ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING
M.Sc. Program in Environmental Engineering

Removal of Iron and Manganese from groundwater by oxidation-filtration hybrid system

A thesis submitted to Addis Ababa Institute of Technology, School of Chemical and Bio engineering in partial fulfillment of the requirements for the Degree of Master of Science in Environmental Engineering

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Addis Ababa Institute of Technology

Graduate Program in Environmental Engineering

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Declaration

I declare that this thesis entitled Removal of iron and manganese from groundwater by oxidation-filtration hybrid system is my own original work done under the supervision of Dr. Shimelis Kebede at School of Chemical and Bio engineering in Addis Ababa Institute of Technology, Addis Ababa University and I have not previously submitted it entirely or in part for obtaining any qualification at any other university.

Lemlem Belay ___________________________

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Abstract

Groundwater is naturally available water that exists in pore spaces and fractures in rock and sediment beneath the earth's surface that fills the opening in beds of rocks and sand. In developing countries both groundwater and surface water are used for irrigated agriculture and urban water supply. In Ethiopia groundwater is mostly utilized for drinking and industrial utility. In deeper wells the natural presence of metallic elements iron and manganese together is common .Their presence in limited amount is essential for all living organisms. However, the existence of iron and manganese are considered as contaminants above the limited concentration of 0.3mg/L and 0.1mg/L respectively. From many wells found in and around Addis Ababa some of them have high iron and manganese concentration which is found to be a problem on using groundwater to supply the high-water demand in the city.

The aim of this study was removal of iron and manganese from groundwater by oxidation by air and sodium hypochlorite followed by sand filtration. Experimental set up was done at AAiT 5 kilo campus. The sand bed was prepared for filtration process with bed depth 0.6m and grain size of ES=0.71mm, UC=1.70 and d_{60}=1.2mm. Electrolytic sodium hypochlorite Produced using titanium and stainless steel electrodes at electrolytic reaction time 72 min in one liter electrolytic cell 2 cm gape and 7volte. The result hypochlorite resulted had concentration of 4.183 g/lit.

Removal efficiency of the system tested using synthetic water resulted removal efficiency of 95.76333% for iron and 95.65% for manganese. For actual groundwater from Sambanekersa with 5.162mg/l iron and 0.607mg/l manganese concentration oxidation filtration process was performed at optimal point of 7.02mg/l NaOCl, 77min and 1.5 l/min air flow rate the resulted removal efficiency is 87.14% for iron and 26.41% for manganese.

Key words; filtration, sodium hypochlorite, air flow rate, oxidation

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Acronyms

AAiT	Addis Ababa Institute of technology
AAWSA	Addis Ababa water and sewerage authority
ANOVA	Analysis of Variance
APHA	American Public Health Association
BBD	Box – Behnken design
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DC	Direct current
DO	Dissolved oxygen
ES	Effective size
L/min	Liter per minute
MCL	Minimum concentration level
Mm	Millimeter
NaOCl	Sodium hypochlorite
PAN	Pyridylazonaphthol
UC	Uniformity coefficient
WHO	World health organization

Chapter one

1 Background and justification

1.1 Introduction

Water has serious involvement in human daily activities and their lives are depending on it. It is fundamental for the growth and economic development of every country. Water used for domestic, industrial, and used for livestock's in the world. Growing human populations and increasing economic production and consumption activities demand wide-ranging freshwater which covers all water resource components, counting water stored in the soil surface and groundwater possessions [1].Groundwater is naturally available water that exists in pore spaces and fractures in rock and sediment beneath the earth's surface that fills the opening in beds of rocks and sand. From water types that fill in the opening beds, rainwater, and surface water can list as an example[2]. These waters infiltrated into the soils and move downward to the water level in the groundwater reservoir which is called the water table[3]. Groundwater occurs in a deeper zone that is the saturated zone in which all the pore spaces are occupied with water. Groundwater is normally much like a sponge that holds water that presents in soils and sands and able to hold the water[1]. The origin is rainfall or snow that moves through the soil into the groundwater system. Surface water is water found in a river, ponds lakes, swamps, and other parts of the earth that have fresh water. Most World countries' water supply mainly depends on surface water which is easily accessible and distributable[4]. In developed and developing countries, groundwater is preferable for drinking purposes and it is considered the best potable water due to its purity[5]. In developing countries both groundwater and surface water are used for irrigated agriculture and urban water supply. Due to the filtration layers like sand and rocks underneath the ground groundwater has better quality than surface water which is more susceptible for contamination [4]. It is best guesses that Ethiopian groundwater usage reaches 12 to 30 BCM [6]. In Ethiopia groundwater is mostly utilized for drinking and industrial utility [6]. However, groundwater occurrence and accessibility influenced by the geophysical and climatic conditions of the area[6].

Groundwater has characteristics which are different from surface water which makes it suitable for drinking purpose and it is expected to be clean. It has low temperature, low suspended solid content, and low red-ox potential and high carbon dioxide level and high mineral content[7]. In deeper wells the natural presence of metallic elements iron and manganese together is common [8]. Their presence in limited amount is essential for all living organisms. However, the existence of iron and manganese are considered as contaminants above the limited concentration of 0.3mg/L and 0.1mg/L respectively [4],[2]. The natural occurrence of iron and manganese in ground water is as divalent and in most soluble forms [9][10]. In divalent form they possess colorless and organoleptic properties [11]. Their presence above limited concentration in groundwater causes odor, metallic test and staining of laundry and plumping fixtures [12]. In groundwater Fe and Mn found in their soluble forms and when they exposed to air they turns into insoluble forms of $Fe^{+3}$and Mn^{+4} respectively and leave the water with brown- red color [4]. In waters restraining ferrous and manganous salts rust-colored deposits on the walls of tanks, pipes and channels carry-over of deposits into the water may cause due to oxidation by iron bacteria or by exposure to air. Even the presence of iron and manganese in drinking water only have aesthetic issue the removal of this metallic elements are mandatory. In using of groundwater as drinking water source, it can be limited by the availability of iron and manganese as in the case of some wells found in Addis Ababa. From the groundwater wells around Addis Ababa one is closed due to high iron and manganese concentration and other are used in limited amount by diluting with surface water from Legedadi and Gefersa. Manganese and iron are not considered as health hazards but the reddish color they make and the change of test of the water results in low aesthetic value [13]. There are numerous methods used for effective removal of iron and manganese from groundwater depending on the concentration. Methods include Ion exchange, adsorption by activated carbon, bio-sorption, ionic liquid extraction and membrane technology including Nano-filtration. The most effective and economical of those methods include Oxidation by aeration, chlorine, potassium permanganate, hypochlorite, chlorine dioxide and ozone are common ones and filtration or sedimentation follows the oxidation process [4][14].

1.2 Statement of the problem

Since groundwater is clearer than surface water and found abundantly for utilization for different purposes around the world it has to be kept safe and free from contamination. Groundwater can be polluted from natural sources like acid rain during infiltration and degradation of rocks and other oars inside the deep wells [15][16]. There are a lot of source of groundwater pollutant related to human activity which includes linkage from industrial wastes and leaching from waste disposal site or landfills. High concentration of iron and manganese suspected to mostly leak from natural minerals found in deeper wells [17]. This metals mostly iron have only aesthetic problem in high concentration while manganese has both aesthetic and related health effect in high concentration. From many wells found in and around Addis Ababa some of them have high iron and manganese concentration which is found to be a problem on using groundwater to supply the high-water demand in the city. From daily water supply distributed to the city much of it comes from surface water even if the groundwater potential of the city is high. This is due to high iron and manganese concentration. The treatment method the city use to overcome the problem are dilution of groundwater generated from the wells by surface water, and oxidation by air and chlorine followed by sand filtration on one well found in Guskuam which is on ongoing trial bases. Dilution of iron and manganese containing groundwater limits the amount of water that came from groundwater, as the dilution takes only little amount of groundwater to high amount surface water to lower the concentration of both elements. It is great concern that the possibility of not using ground water due to iron and manganese concentration which lead to more water scarcity to the people lives in the city. Using groundwater in its full capacity with strict management practice is what the city needs to solve the current water supply problem. Shutting down of wells rather than treating the water won’t help the city. Even if there is financial limitation over sophisticated and high technology treatment methods it is important to find most economical iron and manganese removal method and assessing their effectiveness will help to solve the problem for both the people and city administrators in this matter. With this thesis the method used for removal of iron and manganese is oxidation followed by sand filtration. The oxidant used was air and sodium hypochlorite and sand filter is the most convenient filter most water treatment plants used.

1.3 Objectives

1.3.1 General objective

The main objective of the study was evaluating iron and manganese removal efficiency of oxidation-filtration hybrid system from groundwater.

1.3.2 Specific objectives

The Specific objectives of this thesis are

- To characterize groundwater collected from wells in Addis Ababa Shiromeda and Kotebe Hana for iron and manganese content
- To statistically investigate iron and manganese removal efficiency of oxidation-filtration hybrid process
- To statistically determine the interaction effects and to optimized some of the selected operational parameters

1.4 Significance of the study

All human being in the world are entitled to clean and safe water. Clean include pure, healthy, good test and appearance of water. Supplying clean water at fulfilling supply is the main goal of water and sanitation authority of Addis Ababa city and other cities and countries of the world. In providing of clean water, different treatment methods to remove contaminants like iron and manganese needs intensive investigation, follow up, and researching. Also new and suitable methods and strategies along with the existing technologies have to be used. In this context doing this research has significance on providing an alternative iron and manganese removal system from groundwater.

1.5 Scope of the study

The scope of this study was investigating removal efficiency of air/hypochlorite oxidation followed by filtration process for iron and manganese. This includes preparation of synthetic water, manufacturing of sodium hypochlorite from sodium chloride salt via electrolytic process, sand bed preparation, and statistical analysis of results and characterization of both sample and the filtrate after the removal process. The work is limited for specific parameter analysis of removal efficiency without consideration of change in pH, temperature or other parameters of a like. This study only focuses on removal efficiency of iron and manganese from groundwater at the state of the groundwater without any other treatment and addition of additives.

Chapter two

2 Literature review

2.1 Iron and Manganese in groundwater

From two main drinking water sources ground water utility is higher in the world than surface water. In Ethiopia groundwater the utility is not limited to drinking purpose it used for breweries, beverage industries and hospitals. Most factories have their own wells on their compound. In Addis Ababa groundwater utility is also considerable however in some areas exhibits high iron and manganese concentration levels greater than Ethiopian standard MCL or WHO standard MCL for drinking water.

Iron and manganese existing in many types of rock having a symbol Fe and Mn respectively they are common elements in the earth's crust. Both are vital elements required in small amounts by all living organisms while their concentration is higher it has low aesthetic value and unpleasant color and odor especial found in water [18]. Also presence in higher amount of Fe and Mn caused in metallic taste of water, brown- reddish colored water and rusty-brown stains of products like paper, cloths, and plastics and promote the growth of iron bacteria [15][19]. Anaerobic groundwater may have ferrous iron at concentrations high as several milligrams per liter without color change or turbidity in the water[20]. Ferrous iron oxidizes to ferric iron giving an objectionable reddish-brown color to the water when it exposed to the atmosphere [21]. Also Iron bacteria drive their energy by oxidizing ferrous iron to ferric iron this process cause slimy coating on piping. In addition to the unpleasant test in drinking water manganese cause undesirable taste in beverage and stains sanitary ware and laundry on concentration greater than 0.1mg/l. In some cases at higher concentration manganese cause health effect[22].

The world health organization (HWO) standard for Fe and Mn concentration in drinking water is 0.3mg/L and 0.05mg/L respectively[23][4].

2.2 Source of Iron and Manganese

In little and or no oxygen available deep wells Iron and manganese found in their insoluble forms or divalent form. The source of these metallic elements can be both natural and anthropogenic.

Natural sources include soil and rocks found in deeper wells which degrade and leak to ground water.

2.3 Origin and Chemistry of Iron and Manganese in groundwater

2.3.1 Iron

Iron is the fourth abundant element in the earth. It is believed by scientists that large part of the earth core consisted iron. It found in different forms of ores, the most known are hematite or ferric oxide (Fe2O3), limonite or hydrated ferric oxide, magnetite or (Fe3O4) and siderite or carbonate (FeCO3)[24].Iron is a very active metal and combines with oxygen in moist air and produce, iron oxide (Fe2O3), is recognized as rust. Iron also reacts with very hot water and steam to produce hydrogen gas[18]. It also dissolves in most acids and reacts with many other elements[25]. Iron in water supplies can exist in divalent ferrous iron Fe^{+2} (soluble form) and trivalent ferric iron Fe^{+3} (insoluble form).The process of oxidizing divalent ferrous ion (Fe^{+2}) to trivalent ferric ions (Fe^{+3}) can be described by

$$Fe^{+2} = Fe^{+3} + e^{-} \qquad (a)$$

Where high concentration of dissolved oxygen occurs, the trivalent ferric ion can further react with hydroxyl groups to precipitate in solid form

$$Fe^{+3} + 3OH^{-} = Fe\,(OH)_3 \qquad (b)$$

And whole oxidation-reduction reaction can be written as

$$Fe^{+2} + 3H_2O = Fe\,(OH)_3 + 3H^{+} + e-$$

The stability of iron ion is dependent on PH and redox potential.

