0.39	0.73	0.68	1.48	1.52	2.02	2.14	2.67	2.55
Mn Concentration After 25 min contact	mg/L	0.15	0.16	0.21	0.24	0.35	0.39	0.43	0.41	0.51	0.59
Mn Concentration After 35 min contact	mg/L	0.01	0	0.02	0.01	0.05	0.03	0.08	0.07	0.08	0.08
Mn Concentration After 30 min settling	mg/L	0	0	0	0	0.03	0.01	0.04	0.02	0.03	0.02
Mn Concentration After Filtration	mg/L	0	0	0	0	0	0	0	0	0	0
Mn Removal After 15 min contact	%	59.80	60.61	63.68	66.34	70.46	69.72	73.10	71.39	73.41	74.53
Mn Removal After 25 min contact	%	85.29	83.84	89.55	88.12	93.01	92.23	94.27	94.52	94.92	94.11

Table B-9 (Continued.): Oxidation of groundwater containing different amount of manganese by chlorination at pH 10.0 with variation in contact time. (Stoichiometry ratio = 1.2)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
Mn Removal After 35 min Contact	%	99.02	100.00	99.00	99.50	99.00	99.40	98.93	99.06	99.20	99.20
Mn Removal After 30 min Settlement	%	100.00	100.00	100.00	100.00	99.40	99.80	99.47	99.73	99.70	99.80
Mn Removal After Filtration	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
pH After Removal		9.72	9.7	9.75	9.69	9.74	9.76	9.68	9.76	9.68	9.74
Eh After Removal	mV	-88	-86	-76	-70	-74	-75	-70	-89	-72	-73
Residual Cl_2	mg/L	0.28	0.26	0.42	0.39	0.81	0.82	0.95	0.99	1.19	1.12
Color After 30 min Settlement	Pt-Co unit	4	6	2	5	0	4	2	0	0	0

Table B-10: Effect of pH on oxidation of manganese in groundwater by chlorine (Stoichiometry ratio = 1.0)

	Unit	1	2	3	4	5	6	7
Initial Mn Content	mg/L	2.01	2.02	2.01	2.0	2.03	2.02	2.04
Adjusted pH		5.2	6.02	7.04	7.5	7.98	9	10.01
Chlorine dose added	mg/L	2.58	2.58	2.58	2.58	2.58	2.58	2.58
Residual Mn After 30 mins Settling	mg/L	1.89	1.84	1.73	1.42	0.86	0.39	0.03
Mn in Solution After Filtration	mg/L	1.84	1.76	1.64	1.15	0.62	0.16	0
Mn Removal After 30 mins Settling	%	5.97	8.91	13.93	29.00	57.64	80.69	98.53
Mn Removal After Filtration	%	8.46	12.87	18.41	42.50	69.46	92.08	100.00
pH After removal		5.47	6.34	7.21	7.46	7.90	8.55	8.73
Eh After rem (mV)	mV	91	36	-23	-42	-71	-88	-100
Residual Cl_2	mg/L	2.08	2.01	1.78	1.52	1.26	0.97	0.51
Color after removal	Pt-Co unit	4	8	12	17	22	8	5

Table B-11: Removal of manganese present in natural groundwater with simple aeration with variation in contact time

	Unit	1	2	3	4	5
Initial Mn Concentration	mg/L	2.03	2.04	2	2.02	2.02
Initial pH		7.04	8.08	9.1	10.02	11
Mn Concentration After 20 min Mixing	mg/L	1.86	1.54	0.82	0.26	0.1
Mn Concentration After 30 min Mixing	mg/L	1.82	1.41	0.63	0.15	0.05
Mn Concentration After 60 min Mixing	mg/L	1.71	0.98	0.22	0.04	0.02
Mn Concentration After Filtration	mg/L	1.68	0.92	0.2	0.02	0.01
Mn Removal After 20 min Mixing	%	8.37	24.51	59.00	87.13	95.05
Mn Removal After 30 min Mixing	%	10.34	30.88	68.50	92.57	97.52
Mn Removal After 60 min Mixing	%	15.76	51.96	89.00	98.02	99.01
Mn Removal After Filtration	%	17.24	54.90	90.00	99.01	99.50
pH After Removal		6.94	7.91	8.86	9.82	10.74
Eh After Removal	mV	5	-72	-110	-170	-228
Color After Removal	Pt- Co unit	0	4	2	4	4