Mostly in ground water iron originated from withering of iron ores like pyrite. Through the Weathering of pyrite in heaps of pit coal, reduced groundwater with a content of Fe^{+2} originates as in the following reaction

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_{4(2)}^{-} + 4H^{+}$$

$$5FeS_2 + 14NO_3- + 4CO_2 + 2H_2O = 5Fe_2 + 10(SO_4)_2- + 7N_2 + 4HCO^{3-}$$

These reactions can induce $(SO4)_2^-$ in pumped raw water. And Iron carbonate reacts with CO_2 and gets Fe into the solution as

$$FeCO_3 + CO_2 + H_20 = Fe^{2+} + 2HCO_3$$

In the presence of enough CO_2 and H donors then it will be possible to remobilize the wide spread Fe^{+3} oxyhydrates as follows;

$$FeO(OH) + (H^+) + 2CO_2 = Fe^{2+} + 2HCO_3^- + e-$$

There are also other minerals and ores in the soil iron can be generated through weathering such as Olivin, Magnetit, Geothit and Pyrite[26].

2.3.2 Manganese

Manganese is a moderately active metal. It combines slowly with oxygen in the air to form manganese dioxide (MnO_2). At higher temperatures, it reacts more rapidly and reacts slowly with cold water. It dissolves in most acids with the release of hydrogen gas. It also combines with fluorine and chlorine to make manganese difluoride (MnF_2) and manganese dichloride ($MnCl_2$)[27][28]. Manganese occurs naturally combined with oxygen or other elements. The most common ores of manganese are pyrolusite, manganite, psilomelane, and rhodochrosite. Manganese is also found mixed with iron ores. It is the 12th most abundant element in Earth's crust. The usual method for producing pure manganese is to heat manganese dioxide (MnO_2) with carbon or aluminum. These elements remove the oxygen and leave pure manganese metal:

$$MnO_2 + C = Mn + CO_2$$

In water, manganese exists in two forms like iron but it is not similar to iron in occurrence and behavior. The two forms are Mn^{2+} manganous oxide (soluble) and insoluble or stable magnic oxide Mn^{4+}[26]. In groundwater manganese originate from soil and rocks which are ores of manganese. And it can be found in different phases as; manganese- oxides, silicates and carbonates ; adsorbed on iron oxide ;in organic compounds and in exchanging (Mn^{+2}) and saluted condition[29].

2.4 Removal methods of iron and manganese from groundwater

Iron and manganese can be effectively removed from water using numeral treatment method depending on both the form and concentration of the metals. The methods mainly include oxidation to convert the dissolved forms of the metals to a solid, followed by a filtration to remove the precipitate. And other methods like sequestration, lime softening, subsurface iron removal, ion exchange and biological iron and manganese removal methods [30].

2.4.1 Sequestration

As an alternative to oxidation and filtration processes for low iron and manganese content groundwater sequestration can be used to remove iron and manganese[31]. in sequestration chemical or sequestering agent forms a bond with iron and manganese ions can be used in allowing them to remain in solution which delay precipitation of oxidized manganese and iron [29][32]. Sequestrating agents that mostly used in iron and manganese removal includes Pyrophosphate, tripolyphosphate, and metaphosphate [29].

2.4.2 Oxidation followed by filtration

For combined levels of iron and manganese overdo 10 mg/L, active treatment involves oxidation followed by filtration. Oxygen or/ and other chemical added to convert any dissolved iron and manganese into the solid, oxidized forms that can then be easily filtered from the water. On filtration slow sand, rapid sand filter media of micro filter can be used. However micro-filter filtration is on ongoing study and have drawback. Oxidants mostly used are air, chlorine, hypochlorite, ozone hydrogen peroxide, or potassium permanganate ($KMnO_4$)[28][25] .

2.4.2.1 Aeration

This method is used in gears of concentration levels higher than 0.3 ppm but less than 32 ppm. Iron is easily oxidized by atmospheric oxygen. Aeration provides the dissolved oxygen needed to convert the iron and manganese from ferrous and manganous (soluble) forms to insoluble oxidized ferric and manganic forms[8]. For oxidizing of 1ppm of iron 0.14 ppm of dissolved oxygen is needed, and to oxidize1ppm of manganese 0.27 ppm of dissolved oxygen needed [29]. Aeration required water flow control, air and flow water need to contact with optimal flow rate [33]. If the flow rate is too high water can’t contact to dissolved oxygen and oxidation will not happen and in slow flow rate water saturation with dissolved oxygen occurs [29]. Aeration can apply by cascading, bubbling, or stripping the gas from the water. Aeration is cost effective and requires no chemical addition. It has advantage of low maintenance cost. But it needs higher investment cost compare to the other [34][32]. The reaction with oxygen for iron and manganese states as follows[35].

$$4Fe\ (HCO_3)_2 + O_2 + 2H_2O\ 4Fe\ (OH)_3 + 8CO_2$$

$$2Mn\ (HCO3)_2 + O_2 + 2H_2O\ 2Mn\ (OH)_4 + 4CO_2$$

2.4.2.2 Oxidation with chlorine

Iron and manganese can also be oxidized by chlorine which converts to ferric hydroxide and manganese dioxide. Adding chlorine to groundwater oxidized soluble iron and manganese and they settle out almost immediately after contact with the chlorine. Contact time needed is approximately 20 minutes to form particles that can be filtered[29]. And the dose is from 1 to 2 part of chlorine to 1 part of iron with optimum chlorination pH about 8.0 and 8.5 for iron and manganese respectively. Free chlorine can rapidly oxidize iron not formed organic complex. Oxidation of manganese at ph less than 8.5 is very slow and which may take several hours. After oxidation of both metals precipitated material can then be removed by filtration [32][23][36].

$$2\ Fe^{2+}+Cl_2+6\ OH^-=2Fe(OH)_3+2Cl^-$$

2.4.2.3 Oxidation with potassium permanganate

Treating iron and manganese contaminate ground water with potassium paermanganate is often used for high concentration of iron and manganese at natural ph. Potassium permanganate is naturally more effective at oxidizing manganese than aeration or chlorination and It is not toxic and expensive[37].

Oxidation of Mn^{2+} and Fe^{2+} using $KMnO_4$ is illustrated in the following Equations;

$$3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + 2K^+ + 4H^+ \qquad (a)$$

$$3Fe^{2+} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_3 + K^+ + MnO_2 + 5H^+ \qquad (b)$$

$$2KMnO_4 + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + K^+ + 2H_2O \qquad (c)$$

2.4.2.4 Ozone oxidation

Iron and manganese can also be oxidized by ozone at lower detention time for manganese around pH value of 8 or higher pH value. Oxidation may require higher than stoichiometric does. Ozone used for removal process need to prepare onsite and carefully handled[36] [38].

2.4.2.5 Oxidation with chlorine dioxide

Onsite generated chlorine dioxide use as alternative oxidant for iron and manganese it is very effective as that of potassium permanganate for both elements. The drawback on using chlorine dioxide is it need specialized system and well trained handler which made its utility limited for small system[26][36].

2.4.2.6 Oxidation with hypochlorite (sodium hypochlorite)

Sodium hypochlorite produced in the same fashion with chlorine via electrolytic method. Hypochlorite produced in liquid forms which can be handled easily in opposite to chlorine[39]. On site hypochlorite production and utility are common in many areas of water and wastewater treatment. As that of chlorine and chlorine dioxide sodium hypochlorite use as disinfectant and oxidant in water treatment as for iron and manganese removal by oxidation[40][41].

2.4.2.7 Filtration

After oxidation of iron and manganese from water system mostly sand filter used to remove the precipitate. In some studies microfiltration also used for precipitate removal [4]. Both rapid and slow sand filter are used for iron and manganese removal[26][42][43].

2.4.3 Ion exchange

Ion exchange use at small scale or home level removal of iron and manganese it is not recommended for municipal use because of its risk of rapid clogging and its high expense. The removal processes accomplished by using sodium from strong acid cation [26][36].

2.5 Factors affecting the removal of Iron and Manganese

Removal of iron and manganese from ground water affected by different physiochemical factors including pH, temperature, and total organic carbon, total dissolved solid and dissolved oxygen concentration. Removal of iron and manganese accomplished highly by oxidation and filtration are mostly dependent on pH values. oxidation rate is faster at high pH values[44]. In an oxidation by aeration process the pH value for iron starts at 6.3 and 9.3 for manganese. Increased temperature also enhances the oxidation reactions while lower temperature slows down the oxidation process. In general, the rate of reaction will double for every 10-degree Celsius temperature increase[45]. In the presence of higher concentrations of total organic carbon, the oxidation of iron and manganese is reduced due to less available oxygen. And time factor plays great role in oxidation and filtration process[30]. For lower pH value like 7.5 to 8.5 manganese oxidation will be very slow which increase reaction time[35].

2.6 Electrolytic chlorine preparation

Chlorine is one of the most multipurpose chemicals used in water and wastewater treatment. Chlorine as strong oxidizing agent used for disinfection, control of microorganisms, removal of ammonia control of taste and odor, color reduction, destruction of organic matter, hydrogen sulfide oxidation, and iron and manganese oxidation[46]. It also uses carries safety and environmental concerns[47]. Sodium hypochlorite frequently used in place of chlorine gas for safety reasons. It is available for water treatment purposes as a clear solution containing available chlorine. Sodium hypochlorite (NaOCl) is used on a large scale for surface purification, fabric bleaching, odor removal, and water disinfection and iron and manganese removal[40]. Chlorine is generated commercially by the electrolysis of a brine solution, typically sodium chloride, in any of three types of cells: diaphragm, mercury, or membrane. During electrolysis process bonded elements and compounds separate by passing an electric current through them. An ionic compound or salt is dissolved with an appropriate solvent which mostly used is distilled water, so that its ions are available in the liquid. An electrical current is applied between a pair of inert electrodes immersed in the liquid. The negatively charged electrode is called the cathode and the positively charged one is the anode. Each electrode attracts ions that are oppositely charged. Positively charged ions (called cations) move towards the cathode, while negatively charged ions (termed anions) move toward the anode. The energy required to separate the ions, and cause them to gather at the respective electrodes, is provided by a direct electrical power supply (DC). Salt solution electrolysis result on generation of chlorine in the positive side[48].

$$Na^{+} + e^{-} + H_2O = NaOH + 1/_2H_2$$

$$Cl^{-} - e^{-} = 1/_2Cl_2$$

And the overall chemical equation for production of sodium hypochlorite from sodium chloride salt and water is; $NaCl + H_2O \rightarrow NaOCl + H_2$.

On site sodium hypochlorite production; due to handling and transporting problem of chlorine and hypochlorite product onsite production is more advantageous on improving operator safety, quality of chemicals and lower disinfectant by product formation[48][39].

Chapter three

3 Material and methods

3.1 Sample collection and characterization

Based on standard method of APHA samples were collected using grasp composite sample collection system from two different wells found in Shiromeda /Sambanekersa and Kotebe hana Mariam site for comparison of concentration of iron and manganese. Samples were collected using plastic sample bottles after sterilization by sulphuric acid and washed with distilled water. Samples were transported in ice box for metal analysis at Horticoop Ethiopia laboratory and analyzed using Wet Djestion with strong AcidDjestion+ICP-OES Determination. After analysis the sample with high concentration of iron and manganese was selected for further work of the study. Selected area sample groundwater was characterized by its physic chemical parameters before and after treatment based on standard method of characterization listed in section (3.4) parameters like pH, conductivity and DO were analyzed on cite and other parameters and effluent was characterized in the laboratory.

3.2 Materials

Groundwater sample was collected from two different wells and synthetic water was prepared in the laboratory with Manganous chloride ($MnCl_2 \cdot 4H_2O$), purity 99.1% and Ferrous sulphate ($FeSO4 \cdot 7H_2O$) with purity 99.8%. For electrolytic production of sodium hypochlorite (NaOCl) sodium chloride(Na_2Cl), potassium iodide(KI), distilled water, sodium thiosulphate ($Na_2S_2O_3$) purity 98.5%, Acetic acid (CH_3COOH), starch indicator, Ethanol(C_2H_5OH) 98% and other indicators and reagents like potassium chloride (0.0100M KCl) was used. Filter bed was prepared from selected sand in 2 litter capacity of plastic measuring cylinder. Small plastic tanks for aeration process, magnetic stirrer, DC power supplier and other materials included among the materials used in this process.

3.3 Methods

3.3.1 Preparation of Synthetic water

For experimental runs in the laboratory synthetic water was prepared for each run prior to the oxidation and filtration process in order to avoid oxidation of sample by atmospheric air. Synthetic solution was prepared from 20 mg of ferrous sulphate and 10mg of manganous chloride have theoretical concentration of 4.02mg/l and 2.77 mg/l in distilled water produced at the laboratory as a methods described in literature [9], [14], [49]. For synthetic water 4.02 mg/l and of iron concentration was selected for a reason which could mimic sample ground water which have approximately 4mg/l iron concentration. From sample ground water highest manganese concentration exhibited was 0.61mg/l however it is difficult to work on the laboratory with less than 10mg of manganous chloride powder therefore 10mg of manganous chloride with theoretical manganese concentration of 2.77mg/l was used.

3.3.2 Standard method of groundwater characterization

Groundwater from Sambanekersa well which exhibited high iron and manganese concentration was characterize based on the water physicochemical properties like pH, turbidity, alkalinity, DO, electric conductivity, total dissolved solid (TDS), total suspended solid (TSS), total solid (TS), total phosphorus and total nitrogen, SO4-, S^{2-} BOD, COD and heavy metal concentration which includes iron and manganese concentration based on methods listed on (**Table 1**).