APPENDIX "C"

Study on Manganese Oxidation in Presence of Iron

Table C-1: Manganese removal from groundwater by oxidation with $KMnO_4$ in presence of dissolved iron in water (Initial Mn concentration = 5.0 mg/L; Stoichiometry ratio =1.2)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
Initial pH		7.65	7.62	7.64	7.62	7.7	7.65	7.61	7.67
Initial Mn Concentration	mg/L	5.02	5.01	4.98	5.01	5.03	5.02	4.99	5.02
Mn Concentration After 30 mins Settlement	mg/L	1.76	1.88	1.54	1.48	1.32	1.26	1.21	1.2
Mn Concentration After Filtration	mg/L	0.08	0.06	0.11	0.12	0.18	0.21	0.49	0.51
Mn Removal After 30 mins settlement	%	64.94	62.48	69.08	70.46	73.76	74.90	75.75	76.10
Mn Removal After Filtration	%	98.41	98.80	97.79	97.60	96.42	95.82	90.18	89.84
Initial Fe Concentration	mg/L	1	1	3	3	5	5	10	10
Fe Concentration After 30 mins Settlement	mg/L	0.33	0.42	1.21	1.29	1.72	1.82	2.87	3.25
Fe Conc after Filtration	mg/L	0	0	0	0	0	0	0	0
Fe Removal After Filtration	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Final pH		7.77	7.72	7.65	7.68	7.84	7.82	7.88	7.85

Table C-2: Manganese removal from groundwater by oxidation with $KMnO_4$ in presence of dissolved iron in water (Initial Mn concentration = 2.0 mg/L; Stoichiometry ratio =1.2)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
Initial pH		7.61	7.64	7.68	7.57	7.59	7.7	7.66	7.58
Initial Mn Concentration	mg/L	2.02	2.01	1.99	2.02	2	2.03	2.03	2.02
Mn Concentration After 30 mins Settlement	mg/L	0.14	0.15	0.25	0.22	0.37	0.35	0.51	0.57
Mn Concentration After Filtration	mg/L	0	0.01	0.04	0.03	0.22	0.2	0.44	0.41
Mn Removal After 30 mins settlement	%	93.07	92.54	87.44	89.11	81.50	82.76	74.88	71.78
Mn Removal After Filtration	%	100.00	99.50	97.99	98.51	89.00	90.15	78.33	79.70
Initial Fe Concentration	mg/L	1	1	3	3	5	5	10	10
Fe Concentration After 30 mins Settlement	mg/L	0.46	0.48	0.71	0.68	1.02	1.08	1.48	1.56
Fe Conc after Filtration	mg/L	0	0	0	0	0.03	0.02	0.06	0.07
Fe Removal After Filtration	%	100.00	100.00	100.00	100.00	99.40	99.60	99.40	99.30
Final pH		7.83	7.8	7.77	7.78	7.84	7.86	7.9	7.92

Table C-3: Manganese removal from groundwater by oxidation with $KMnO_4$ in presence of dissolved iron in water
(Initial Mn concentration = 2.0 mg/L; Stoichiometry ratio =1.0)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
Initial pH		7.55	7.69	7.58	7.71	7.56	7.55	7.7	7.68
Initial Mn Concentration	mg/L	1.98	2.01	1.99	1.98	2.02	1.97	2.02	2.01
Mn Concentration After 30 mins Settlement	mg/L	0.65	0.69	0.8	0.82	1.31	1.28	1.56	1.55
Mn Concentration After Filtration	mg/L	0.08	0.05	0.3	0.35	0.91	0.89	1.42	1.44
Mn Removal After 30 mins settlement	%	67.17	65.67	59.80	58.59	35.15	35.03	22.77	22.89
Mn Removal After Filtration	%	95.96	97.51	84.92	82.32	54.95	54.82	29.70	28.36
Initial Fe Concentration	mg/L	1	1	3	3	5	5	10	10
Fe Concentration After 30 mins Settlement	mg/L	0.28	0.3	0.53	0.54	0.82	0.92	1.7	1.76
Fe Conc after Filtration	mg/L	0	0	0	0	0.05	0.04	0.09	0.08
Fe Removal After Filtration	%	100.00	100.00	100.00	100.00	99.00	99.20	99.10	99.20
Final pH		7.91	7.92	7.87	7.85	7.84	7.83	7.9	7.88

Table C-4: Manganese removal from artificially prepared, low alkalinity and low pH water by oxidation with $KMnO_4$ in presence of dissolved iron at condition. (Stoichiometry ratio =1.0)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
Adjusted pH		7.71	7.68	7.62	7.6	7.74	7.70	7.61	7.64
Adjusted Alkalinity	mg/L as $CaCO_3$	89	91	101	98	100	98	95	102
Initial Mn Concentration	mg/L	2.01	1.99	1.99	2.01	2.03	2.02	2	2.02
Mn After Filtration	mg/L	0.15	0.18	0.37	0.41	1.1	1.08	1.59	1.62
Mn Removal After Filtration	%	92.54	90.95	81.41	79.60	45.81	46.53	20.50	19.80
Initial Fe Concentration	mg/L	1	1	3	3	5	5	10	10
Fe after 15 mins mixing	mg/L	0.88	0.85	2.69	2.8	4.49	4.34	8.04	7.92
Fe Conc after Filtration	mg/L	0	0	0.03	0.04	0.16	0.18	0.3	0.37
Fe Removal After Filtration	%	100.0	100.0	98.88	98.57	96.44	95.85	96.27	95.33
Final pH		7.81	7.77	7.6	7.72	7.61	7.54	7.38	7.41
Color After 30 mins settlement	Pt-Co unit	24	15	84	79	115	118	178	160

Table C-5: Simultaneous removal of manganese and iron from groundwater by oxidation with $KMnO_4$ dose at varying stoichiometric fraction with respect to initial iron and manganese concentrations

	Unit	1a	1b	2a	2b	3a	3b	4a	4b
combined KMnO4 ratio		0.25	0.25	0.5	0.5	0.75	0.75	1	1
Initial pH		6.94	6.93	6.91	7	6.91	6.96	6.94	7.04
Initial Mn Concentration	mg/L	1.99	2.01	1.98	2	2.01	2.03	2.02	1.97
Mn Concentration After 30 min settlement	mg/L	1.83	1.82	1.14	1.19	0.31	0.35	0.55	0.58
Mn Concentration After Filtration	mg/L	1.72	1.75	0.8	0.78	0.14	0.12	0.33	0.3
Mn Removal After 30 mins settlement	%	13.57	12.94	42.42	40.50	84.58	82.76	72.77	70.56
Mn Removal After Filtration	%	8.04	9.45	59.60	61.00	93.03	94.09	83.66	84.77
Initial Fe Concentration	mg/L	5	5	5	5	5	5	5	5
Fe Concentration After 30 mins Settlement	mg/L	0.88	0.87	0.59	0.62	0.41	0.42	0.25	0.3
Fe Concentration After Filtration	mg/L	0	0	0	0	0	0	0	0
Fe Removal After Filtration	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
pH After Removal		7.45	7.42	7.75	7.71	8.1	8.04	7.9	7.79
Color After 30 mins settlement	Pt-Co unit	22	31	61	52	88	93	131	140

Table C-6: Potassium permanganate oxidation of manganese present in groundwater (containing dissolved iron) with pre- oxidation of iron by aeration at elevated pH (Stoichiometric ratio of $KMnO_4$ = 1.0)

	Unit	1a	1b	2a	2b	3a	3b	4a	4b
Adjusted pH		8.1	8.06	8.01	8.09	8.08	8.1	8.11	8.08
Initial Mn Concentration	mg/L	1.99	2.01	1.97	1.99	2.01	1.98	1.98	2.02
Mn Concentration After Filtration	mg/L	0	0	0	0	0	0	0	0
Mn Removal After Filtration	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Initial Fe Concentration.	mg/L	1	1	3	3	5	5	10	10
Fe Concentration after 15 mins stirring	mg/L	0.68	0.71	2.02	1.89	3.14	3.18	5.11	5.26
Fe Concentration after Filtration	mg/L	0	0	0	0	0	0	0	0
Fe Removal after Filtration	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
pH after removal		7.79	7.78	7.74	7.71	7.69	7.7	7.62	7.65
Color after removal	Pt-Co unit	62	58	49	55	70	58	66	72