Table 1; Groundwater characterization standard methods

Parameter	Standard method of analysis
pH	Using PH meter (APHA)
Conductivity	Using conductivity meter (APHA)
Turbidity	Using turbid meter (APHA)
DO	Using DO meter (APHA)
TDS	APHA standard method
TSS	APHA standard method
Alkalinity	Examination of Water and Wastewater standard method
BOD	Winkiler method with azide modification (APHA standard method)
TP	Digestion colorimetric method of ascorbic acid (APHA standard method)
TN	APHA standard method
COD	Closed reflux colorimetric method using COD digester (APHA standard method)
Microbial	Selective media membrane filtration
Sulphate	Turbid metric method (APHA standard method)
Sulfide	Methylene blue method (APHA standard method)
Free ammonia	APHA standard method
Metal analysis	Wet Digestion with strong Acid Digestion + ICP-OES Determination(ASTM standards)
Fe	UV/VIS spectrophotometer by pyridylazonaphthol (PAN) (feron indicator)
Mn	UV/VIS spectrophotometer by pyridylazonaphthol (PAN)
Sodium hypochlorite	Iodometric titration (Standard Methods for the Examination of Water and Wastewater)

3.3.3 Electrolytic process laboratory setup

Sodium hypochlorite was produced at the laboratory using rectangular PVC as electrolysis chamber (which can be filled with up to 1 L of electrolyte) and direct current (DC) power supply (with yield voltage run of 7.13) from 35.65 g of sodium chloride salt and one litter distilled water produced at the lab. The production were carried out in 1000ml rectangular PVC cell with the electrodes IrO_2/Ti sort as anode and stainless-steel plate as cathodes. Electrode spaces were designed at 2cm and the electrode plates were confronted each other in order to maximize ion exchange between electrodes[39]. The time used for one batch production is 72 minutes [48][50]. For this work titanium and stainless steel was used as electrodes due to their availability, high electron conductivity capacity to catalyze the electrode reaction and erosion resistivity[51][47]. Before use the electrodes were soaked in acetone 1% for 3 h then washed with distilled water. And soaked in ethanol 1% for 10 min and were washed three times with distilled water and dried for 24 h after that they were set in desiccators. Laboratory set up picture presented on appendix.

3.3.4 Sand bed filtration laboratory setup

Sand bed preparation was done through processes which includes sand selection and preparation, sieve analysis and bed building. The sand was collected from Dire Dawa, Ashewa area. The sand was washed till it became pure and dried at 105 ^{0}c for four hours. After measuring 4kg sand sieve analysis done by available sieves in the laboratory of unit operation at five kilo campus which have different size. The analysis continued until the chosen effective diameter of 0.71 and uniformity coefficient between 1.3 and 1.7 was reach based on American standard [52][53] detailed mesh analysis and result is stated at appendix C. and the laboratory set up pictures showed on appendix.

3.3.5 Aeration system laboratory setup

For synthetic water 20mg ferrous sulphate and 10 mg of managous chloride was dissolved in one litter distilled water and aerated for 30,60 and 90 minutes based on the experimental design run. For iron the minimum oxidizing time in literature was 20min and for manganese 90 minute oxidizing time or more is needed therefore for oxidizing both metals 30 to 90 minute oxidation time were set[21][54]. Air pump of capacity 2.5 lit per minutes was used for air flow to aeration tank in different rate of 0.5,1 and 1.5 lit/min[55][54][56]. And for groundwater sample collected from Sambanekersa at optimum design parameters the same aeration procedure was used.

3.3.6 Oxidation- Filtration process

Oxidation of synthetic water and natural groundwater by hypochlorite (obtained from electrolytic process) was done in aeration tank and the process was simultaneous with aeration. Sodium hypochlorite was added to the system in different concentration 0, 8 and 16 mg/l based on the experimental design results before aeration began.

After oxidation process was done filtration followed by prepared filter bed by pouring oxidized water by hand. The filtrate was collected from the bottom of the bed. The bed was washed after each experimental run and stabilized with tap water.

The result of the process measured in removal percentage after analysis of each run all filtered samples Fe and Mn concentration were determined using the UV/VIS spectrophotometer by pyridylazonaphthol (PAN).

And efficiency of removal calculated as follows

$$\% \, removal = \frac{ci-co}{ci} * 100 \qquad (1)$$

Where

Ci- initial concentration, Co- final concentration

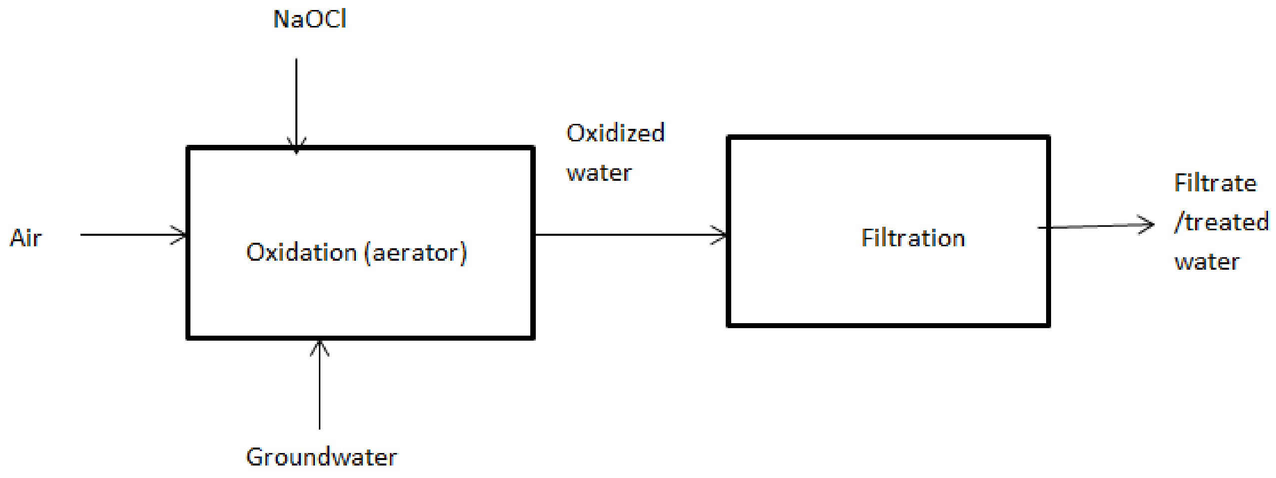


Figure 1; Flowchart for oxidation-filtration process

3.3.7 Statistical Experimental Designs

In this work the experimental design was conducted using design expert software 7.0.0 and selected design experiment surface response method Box-Behnken design. The design experiment helps to optimize and set different process parameters combinations to a minimum design runs. This also shows the interaction between parameters and their effect. Box-Behnken design was used to optimize the experiment with three design parameters and fifteen experimental runs with three center points per block to evaluate the three parameters which are time, airflow rate and sodium hypochlorite concentration on response of both iron and manganese removal efficiency. The responses function was partitioned into linear, quadratic, and interactive components. The model adequacies were checked in terms of the values of R^2 and adjusted R^2. Analysis of variance (ANOVA) was employed to determine the significance of the models. Verification of optimized conditions and predicted values were done in triplicate to confirm the validity of the models. Number of experimental runs were determined on fifteen based on the following formula.

$$N = k^2 + k + cp = 3^2 + 3 + 3 = 15 \qquad (2)$$

Where

K= number of factors

Cp = center point chosen from 3 or 5

Response variable were removal efficiency of iron and manganese express in percentages.

Table 2; Coded level of the independent variable used in the RSM design

Code symbol	Experimental variable /factor	Units	Levels		
			Low (−1)	Middle (0)	High (+)
A	NaOCl(sodium hypochlorite)	Mg/l	0	8	16
B	Air flow rate	L/min	0.5	1	1.5
C	Time	Minute	30	60	90

Table 3; Experimental runs which are arranged according to Response surface Box-Behnken actual design

Run	Factor			Response			
	A NaOCl (mg/l)	B air flow rate (lit/min)	C Time (min)	Fe removal (%) predicted	Fe removal (%) actual	Mn removal (%) predicted	Mn removal (%)actual
1	0.00	1.50	60.00	87.94	89.77	89.00	92.09
2	8.00	0.50	90.00	97.66	95.26	99.20	96.24
3	8.00	0.50	30.00	89.61	93.26	91.51	93.61
4	16.00	0.50	60.00	98.84	97.5	99.06	98.61
5	8.00	1.00	60.00	86.50	94.51	87.41	95.23
6	8.00	1.00	60.00	98.22	96.25	97.40	96.02
7	8.00	1.50	90.00	90.80	96	90.17	96.35
8	8.00	1.50	30.00	98.03	94.76	97.92	94.78
9	8.00	1.00	60.00	92.89	97.25	93.57	94.98
10	16.00	1.00	30.00	94.70	98	95.28	97.94
11	16.00	1.50	60.00	95.32	99	95.74	99.02
12	0.00	1.00	90.00	96.38	91.02	96.39	89.63
13	0.00	1.00	30.00	96.00	86.28	95.41	87.32
14	0.00	0.50	60.00	96.00	87.78	95.41	89.04
15	16.00	1.00	90.00	96.00	98.25	95.41	98.01

Chapter four

4 Result and discussion

In this chapter all the analysis and experimental procedures results which used to justify and express the general objective of the thesis are discussed.

4.1 Metal analysis

From comparison based on metal analysis from the two recommended wells for high iron and manganese concentration the results showed that Shiromeda exibits high values on both parameters.

Table 4; Heavy metal analysis result for Sambanekersa and Kotebe hana (Hana mariam/selam) site

Metal analysis

Lab code	*Description*	*Concentration*	*Parameters*											
			As	*Pb*	*B*	*Zn*	*Cd*	*Hg*	*Cu*	*Ni*	*Co*	*Fe*	*Mn*	*Cr*
			mg/l	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*
HWA 2636/20	*Shiro meda*	*Conc.1*	*0.776*	*0.578*	*0.029*	*0.0230*	*0.0270*	*0.2280*	*0.0360*	*0.1900*	*0.0660*	*3.5300*	*0.3940*	*0.1720*
		Conc.2	*0.647*	*0.693*	*0.038*	*0.0210*	*0.0310*	*0.2300*	*0.0360*	*0.1830*	*0.0560*	*3.5900*	*0.5230*	*0.1640*
		Conc.3	*0.606*	*0.665*	*0.040*	*0.0230*	*0.0300*	*0.2530*	*0.0340*	*0.1510*	*0.0560*	*3.5030*	*0.5250*	*0.1660*
		Mean	*0.676*	*0.645*	*0.036*	*0.022*	*0.029*	*0.237*	*0.035*	*0.175*	*0.059*	*3.541*	*0.481*	*0.167*
		SD	*0.089*	*0.060*	*0.006*	*0.001*	*0.002*	*0.014*	*0.001*	*0.021*	*0.006*	*0.045*	*0.075*	*0.004*
HWA 2637/20	*Kotebe Hana*	*Conc.1*	*0.818*	*0.7050*	*0.0250*	*0.0380*	*0.0790*	*0.3810*	*0.0190*	*0.2650*	*0.0390*	*0.2200*	*0.0680*	*0.1800*
		Conc.2	*0.963*	*0.6040*	*0.0310*	*0.0370*	*0.1010*	*0.4050*	*0.0180*	*0.2440*	*0.0340*	*0.2200*	*0.0640*	*0.1560*
		Conc.3	*0.887*	*0.6930*	*0.0230*	*0.0340*	*0.0960*	*0.4150*	*0.0170*	*0.2400*	*0.0360*	*0.2080*	*0.0670*	*0.1830*
		Mean	*0.889*	*0.667*	*0.026*	*0.036*	*0.092*	*0.400*	*0.018*	*0.250*	*0.036*	*0.216*	*0.066*	*0.173*
		SD	*0.073*	*0.055*	*0.004*	*0.002*	*0.012*	*0.017*	*0.001*	*0.013*	*0.003*	*0.007*	*0.002*	*0.015*

4.2 Hypochlorite production

Electrolytic reaction takes place for 72 min in one liter electrolytic cell 2 cm gape and 7volte. The result hypochlorite found was tested by titration and Based on (equation (4) Appendix C) concentration of the result was calculated found to be 4.183 g/lit [40][41].

4.3 Experimental design and statistical data analysis of synthetic water

After each run all filtered samples Fe and Mn concentration were determined and result converted it to percentage and entered design expert 7.0 software at study type RSM, initial design Box-Behnken with 15 runs with three center points and quadratic model with no blocks. The analysis table from the software presented as follows.

4.4 Analysis of variance

Based on the analysis of variance (ANOVA) as shown in Table 5 and 6, the models which correlate the study parameters with the responses iron and manganese removal efficiency were found significant with F-values 26.75 and 42.10 (P<0.001). Values of "Prob > F" less than 0.0500 indicate model terms are significant howeve Values greater than 0.1000 indicate the model terms are not significant. Hence for iron removal A, Cand A^2 were found to be significant and for manganese removal siginificant model terms are A, Cand A^2.

For iron removal "Lack of Fit F-value" of 0.10with a 95.27% chance that a "Lack of Fit F-value" this large could occur due to noise. Similarly Manganses removal exibits "Lack of Fit F-value" of 2.02 with a 34.76% chance that a "Lack of Fit F-value" this large could occur due to noise. For both cases Lack of Fit is not siginificant which implies that the model equations are adequate for predicting removal eficiency of iron and manganase.

From Tables 5 and 6, one can observe that the most important effects are sodium hypochlorite concentraion and time.

Table 5; Analysis of variance table for iron removal

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	212.95	9	23.66	26.75	0.001	significant
A-NaOCl	179.55	1	179.55	202.97	< 0.0001	
B- Air flow rate	4.1	1	4.1	4.64	0.0838	
C-time	8.47	1	8.47	9.57	0.027	
AB	0.06	1	0.06	0.068	0.8049	
AC	5.04	1	5.04	5.7	0.0626	
BC	0.14	1	0.14	0.16	0.7029	
A^2	14.21	1	14.21	16.06	0.0102	
B^2	1.03	1	1.03	1.17	0.329	
C^2	1.58	1	1.58	1.79	0.239	
Residual	4.42	5	0.88			
Lack of Fit	0.58	3	0.19	0.1	0.9527	not significant
Pure Error	3.85	2	1.92			
Cor Total	217.38	14				

Table 6; Analysis of variance table for manganese removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	180.26	9	20.03	42.1	0.0003	significant
A-NaOCl	157.53	1	157.53	331.12	< 0.0001	
B-Air flow rate	2.81	1	2.81	5.9	0.0594	
C-time	5.41	1	5.41	11.38	0.0198	
AB	1.74	1	1.74	3.66	0.1138	
AC	1.25	1	1.25	2.64	0.1653	
BC	0.28	1	0.28	0.59	0.477	
A^2	6.93	1	6.93	14.57	0.0124	
B^2	1.56	1	1.56	3.28	0.1299	
C^2	2.45	1	2.45	5.16	0.0724	
Residual	2.38	5	0.48			
Lack of Fit	1.79	3	0.6	2.02	0.3476	not significant
Pure Error	0.59	2	0.29			
Cor Total	182.63	14				

4.5 Model fit summary

From sequential model fitting table 7 and 8 and model summary statistics Table 9 and 10 for both experimental responses by design expert quadratic model were suggested and from lack of fit test second order quadratic model was suitable with insignificant lack of fit.

Table 7; Sequential model fitting for iron removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	1.335E+005	1	1.335E+005			
Linear vs Mean	192.12	3	64.04	27.89	< 0.0001	
2FI vs Linear\	5.24	3	1.75	0.70	0.5785	
Quadratic vs 2FI	15.59	3	5.20	5.87	0.0429	Suggested
Cubic vs Quadratic	0.58	3	0.19	0.10	0.9527	Aliased
Residual	3.85	2	1.92			
Total	1.337E+005	15	8911.89			

Table 8; Sequential model fitting for manganese removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	1.342E+005	1	1.342E+005			
Linear vs Mean	165.75	3	55.25	36.00	< 0.0001	
2FI vs Linear\	3.28	3	1.09	0.64	0.6090	
Quadratic vs 2FI	11.23	3	3.74	7.87	0.0244	Suggested
Cubic vs Quadratic	1.79	3	0.60	2.02	0.3476	Aliased
Residual	0.59	2	0.29			
Total	1.344E+005	15	8959.70			

Table 9; Model Summary Statistics for iron removal

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	1.52	0.8838	0.8521	0.8074	41.88	
2FI	1.58	0.9079	0.8389	0.7459	55.24	
Quadratic	0.94	0.9797	0.9430	0.9176	17.90	Suggested
Cubic	1.39	0.9823	0.8762		+	Aliased

Table 10; Model Summary Statistics for manganese removal

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	1.24	0.9076	0.8823	0.8162	33.57	
2FI	1.30	0.9255	0.8696	0.6628	61.59	
Quadratic	0.69	0.9870	0.9635	0.8360	29.96	Suggested
Cubic	0.54	0.9968	0.9774		+	Aliased

In the present study the "Pred R-Squared" of 0.9176 is in reasonable agreement with the "Adj R-Squared" of 0.9430 for iron removal and "Pred R-Squared" of 0.8360 is in reasonable agreement with the "Adj R-Squared" of 0.9635 for manganase . "Adeq Precision" measures the signal to noise ratio and ratio greater than 4 is desirable. The study stated the ratio of 16.075 and 20.935 for iron and manganese removal which indicates an adequate signal to noise ratio. Therefore this model used to navigate the design space. The coeficicent of determination R^2 exibited were 0.9797 for iron and 0.9870 for manganese. which indicated that method is accounted for 97.97% and 98.70 % variability within the expirmental range.

4.6 Regression model equations

The model equations that correlate the responses to the pelletization process variables in terms of actual value are given in equasion 3 and 4.

Fe removal =+77.830+1.393* Al +6.670 * B +0.171 * C -0.030 * A * B -4.678-003* A * C-0.012* B * time-0.030 *A ^{2}-2.11 * B ^{2}-7.26-004 * C^{2} …………………………….(3)

Mn removal = +82.612+1.202* A -1.635*B+0.172* C-0.165 * A * B -2.333-003* A * C-0.0176* B * C-0.021* A ^2+2.600* B ^2-9.055-004 * C^2 ……………………… (4)

Where

A= NaOCL, B=Air flow rate C= Time

The actual factors in the equation used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. Because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space this equation should not be used to determine the relative impact of each factor.

4.7 Diagnostics plots Iron and Manganese removal

In this section the precision of the models was measured by read-through the diagnostic plots of the experiment and model results. Figure 2a and b shows the normal % probability of residual plot for responses and was normally distributed ,as the points lie reasonably close to the traight line and variance deviation was not observed. The present model effectively enhanced the relationship between the process variables and the response.

Figure 3 a and b show internally Studentized residuals design which were constructed to visualize the satisfactory fit of the developed model and the plots show that the points lie inside (±3) limit.

The pridicted versus actual plot stright line and the data points which spread around the line implies that the difference between the predicted values and actual values are reasonably alined as shown in figure 4a and b.

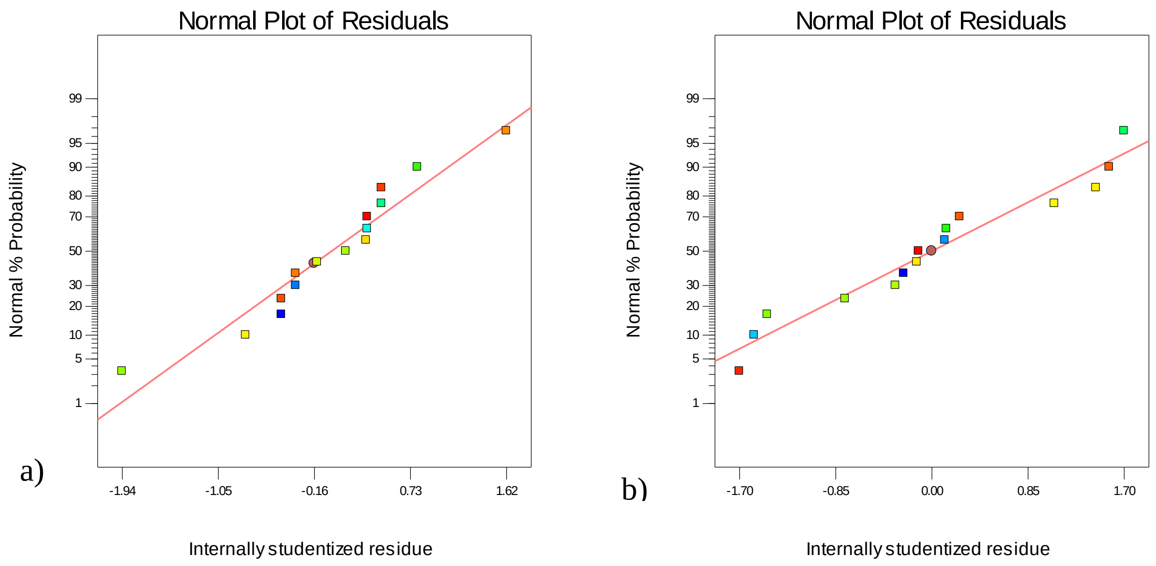


Figure 2; Normal % probability of residual plot a) Iron removal b) Manganese removal

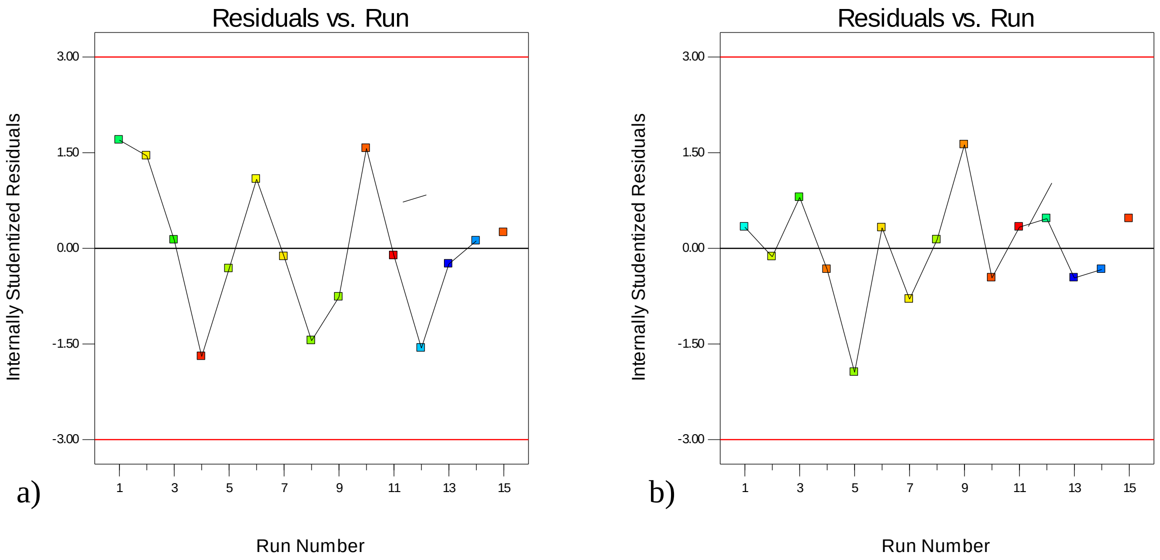


Figure 3; Residual versus run plots a) Iron removal b) Manganese removal

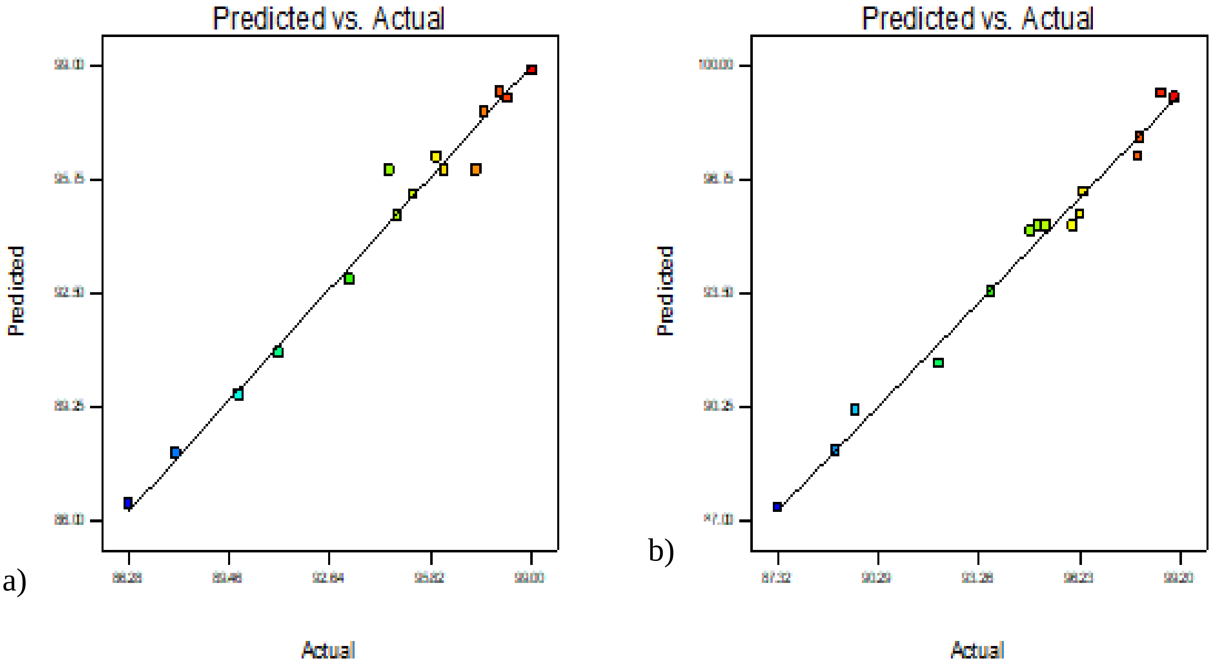


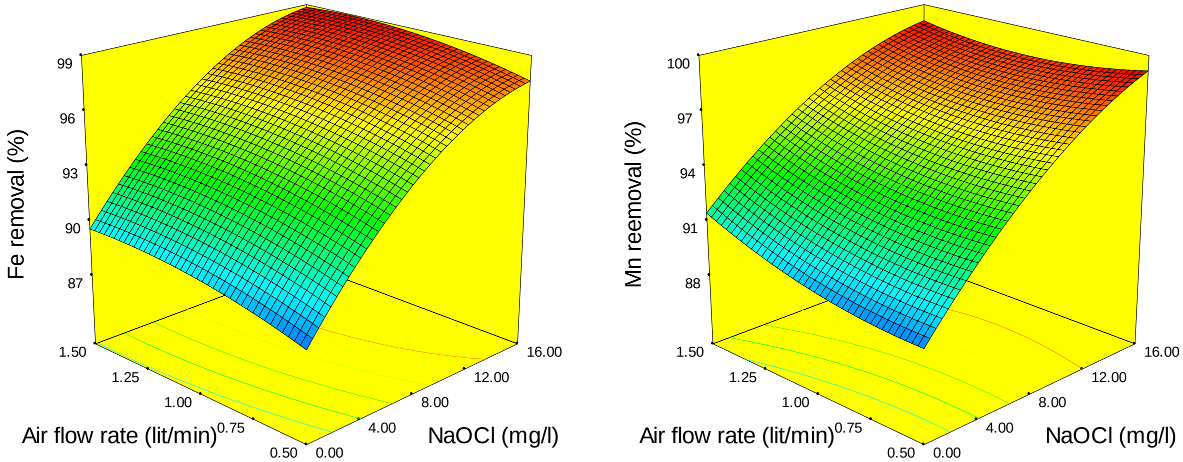
Figure 4; Predicted versus actual plot for a) Iron removal b) Manganese removal

4.8 Linear and interaction effects of selected operational parameters on iron and manganese removal

The BBD model resulted in 3D response surface graphs for iron and manganese was studied. based on this study thefollowing discusion was made in line with figures.