Table C-7: Oxidation of manganese by aeration in presence of iron in groundwater in varying concentration

	Unit	1a	1b	2a	2b	3a	3b	4a	4b
Initial pH		7.68	7.65	7.71	7.7	7.69	7.74	7.7	7.72
Initial Mn Concentration	mg/L	2.03	2.02	2.03	2.01	2.01	2.03	2.02	2.01
Mn Concentration After 30 min settlement	mg/L	1.78	1.75	1.74	1.71	1.44	1.39	1.74	1.78
Mn Concentration After Filtration	mg/L	1.56	1.58	1.59	1.58	1.62	1.65	1.66	1.65
Mn Removal After 30 mins settlement	%	12.32	13.37	14.29	14.93	28.36	31.53	13.86	11.44
Mn Removal After Filtration	%	23.15	21.78	21.67	21.39	19.40	18.72	17.82	17.91
Initial Fe Concentration	mg/L	1	1	3	3	5	5	10	10
Fe Concentration After 30 mins Settlement	mg/L	0.17	0.14	0.53	0.54	1.42	1.39	3.99	4.28
Fe Concentration After Filtration	mg/L	0.08	0.09	0.45	0.41	1.26	1.24	3.56	3.5
Fe Removal After 30 mins Settlement	%	83.00	86.00	82.33	82.00	71.60	72.20	60.10	57.20
Fe Removal After Filtration	%	92.00	91.00	85.00	86.33	74.80	75.20	64.40	65.00
pH After Removal		7.84	7.81	7.78	7.8	7.74	7.75	7.8	7.82

APPENDIX "D"

Study on Manganese Removal by Coagulation-Adsorption- Coprecipitation

Table D-1: Removal of manganese from groundwater by coagulation-adsorption-coprecipitation using ferrous sulfate [Fe(II)] as coagulant with addition of potassium permanganate as oxidant (Stoichiometry ratio for $KMnO_4$ =1.0)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
Initial pH		7.55	7.52	7.6	7.62	7.61	7.58	7.49	7.54	7.64	7.6
Initial Mn Concentration	mg/L	2.01	2.01	1.99	1.98	1.99	2.01	1.98	2.02	2.03	2.02
Fe (II) Dose	mg/L	25	25	15	15	10	10	5	5	2	2
Mn Concentration After Coagulation	mg/L	0.35	0.33	0.47	0.44	0.77	0.79	0.68	0.67	0.46	0.49
Mn Concentration After Filtration	mg/L	0.27	0.28	0.42	0.38	0.73	0.75	0.63	0.61	0.4	0.43
Mn Removal After Coagulation	%	82.59	83.58	76.38	77.78	61.31	60.70	65.66	66.83	77.34	75.74
Mn Removal After Filtration	%	86.57	86.07	78.89	80.81	63.32	62.69	68.18	69.80	80.30	78.71
Fe Concentration After Coagulation	mg/L	4.79	4.96	2.87	2.71	0.68	0.74	0.39	0.33	0.05	0.08
Fe Concentration After Filtration	mg/L	0.04	0.03	0.04	0.05	0.03	0.04	0.01	0	0	0
pH After Removal		7.77	7.69	7.78	7.71	7.75	7.7	7.7	7.76	7.72	7.73
Color After Coagulation	Pt-Co unit	90	88	84	80	90	79	89	90	85	88

Table D-2: Removal of manganese from groundwater by coagulation-adsorption-coprecipitation using ferrous sulfate [Fe(II)] as coagulant without addition of potassium permanganate