As shown in 3D (Figure 5a) sodium hypochlorite concentration increment showed significant effect on iron removal. Maximizing the concentration would maximize removal efficiency of iron. Likewise NaOCl have significant effect on manganese removal as the concentration increase removal efficiency of manganese increases (Figure 5b). However for air flow rate ANOVA showed slightly significant effect for both cases and the increment of air flow rate increase removal of iron and manganese this is because NaOCl is more active oxidant than air[57]. For iron removal air flow rate increment and NaOCl increment have slightly significant effect the relation showed that as both parameters increase removal efficiency increased. And based on a study [18] it is clear that aeration increase oxidation of iron to its insoluble form which facilitates removal of ferric oxide by filtration afterwards. For manganese removal at maximum air flow rate and NaOCl concentration point the removal efficiency become maximum and for the interaction effect at lower points the change showed similar way (Figure 5b).

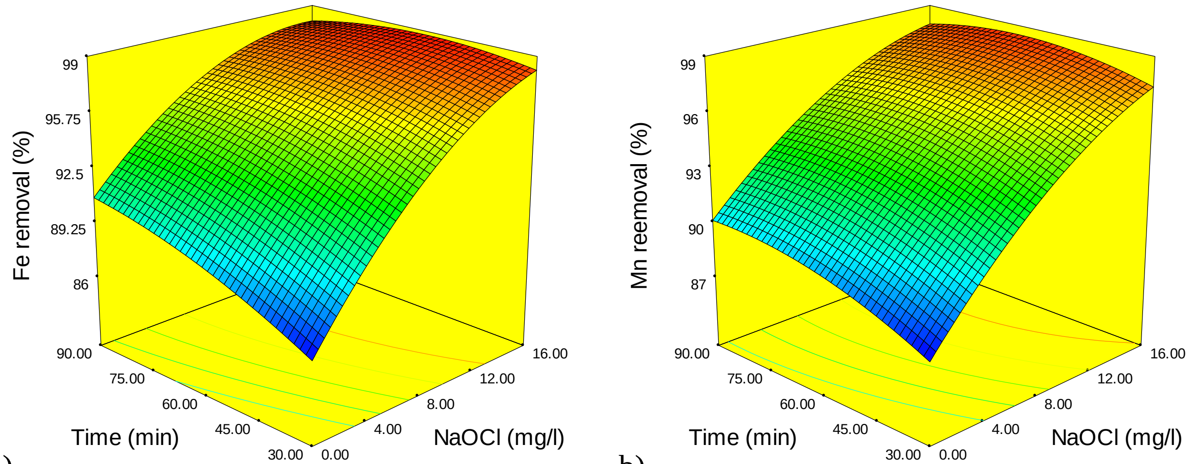
Figure 6a shows that time has significant effect on iron removal when we compare the effect of time with sodium hypochlorite concentration it is less effective and compare to air flow rate it is more effective on increasing removal efficiency of iron. Contact time has effect on oxidation of iron for both air oxidation and oxidation by NaOCl. In case of manganese removal (Figure 6b) contact time has significant effect. Oxidation of both manganese and iron increase with increase in oxidation time. In Figure 6a and b as both time and NaOCl increase removal of both iron and manganese removal increased. The maximum removal efficiency found at maximum sodium hypochlorite concentration of 16mg/l and time 90 min. The interaction effect of NaOCl and time showed in the 3D responses stated that the removal of both metals was affected by time NaOCl interaction.



a)

b)

Figure 5; 3D plots of a removal of iron and b manganese removal as functions of NaOCl and air flow rate



a)

b)

Figure 6; 3D plots of a removal of iron and b manganese removal as functions of NaOCl and time

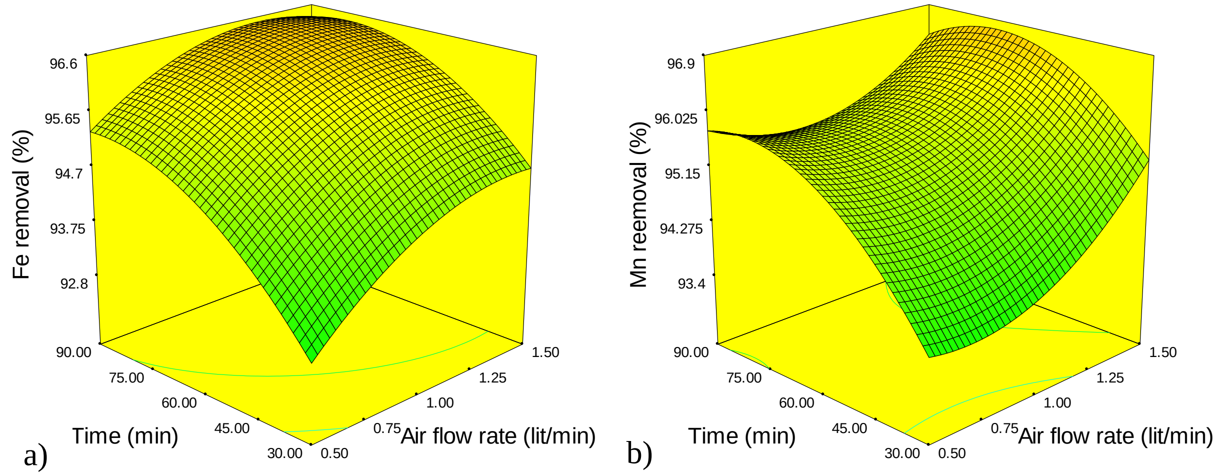


Figure 7; 3D plots of a removal of iron and b manganese removal as functions of time and air flow rate

For time air flow rate interaction (Figure 7) in both cases removal at higher air flow rate and time the removal efficiency exhibits higher value. For instance at 90minuet and 1.5 lit/min flow rate the removal of iron reached 96% likewise manganese removal reach 96.25%. However from the 3D plot of time air flow rate interaction for manganese removal doesn’t follow increment phase as that of iron instead it lowers around time of 75 minute and then increase to higher removal point.

4.9 Optimization of the process parameters and validation

After the process of analysis the process variables optimized in order to find a positive working condition for maximum iron and manganese removal efficiency according to the Box–Behnken design, joined with the numerical optimization technique within selected parameters. For the optimization the independent variable sodium hypochlorite concentration was minimized to reduce chemical concentration on the system and air flow rate and time was set in rage value (with 0-16 mg/l, 30-90 min and 0.5- 1.5lit/min) as the ramps graph showed in Figure 8. Based on the criteria given above the forecasted result for iron removal was 95.934% and 96.2712% for manganese at optimum point of time 77 min, NaOCl 7.02mg/l and 1.5lit/min air flow rate with desirability of 0.688.

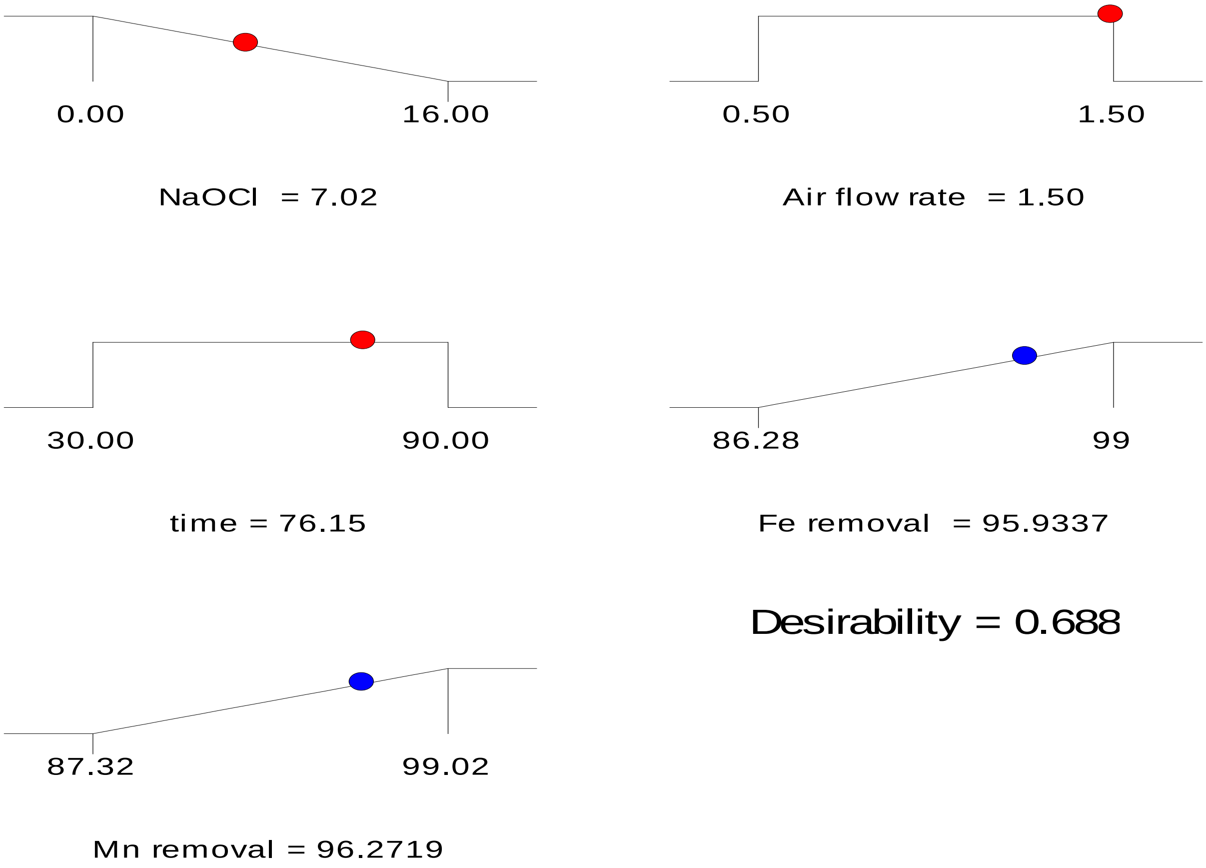


Figure 8; Ramps for optimum point solution for chosen solution

To validate the optimum condition predicted by the model, triplicate experiments were conducted at the optimized conditions. The result found from the experiment was 95.76333% for iron and 95.65% for manganese which is in best agreement with the predicted data from optimization analysis.

Table 11; validation experimental run results

Response	Run 1	Run 2	Run 3	Average	Standa	Stdev.s
Fe removal	96.33	95.01	95.95	95.76	0.554	0.679
Mn removal	95.99	95.30	95.66	95.65	0.281	0.345

After the validation of the model actual groundwater sample from Sambanekersa well was treated at optimum point. The removal efficiency of both iron and manganese for sample groundwater from Sambanekersa is showed in Table 12. 87.14%

Table 12; Iron manganese removal result for groundwater sample Sambanekersa

Response	Test 1	Test 2	Test 3	Average
Fe removal	87.60 %	85.85%	87.98 %	87.14%
Mn removal	30.80 %	24.21%	24.21 %	26.41%

4.10 Characterization of Sample and treated groundwater

Table 13; metal analysis for Shiromeda well groundwater sample

			Parameters											
Lab Code	*Description*	*Concentration*	*As*	*Pb*	*B*	*Zn*	*Cd*	*Hg*	*Cu*	*Ni*	Co	Fe	Mn	Cr
			mg/l	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*
21HWA 2014	*Raw H.M*	*Conc.1*	*1.324*	*0.599*	*< 0.001*	*< 0.013*	*< 0.024*	*0.395*	*< 0.012*	*0.196*	*0.06*	*4.98*	*0.64*	*0.16*
		Conc.2	*1.417*	*0.512*	*< 0.001*	*< 0.013*	*< 0.024*	*0.412*	*< 0.012*	*0.112*	*0.06*	*5.14*	*0.63*	*0.14*
		Conc.3	*1.031*	*0.592*	*< 0.001*	*< 0.013*	*< 0.024*	*0.478*	*< 0.012*	*0.195*	*0.06*	*5.37*	*0.55*	*0.12*
		Mean	*1.257*	*0.568*	*< 0.001*	*< 0.013*	*< 0.024*	*0.428*	*< 0.012*	*0.167*	*0.059*	*5.162*	*0.607*	*0.142*
		Stdv	*0.201*	*0.048*	*-*	*-*	*-*	*0.044*	*-*	*0.048*	*0.0028*	*0.200*	*0.05*	*0.020*
21HWA 2015	*Treated*	*Conc.1*	*0.879*	*0.418*	*< 0.001*	*< 0.013*	*< 0.024*	*0.292*	*< 0.012*	*0.110*	*0.09*	*0.64*	*0.42*	*0.21*
		Conc.2	*0.749*	*0.417*	*< 0.001*	*< 0.013*	*< 0.024*	*0.244*	*< 0.012*	*0.120*	*0.04*	*0.73*	*0.46*	*0.28*
		Conc.3	*0.886*	*0.442*	*< 0.001*	*< 0.013*	*< 0.024*	*0.214*	*< 0.012*	*0.161*	*0.06*	*0.62*	*0.46*	*0.25*
		Mean	*0.838*	*0.425*	*< 0.001*	*< 0.013*	*< 0.024*	*0.250*	*< 0.012*	*0.130*	*0.063*	*0.667*	*0.447*	*0.25*
		Stdv	*0.077*	*0.014*	*-*	*-*	*-*	*0.04*	*-*	*0.027*	*0.023*	*0.059*	*0.0201*	*0.04*

After treatment of groundwater from Sambanekersa well by oxidation filtration process all parameter were analyzed and the results showed significant difference on each parameter except for microbial analysis. As the results of onsite and laboratory analysis are listed in Table 14 the following discussion was made.

Since groundwater is less susceptible for microorganism growth except for iron bacteria, both total coliform and E-coli were not detected before and after treatment.

The pH and DO showed increments. The reason for dissolved oxygen changed from 3.9 to 7.2 mg/l s due to aeration which influence amount of dissolved oxygen presence. And addition of sodium hypochlorite is responsible for pH change from 6.47 to 8.4.

BOD, COD, sulfide, sulphate, phosphorus, free ammonia and total nitrogen showed reduction on their concentration after treatment since, aeration and NaOCl addition can reduce hydrogen sulfide and other undesirable restraints from groundwater[18]. This shows that the treatment method had significance on treating groundwater.

In addition to iron and manganese other heavy metals like As, Pb, Hg and Ni showed reduction in concentration as heavy metal analysis showed on table 13.

Removal of iron and manganese efficiency of the system for sample groundwater differs from removal efficiency of the system for synthetic water prepared in the laboratory. The main difference resulted from the composition of the water itself. Since the synthetic water has not prepared in the fashion which mimic every characteristics and contain each compound that the real groundwater contains, the removal efficiency was high up to 98% for manganese and 97% iron.

While from sample groundwater collected from Sambanekersa with concentration of iron 5.16 and manganese 0.607 the removal efficiency resulted was 87.14 and 26.41 percent. The highest withdraw of manganese removal efficiency might be due to sample pH value and manganese oxidation potential [42],[18]. For manganese the optimal pH value for oxidation by air and NaOCl is higher than that of iron. Iron can oxidized easily by air and other oxidants at pH value greater than 7, however manganese exhibits pH value of 8.5 and above for aeration and NaOCl oxidation [26],,[49][58]. For other strong oxidants like potassium permanganate, chlorine dioxide and chlorine the pH value starts at 7 [26]. Based on a study conducted on iron and manganese removal by oxidation followed by hollow -fiber microfiltration, iron oxidized easily by air and sodium hypochlorite than manganese. The removal of iron after oxidation reached 70% from 0.4mg/l and further treatment by MF increased the removal efficiency[59]. However for manganese removal at same procedure before MF oxidation of manganese was above accepted level[59].

Table 14; Characterization of groundwater before and after treatment

NO	Parameter	Unit	Raw groundwater	Treated groundwater
1	pH	-	6.47	7.84
2	DO	mg/l	3.9	7.2
3	Turbidity	NTU	20.1	2.73
4	Electro conductivity	µmho/cm	196.3	177.9
5	Total ALKALINITY	mg/l	79.4	51
6	TSS	mg/l	0.268	0.0596
7	TDS	mg/l	93	85
8	BOD	mg/l	56.3	7.06
9	COD	mg/l	75.8	10.69
10	Sulfide	µg/l	23.8	11.16
11	Sulphate	mg/l	23.5	6.83
12	Total nitrogen	mg/l	1.276	0.281
13	Phosphorus	mg/l	0.32	0.1347
14	Free ammonia	mg/l	0.089	0.0613
15	Microbial test			
	1.Total coliform		Not detected	Not detected
	2.E-coli		Not detected	Not detected
16	Heavy metal			
	1. Iron	mg/l	5.162	0.667
	2. Manganese	mg/l	0.607	0.447
17	TS	mg/l	93.268	85.06

Chapter five

5 Conclusion and recommendation

5.1 Conclusion

In summary iron and manganese removal from synthetic water and actual groundwater collected from selected well Sambanekersa was investigated during this study. The oxidation filtration process efficiency was analyzed in terms of removal efficiency of iron and manganese from groundwater. For characterizing and analyzing the experimental procedures sample groundwater the setup was studied using synthetic water.

In this study the analysis was modeled using RMS experimental analysis method of expert design 7.0. Optimum value was found from the analysis in which it was validated at optimal values of NaOCl concentration of 7.02, time 77 min and 1.5 l/min air flow rate with synthetic water and the result of validation was 95.76%, 95.65% for iron and manganese respectively. At the same optimum point sample collected from Sambanekersa well for both metals and it exhibited the result of 87.14% for iron and 26.41% for manganese removal. From which I concluded that the removal efficiency of oxidation filtration process is well worked for iron and for manganese. And pH adjustment of groundwater can increase removal efficiency of manages too.

The result showed that iron and manganese oxidation by air and sodium hypochlorite is attainable. However manganese removal efficiency of the system had highly significant difference for synthetic water and sample groundwater. In which the difference between iron and manganese removal on sample groundwater was resulted due to pH value sensitivity of manganese during oxidation. Since oxidation of manganese needs to have pH value greater than 8.5 to be oxidized by both air and sodium hypochlorite the result can be expected. And it is well known to use other strong oxidants for further reduction to reach the WHO standard of iron and manganese level in ground water.

The study also showed that some physic chemical parameters like DO, sulfide, BOD, COD and other show difference which indicate that the system worked well for groundwater treatment.

5.2 Recommendations

Iron and manganese removal from ground water have different treatment methods including oxidation by air and sodium hypochlorite followed by filtration process. This study was limited for analysis of removal efficiency of iron and manganese using sodium hypochlorite and air as oxidant. The result showed that removal of iron can be achieved using this process while manganese removal efficiency exhibited low percentage. Based on the result the following recommendations are made.

1. By widening the scope of the study further to see the effect of pH on iron and manganese removal with the same system can be performed.
2. The system working principles can be adjusted and see the effect on lower iron and manganese concentration.
3. For well of Sambanekersa which exhibited high iron and manganese concentrations may result from leaching of hospital waste water from nearby wastewater stream around the well. Therefore further studies can be conducted and solve long term problem and make the water usable.
4. This study can be used for small scale wells which are low iron and manganese concentration with above MCL by further studying its economical visibility.
5. The study can be also used as starting point for other related studies performed on iron and manganese removal using oxidation filtration or other methods which are applicable for finding similar output.

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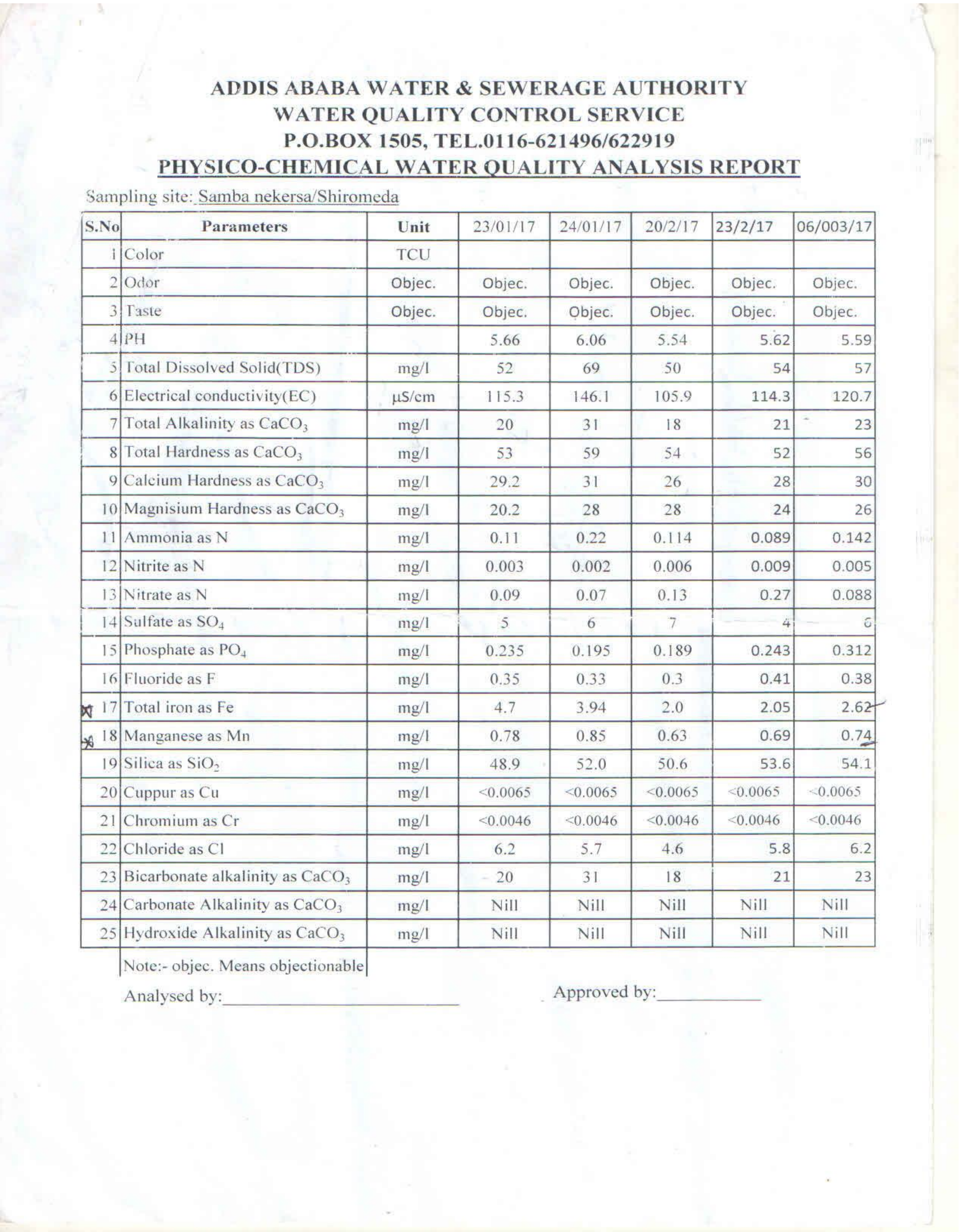
Appendix A

Appendix A -1 Physico-chemical water quality analysis report for Sambanekersa /Shiromeda