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
Initial pH		7.61	7.65	7.62	7.63	7.69	7.64	7.7	7.68	7.66	7.59
Initial Mn Concentration	mg/L	2.01	2.01	1.99	1.98	1.99	2.01	1.98	2.02	2.03	2.02
Fe (II) Dose	mg/L	25	25	15	15	10	10	5	5	2	2
Mn Concentration After Coagulation	mg/L	1.59	1.58	1.48	1.47	1.41	1.4	1.36	1.35	1.31	1.32
Mn Concentration After Filtration	mg/L	1.35	1.36	1.31	1.33	1.29	1.31	1.24	1.21	1.26	1.22
Mn Removal After Coagulation	%	20.90	21.39	25.63	25.76	29.15	30.35	31.31	33.17	35.47	34.65
Mn Removal After Filtration	%	32.84	32.34	34.17	32.83	35.18	34.83	37.37	40.10	37.93	39.60
Fe Concentration After Coagulation	mg/L	5.29	5.16	3.32	3.44	1.68	1.61	0.77	0.73	0.32	0.29
Fe Concentration After Filtration	mg/L	2.38	2.51	1.36	1.49	0.84	0.79	0.26	0.28	0.15	0.13
Fe Removal After Coagulation	%	78.84	79.36	77.87	77.07	83.20	83.90	84.60	85.40	84.00	85.50
pH After Removal		6.68	6.69	6.78	6.72	6.9	6.94	7.02	7.1	7.4	7.42

Table D-3: Removal of manganese from groundwater by coagulation-adsorption-coprecipitation using ferric chloride [Fe(III)] as coagulant with addition of potassium permanganate as oxidant (Stoichiometry ratio for $KMnO_4$ =1.0)

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**
Initial pH		7.71	7.67	7.72	7.7	7.64	7.61
Fe (III) Dose	mg/L	10	10	15	15	25	25
Initial Mn Concentration	mg/L	1.99	1.98	2.01	2	1.98	1.97
Mn Concentration After Coagulation	mg/L	0.14	0.15	0.1	0.09	0.07	0.08
Mn Concentration After Filtration	mg/L	0.02	0.03	0	0.01	0	0
Mn Removal After Coagulation	%	92.96	92.42	95.02	95.50	96.46	95.94
Mn Removal After Filtration	%	98.99	98.48	100.00	99.50	100.00	100.00
pH after removal		7.83	7.88	7.89	7.9	7.94	7.91
Color after removal	Pt-Co unit	92	109	126	131	166	155

Table D-4: Removal of manganese from groundwater by coagulation-adsorption-co precipitation using ferric chloride [Fe(III)] as coagulant without addition of potassium permanganate as oxidant

	Unit	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**
Initial pH		7.64	7.6	7.59	7.6	7.68	7.64
Fe (III) Dose	mg/L	10	10	15	15	25	25
Initial Mn Concentration	mg/L	2	2.02	2.03	2.02	2.03	2.03
Mn Concentration After Coagulation	mg/L	1.51	1.49	1.38	1.37	1.26	1.29
Mn Concentration After Filtration	mg/L	1.42	1.41	1.33	1.32	1.22	1.19
Mn Removal After Coagulation	%	24.50	26.24	32.02	32.18	37.93	36.45
Mn Removal After Filtration	%	29.00	30.20	34.48	34.65	39.90	41.38
pH after removal		6.86	6.91	6.94	6.92	6.8	6.85
Color after removal	Pt-Co unit	23	18	27	30	35	42

Table D-5: Effect of pH on Mn removal by coagulation using ferric chloride [Fe(III)] as coagulant

	Unit	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Initial pH		7	7.25	7.7	8.3	9	10	11
Initial Mn Concentration	mg/L	15	15	15	15	15	15	15
Fe (III) Dose	mg/L	1.97	2.01	1.98	1.95	2.01	2.03	1.97
Mn Concentration After Coagulation	mg/L	1.58	1.56	1.41	1.35	1.28	0.46	0.02
Mn Concentration After Filtration	mg/L	1.45	1.40	1.26	1.25	1.15	0.31	0.01
Mn Removal After Coagulation	%	19.80	22.39	28.79	30.77	36.32	77.34	98.98
Mn Removal After Filtration	%	26.40	30.35	36.36	35.90	42.79	84.73	99.49
Fe Concentration After Filtration	mg/L	0.02	0.04	0	0	0	0	0.04
Fe Removal After Filtration	%	99.87	99.73	100.00	100.00	100.00	100.00	99.73
pH after removal		6.78	6.91	7.02	7.67	7.29	7.89	9.36