ADDIS ABABA WATER & SEWERAGE AUTHORITY
WATER QUALITY CONTROL SERVICE
P.O.BOX 1505, TEL.0116-621496/622919

PHYSICO-CHEMICAL WATER QUALITY ANALYSIS REPORT

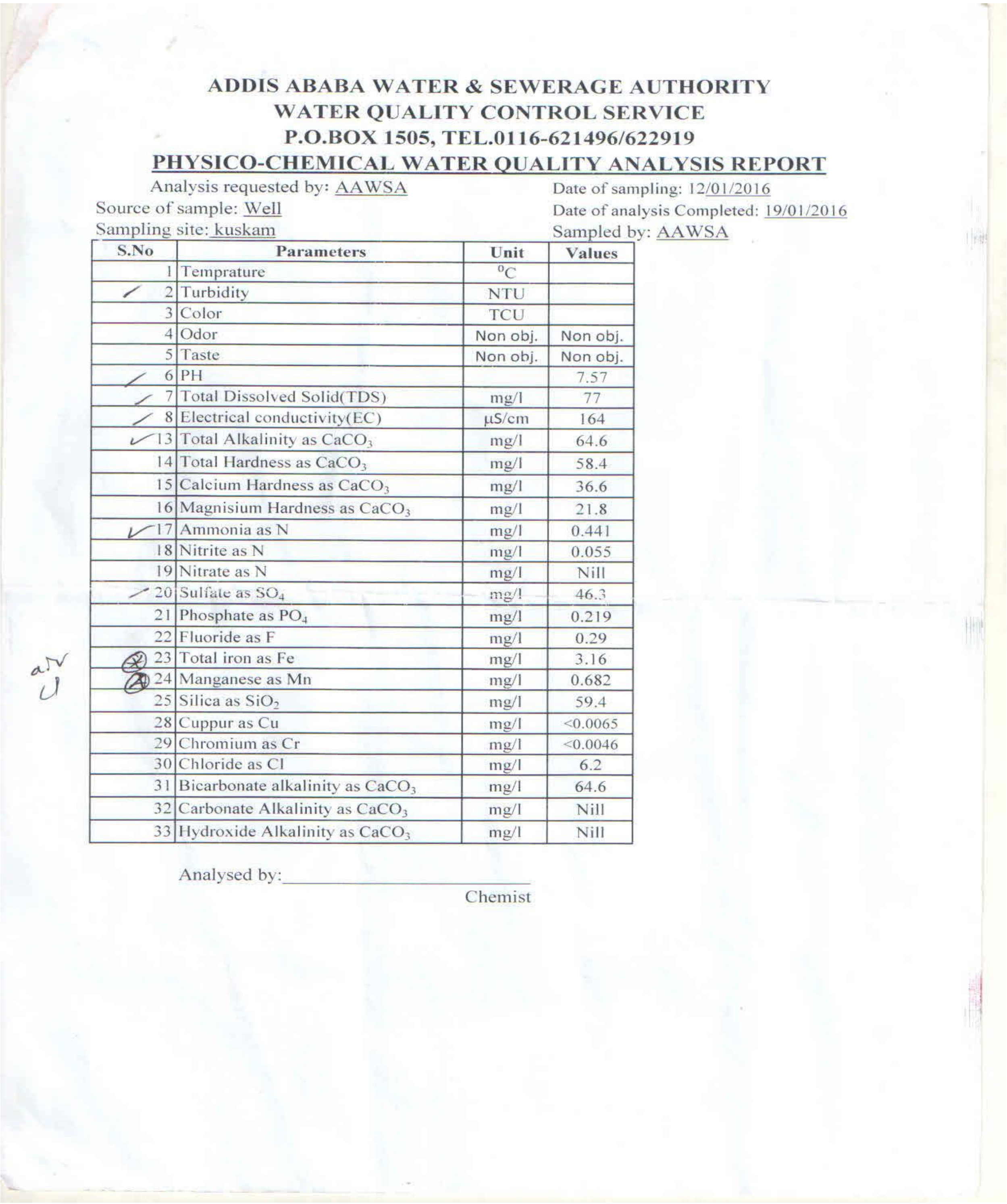
Sampling site: Samba nekersa/Shiromeda

S.No	Parameters	Unit	23/01/17	24/01/17	20/2/17	23/2/17	06/003/17
1	Color	TCU					
2	Odor	Objec.	Objec.	Objec.	Objec.	Objec.	Objec.
3	Taste	Objec.	Objec.	Objec.	Objec.	Objec.	Objec.
4	PH		5.66	6.06	5.54	5.62	5.59
5	Total Dissolved Solid(TDS)	mg/l	52	69	50	54	57
6	Electrical conductivity(EC)	µS/cm	115.3	146.1	105.9	114.3	120.7
7	Total Alkalinity as $CaCO_3$	mg/l	20	31	18	21	23
8	Total Hardness as $CaCO_3$	mg/l	53	59	54	52	56
9	Calcium Hardness as $CaCO_3$	mg/l	29.2	31	26	28	30
10	Magnisium Hardness as $CaCO_3$	mg/l	20.2	28	28	24	26
11	Ammonia as N	mg/l	0.11	0.22	0.114	0.089	0.142
12	Nitrite as N	mg/l	0.003	0.002	0.006	0.009	0.005
13	Nitrate as N	mg/l	0.09	0.07	0.13	0.27	0.088
14	Sulfate as SO_4	mg/l	5	6	7	4	6
15	Phosphate as PO_4	mg/l	0.235	0.195	0.189	0.243	0.312
16	Fluoride as F	mg/l	0.35	0.33	0.3	0.41	0.38
17	Total iron as Fe	mg/l	4.7	3.94	2.0	2.05	2.62
18	Manganese as Mn	mg/l	0.78	0.85	0.63	0.69	0.74
19	Silica as SiO_2	mg/l	48.9	52.0	50.6	53.6	54.1
20	Cuppur as Cu	mg/l	<0.0065	<0.0065	<0.0065	<0.0065	<0.0065
21	Chromium as Cr	mg/l	<0.0046	<0.0046	<0.0046	<0.0046	<0.0046
22	Chloride as Cl	mg/l	6.2	5.7	4.6	5.8	6.2
23	Bicarbonate alkalinity as $CaCO_3$	mg/l	20	31	18	21	23
24	Carbonate Alkalinity as $CaCO_3$	mg/l	Nill	Nill	Nill	Nill	Nill
25	Hydroxide Alkalinity as $CaCO_3$	mg/l	Nill	Nill	Nill	Nill	Nill

Note:- objec. Means objectionable

Analysed by:____________________ Approved by:__________

Appendix A-2 Physico-chemical water quality analysis report for Kuskam



ADDIS ABABA WATER & SEWERAGE AUTHORITY
WATER QUALITY CONTROL SERVICE
P.O.BOX 1505, TEL.0116-621496/622919

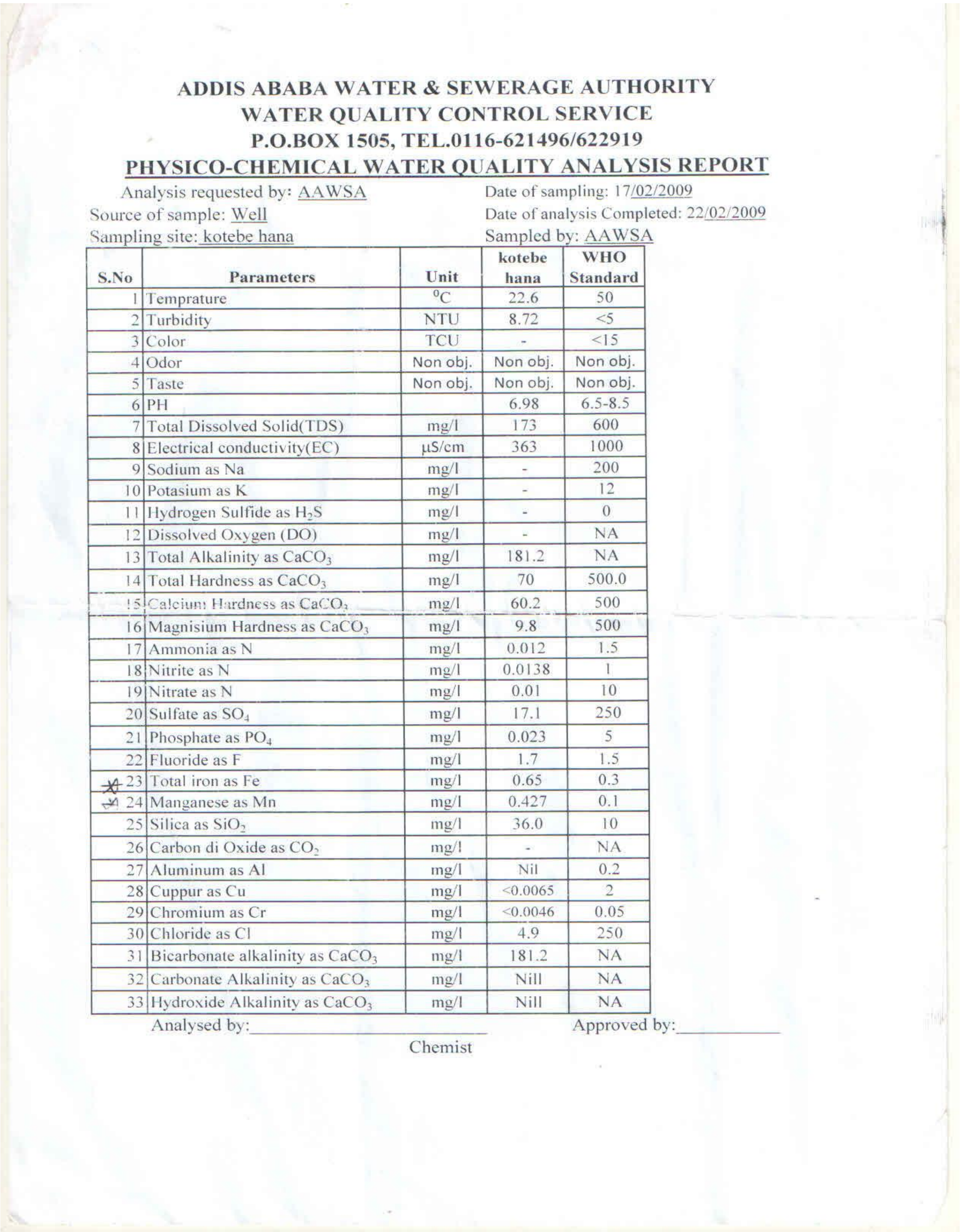
PHYSICO-CHEMICAL WATER QUALITY ANALYSIS REPORT

Analysis requested by: AAWSA
Date of sampling: 12/01/2016
Source of sample: Well
Date of analysis Completed: 19/01/2016
Sampling site: kuskam
Sampled by: AAWSA

S.No	Parameters	Unit	Values
1	Temprature	^0C	
2	Turbidity	NTU	
3	Color	TCU	
4	Odor	Non obj.	Non obj.
5	Taste	Non obj.	Non obj.
6	PH		7.57
7	Total Dissolved Solid(TDS)	mg/l	77
8	Electrical conductivity(EC)	µS/cm	164
13	Total Alkalinity as $CaCO_3$	mg/l	64.6
14	Total Hardness as $CaCO_3$	mg/l	58.4
15	Calcium Hardness as $CaCO_3$	mg/l	36.6
16	Magnisium Hardness as $CaCO_3$	mg/l	21.8
17	Ammonia as N	mg/l	0.441
18	Nitrite as N	mg/l	0.055
19	Nitrate as N	mg/l	Nill
20	Sulfate as SO_4	mg/l	46.3
21	Phosphate as PO_4	mg/l	0.219
22	Fluoride as F	mg/l	0.29
23	Total iron as Fe	mg/l	3.16
24	Manganese as Mn	mg/l	0.682
25	Silica as SiO_2	mg/l	59.4
28	Cuppur as Cu	mg/l	<0.0065
29	Chromium as Cr	mg/l	<0.0046
30	Chloride as Cl	mg/l	6.2
31	Bicarbonate alkalinity as $CaCO_3$	mg/l	64.6
32	Carbonate Alkalinity as $CaCO_3$	mg/l	Nill
33	Hydroxide Alkalinity as $CaCO_3$	mg/l	Nill

Analysed by:____________________
Chemist

Appendix A-3 Physico-chemical water quality analysis report for Kotebe hana



ADDIS ABABA WATER & SEWERAGE AUTHORITY
WATER QUALITY CONTROL SERVICE
P.O.BOX 1505, TEL.0116-621496/622919

PHYSICO-CHEMICAL WATER QUALITY ANALYSIS REPORT

Analysis requested by: AAWSA
Date of sampling: 17/02/2009
Source of sample: Well
Date of analysis Completed: 22/02/2009
Sampling site: kotebe hana
Sampled by: AAWSA

S.No	Parameters	Unit	kotebe hana	WHO Standard
1	Temprature	^0C	22.6	50
2	Turbidity	NTU	8.72	<5
3	Color	TCU	-	<15
4	Odor	Non obj.	Non obj.	Non obj.
5	Taste	Non obj.	Non obj.	Non obj.
6	PH		6.98	6.5-8.5
7	Total Dissolved Solid(TDS)	mg/l	173	600
8	Electrical conductivity(EC)	µS/cm	363	1000
9	Sodium as Na	mg/l	-	200
10	Potasium as K	mg/l	-	12
11	Hydrogen Sulfide as H_2S	mg/l	-	0
12	Dissolved Oxygen (DO)	mg/l	-	NA
13	Total Alkalinity as $CaCO_3$	mg/l	181.2	NA
14	Total Hardness as $CaCO_3$	mg/l	70	500.0
15	Calcium Hardness as $CaCO_3$	mg/l	60.2	500
16	Magnisium Hardness as $CaCO_3$	mg/l	9.8	500
17	Ammonia as N	mg/l	0.012	1.5
18	Nitrite as N	mg/l	0.0138	1
19	Nitrate as N	mg/l	0.01	10
20	Sulfate as SO_4	mg/l	17.1	250
21	Phosphate as PO_4	mg/l	0.023	5
22	Fluoride as F	mg/l	1.7	1.5
23	Total iron as Fe	mg/l	0.65	0.3
24	Manganese as Mn	mg/l	0.427	0.1
25	Silica as SiO_2	mg/l	36.0	10
26	Carbon di Oxide as CO_2	mg/l	-	NA
27	Aluminum as Al	mg/l	Nil	0.2
28	Cuppur as Cu	mg/l	<0.0065	2
29	Chromium as Cr	mg/l	<0.0046	0.05
30	Chloride as Cl	mg/l	4.9	250
31	Bicarbonate alkalinity as $CaCO_3$	mg/l	181.2	NA
32	Carbonate Alkalinity as $CaCO_3$	mg/l	Nill	NA
33	Hydroxide Alkalinity as $CaCO_3$	mg/l	Nill	NA

Analysed by:______________________ Approved by:__________
Chemist

Appendix B

Methods of characterization used for groundwater

Onsite analysis

On site analysis of pH, conductivity and dissolved oxygen (DO) were conducted based on APHA standard using pH meter, DO_2 meter and conductivity meter respectively.

Conductivity

Conductivity of the samples was measured using conductivity meter Qcond 2200 based on APHAS. Standard reference solution was prepared with 0.0100M potassium chloride which used as a reference at 1412µmlos/cm at 25 ºC. Conductivity meter was rinsed at each measurement to avoid interference.

Reagent

- 0.0100M KCl

pH

PH measurements were performed in the field using pH meter (VOLTCRAFT PV- 100ATC). pH meter was rinsed with deionized water to avoid contamination. And turbidity was also measured in the lab using turbidity meter.

Dissolved oxygen

Oxygen is slightly soluble in water, the solubility being temperature dependent. At 5°C the solubility is about 12 mg/L and at 24°C it is about 8 mg/L. Dissolved oxygen was measured using DO2 meter (970 Temway) found in environmental laboratory at the field.

Laboratory analysis

Total Suspended Solids

Total suspended solids are measured gravimetrically by weighing the fraction remaining on filter paper dried at 105 °C, after filtration of a measured volume of sample 100ml. The method is described in APHA (2005), (Standard Methods for the Examination of Water and Wastewater, 21st Edition, (2005) American Public Health Association, Washington DC. Method 2540 D. Total Suspended Solids Dried at 103 - 105 °C.

$$\frac{Mg\ total\ suspended\ \ solid}{L} = (\mathrm{A} - \mathrm{B}) * \frac{1000}{\mathrm{samplevolume\ ml}} \qquad (1)$$

Where

A=weight of filter plus dried residue mg

B=weight of filter

Total Dissolved Solids

Total dissolved solids are measured gravimetrically by weighing that fraction passing through a filter, dried at 105 °C, after vacuum filtration of a measured volume of sample. The method is described in APHA (2005).Standard Methods for the Examination of Water and Wastewater. 21st Edition (2005) American Public Health Association, Washington DC,.

$$\frac{Mg\ total\ dissolved\ solid}{L} = (\mathrm{A} - \mathrm{B}) * \frac{1000}{\mathrm{samplevolume\ ml}} \qquad (2)$$

Where

A=weight of crucible plus dried residue mg

B=weight of crucible

Alkalinity

Alkalinity was analyzed by titration with 0.02N sulfuric acid based on APHA. It measured by the amount of sulfuric acid needed to bring a sample to its end point PH which is 4.2 and it measured in mg/l.

Alkalinity total mg/L= ml titrant *20 (3)

Where

20= digits multiplier used

Heavy metals

The analyses of heavy metals such as Cu, Zn, Mg, Fe, Cd, Pb, Cr, As, Hg, and Mn were carried out based on ASTM standards ,which are approved by APHA using Wet Digestion with strong Acid Digestion + ICP-OES Determination.

Effluent iron and manganese concentration

Iron and manganese concentration was measured for each experimental run in each day of the experiment using calorimetric spectroscopy at Addis Ababa water and sewerage authority laboratory.

Chemical Oxygen Demand (COD)

COD was analyzed with closed reflux colorimetric method using COD digester.

Biological oxygen demand

Biological oxygen demand is Measurements of oxygen consumed in a 5-d test period (5-d BOD or BOD5, 5210B). BOD was measured via the winkiler method with azide modification.

Elemental analysis and microbial analysis

Elemental analysis for total phosphorus, total nitrogen, sulphate and sulfide was performed at Addis Ababa university 4 kilo campus based on standard water and waste water analysis methods and American public health association methods.

Total phosphorus was analyzed using Digestion colorimetric method of ascorbic acid method. Determine per sulfate digestion method. Sulphate was analyzed by turbid metric method based on. And Sulfide was determined using methylene blue method.

Microbial analysis of sample and treated water was observed for total coli form and E-coli at bioengineering lab using selective media membrane filtration.

Sodium hypochlorite concentration

Sodium hypochlorite concentration was determined using iodometric methods. Iodometric titration following the Standard Methods for the Examination of Water and Wastewater

Reagent

- 1.581g of sodium thiosulphate
- Potassium iodide (KI)
- starch solution
- acetic acid

And the residual chlorine concentration calculated by

$$\text{Residual chlorine (g/l)} = \frac{V_{Na_2S_2O_3} \times N \times eq_{wt\ of\ Cl}}{V_{sample}} \qquad (4)$$

Appendix C

Sand bed preparation/ filter bed preparation

Sand bed prepared using two plastic measuring cylinders of 2 lit capacity or 45 cm long by molding one above the other which gives total height of 90 cm. which was filled by sand till 60cm based on American standard for iron and manganese filtration (Fable 15).

Sieve analysis result

Washed sand undergoes sieve analysis reputedly until effective diameter of 0.7mm, uniformity coefficient 1.71 and d_{60} of 1.2 was reached. The tables and figures below show the consecutive results of sieve analysis.

Table 15; Sieve analysis first sieving (d10= 0.6, d60= 1.55, UC =2.55)

Sieve size	Weight retained stock(g)	Cumulative weight retained (g)	Cumulative weight passing (g)	Cumulative weight passing %
4	0	0	4000	100
3.55	114	114	3886	97.15
3.15	67	181	3819	95.475
2.5	141	322	3678	91.95
2	267	589	3411	85.275
1	2407	2996	1004	25.1
0.5	756.9	3752.9	247.1	6.1775
0.25	155	3907.9	92.1	2.3025
0	92.1	4000	0	0

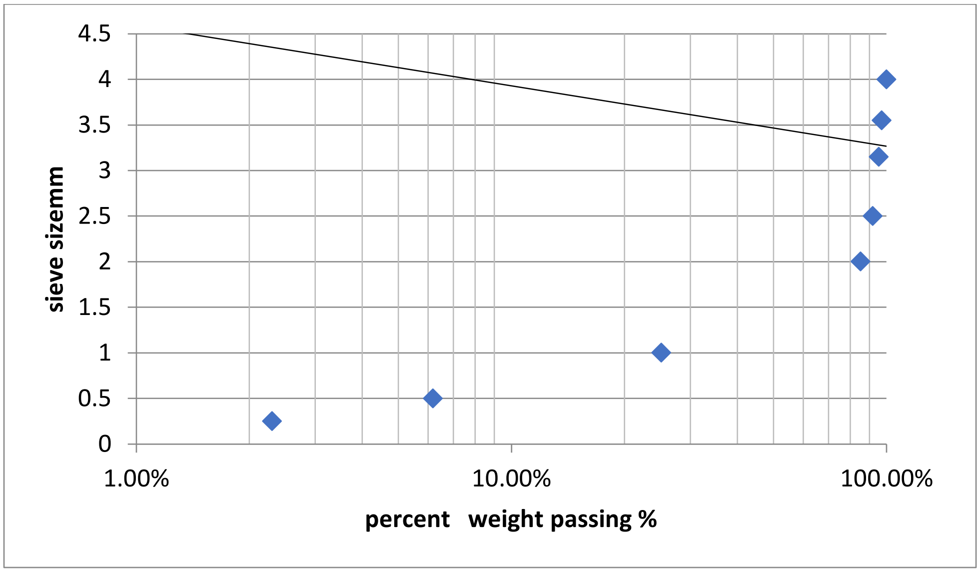


Figure 12; Log graph for first sieve analysis

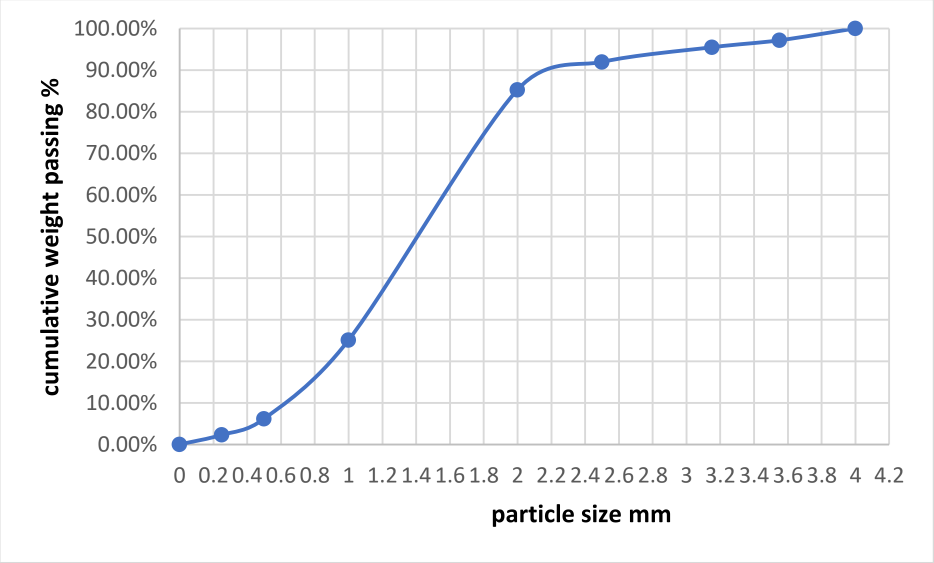


Figure 9; Cumulative percentage passing for first sieve analysis

After the first sieve analysis the finest and the core particles were removed and second sieving was done with sieve of different sizes. And the result was done on excel for cumulative percent passing, d $_{60}$ and ES calculated from graph.

Table 16; Sieve analysis second sieving (d10= 0.68, d60=1.45, UC=2.13)

Sieve size	weight retained treated(g)	Cumulative weight retained (g)	Cumulative weight passing (g)	Cumulative weight passing %
4	0	0	2723.1	100
3.55	0	0	2723.1	100
3.15	267.1	267.1	2456	90.19132606
2.5	9.2	276.3	2446.8	89.85347582
2	133	409.3	2313.8	84.96933642
1.8	158.1	567.4	2155.7	79.16345342
1.4	579	1146.4	1576.7	57.90092174
1	964.6	2111	612.1	22.4780581
0.6	612.1	2723.1	0	0
0.5	0	2723.1	0	0
0	0	2723.1	0	

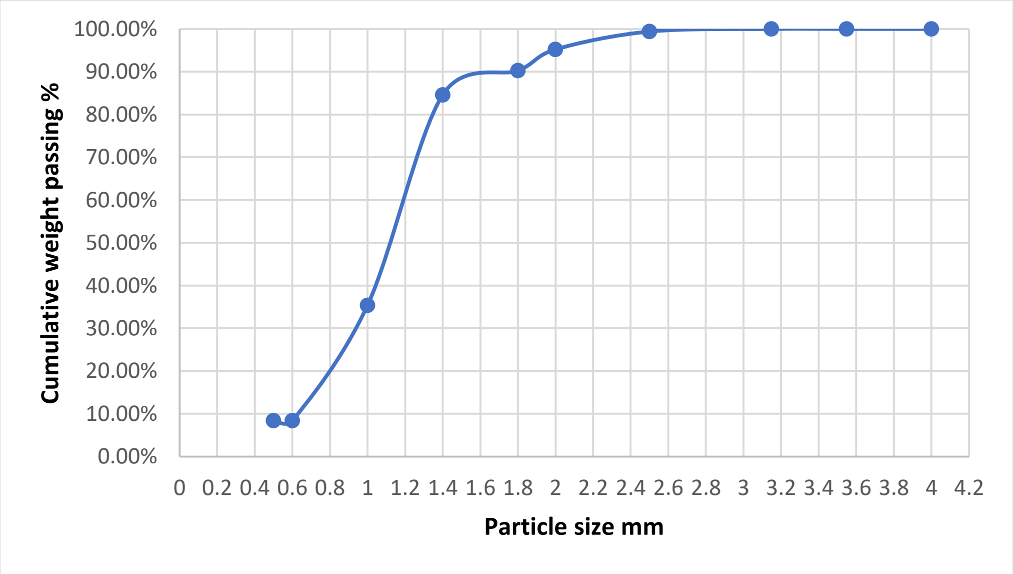


Figure 10; Cumulative percentage passing for second sieve analysis

After the second sieve analysis the finest and the core particles were removed and consecutive sieving was done with sieve of different sizes. Finally the desired effective size and uniformity coefficient was found and the result was done on excel for cumulative percent passing, d $_{60}$ and ES calculated from graph. Based on American water and waste water treatment gain size of sand bed for iron and manganese removal can be up to 8mm and UC of 1.71 of less. Therefore the grain size distribution for the experiment was decided to have d_{10}= 0.71, d_{60}= 1.2, UC=1.70.

Then the bed was prepared with particle size ranged from 0.6mm to 1.4 mm with bed length 0.6m.

Table 17; Final sieve analysis d10= 0.71, d60= 1.2, UC=1.70

sieve size	weight retained treated (g)	cumulative weight retained (g)	cumulative weight passing (g)	Cumulative weight passing (%)
2.5	0	0	2570.4	100
2	267	163.4	2407	93.64301276
1.8	285.2	448.6	2121.8	82.54746343
1.4	213.5	662.1	1908.3	74.24136321
1	540.8	1202.9	1367.5	53.20183629
0.85	855.7	2058.6	511.8	19.91129785
0.71	265.5	2324.1	246.3	9.5821662
0.6	246.3	2570.4	6.25278E-13	2.43261E-14
0.5	0	2570.4	0	0
0	0	2452.8	0	0

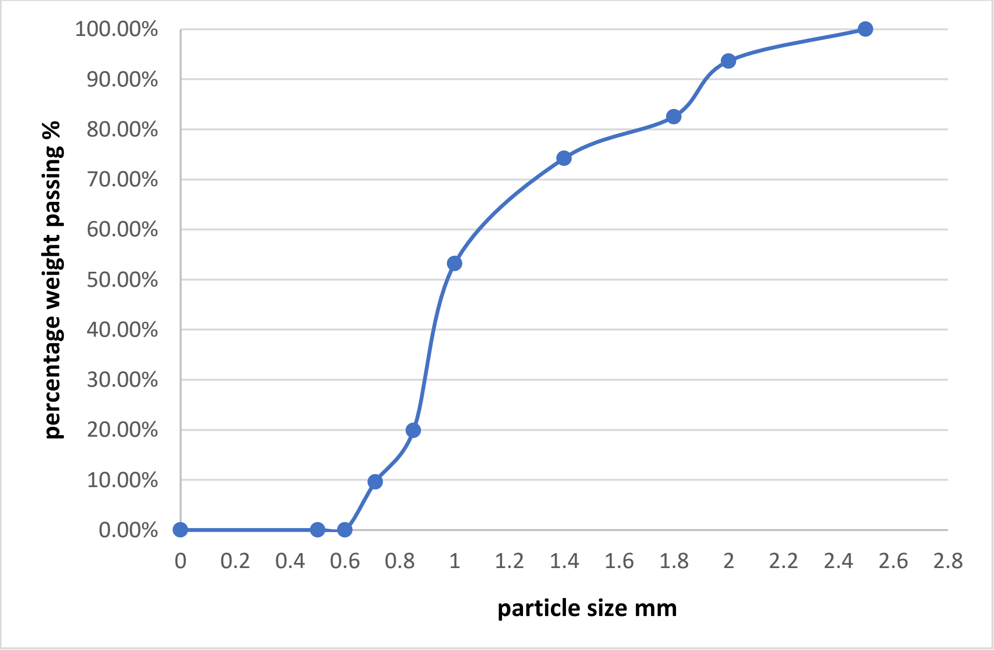


Figure 11; Cumulative percentage passing for final sieve analysis

Table 18; Iron and manganese removal results final concentration of filtrate

Run	Co		$\frac{Ci-Co}{Ci}*100$ Ci=4.02 Fe , Ci=2.77Mn	
	Fe	Mn	Fe	Mn
1	0.411	0.219	89.77	92.09
2	0.190	0.104	95.26	96.24
3	0.270	0.177	93.26	93.61
4	0.100	0.038	97.5	98.61
5	0.220	0.123	94.51	95.23
6	0.150	0.110	96.25	96.02
7	0.160	0.101	96	96.35
8	0.210	0.144	94.76	94.78
9	0.110	0.144	97.25	94.98
10	0.080	0.139	98	97.94
11	0.040	0.027	99	99.02
12	0.360	0.287	91.02	89.63
13	0.551	0.351	86.28	87.32
14	0.491	0.303	87.78	89.04
15	0.070	0.055	98.25	98.01

Some picture from laboratory set up