ASSESSMENT OF HEAVY METALS CONTAMINATION IN GROUNDWATER AND ADSORPTIVE REMOVAL OF IRON, MANGANESE, CADMIUM, COPPER AND ZINC USING PEAT MOSS: THE CASE OF KEMBATA TEMBARO ZONE

M.Sc. THESIS

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MASTERS OF SCIENCE IN WATER RESOURCE ENGINEERING AND MANAGEMENT

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DECLARATION

I hereby declare that this Master of Science Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

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DEDICATION

This thesis is dedicated to the Almighty God, through whom I had the strength to start and complete this work.

Glory to Almighty God!

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LISTS OF ABBREVATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
EDWS	Ethiopian Drinking Water Standard
EMH	Egyptian Ministry of Health
EPA	Environmental Protection Authority
GAC	Granular Activated Carbon
GPS	Global Positioning System
HEI	Heavy Metals Evaluation Index
HPI	Heavy Metals Pollution Index
MCL	Maximum Contaminant Levels
MWEE	Ministry of Water and Energy of Ethiopia
pH	Power of Hydrogen
rpm	round per minute
SNNPR	South Nation Nationalities and Peoples Region
TDS	Total Dissolved Solids
WHO	World Health Organization

ABSTRACT

Heavy metal contamination is one of the most significant health issues. Heavy metals in groundwater were assessed and analyzed using atomic absorption spectrometer. The HPI, C_{deg} and HEI indices were greater than their critical values of pollution indices. The result showed that Fe^{2+} and Mn^{2+} are the major groundwater contaminant's in the study area. Chemicals are mostly used to purify contaminated water. Adsorptive removal is most important to reduce heavy metals in water to acceptable levels and to minimize the cost of chemicals and health effects of chemicals. Thus, research was carried out to observe the effect of *Sphagnum* moss (peat moss) as non-chemical natural adsorbent. The *Sphagnum* moss was obtained from SNNPR, Kembata Tembaro Zone, Hambericho Mountain. The 500 and 1000 mg of peat moss were used to examine the effectiveness of peat moss to remove different concentration of iron, manganese, cadmium, copper and zinc. For removal of iron, manganese, cadmium, copper and zinc from contaminated boreholes and shallow wells water, batch experiment were employed. The contact time, pH, temperature and adsorbate concentration effects were studied during the adsorption of iron, manganese, cadmium, copper and zinc. The relationship between pH, time and concentration required adsorbing 5-15 mg/L of iron, manganese, cadmium, copper and zinc from the aqueous solution were observed. The average adsorption (93.72%) result indicated that there was a reduction of iron, manganese, cadmium, copper and zinc concentration in the water samples at pH 6.0. The 1000 mg peat moss was effective to remove 96.3% of 5 mg/L of iron, at pH 6, with the contact time 60 minutes. Adsorption equilibrium was attained after 60' minutes of contact time and it was described by kinetics studies. From (R^2) values Zn^{2+} and Cd^{2+} best fit Langmuir adsorption isotherm model. All of the tested metals best fit Freundlich adsorption isotherm model.The model should be developed for large-scale treatment using peat moss for effective water purification.

Key words: Heavy metal contamination, Adsorption, *Sphagnum,* Heavy metals and Groundwater

1. INTRODUCTION

1.1. Background of the study

Water is the basis of life, an ecological resource for the earth's flora and fauna and a fundamental necessity for human life. If there is no adequate supply of safe water, we have no hope of improving the health of the people (Adebayo, *et al.,* 2007 and Eddy and Ekop, 2007). About 80% of the diseases in developing countries are related to contaminated water and the resulting death toll is as much as 10 million per year (Anonymous, 2004).

Globally, marine water constitutes about 97%, while 3% is fresh water. Out of the 3% freshwater, 79% is stored in polar ice caps and high mountain glaciers, aquifers, and soil moisture contains 20% and 1% is from surface water, which is basically lakes and rivers. Besides the limited amount of fresh water availability, the intensification of climate change, coupled with increasing human population and industrial development are putting severe pressure on fresh water, resulting in concerns to seek for sustainable source of drinking water (World Atlas, 2019).

Groundwater is an inevitable component of natural resources and plays an important role to serve as many purposes like drinking, irrigation, and other domestic usage (Azad, 2003) in many countries across the world. It represents 97% of the world's available freshwater resources (Guppy, *et al.,* 2018) and it is about 60 times more plentiful than the surface water (Groundwater Association, 2012). Most of it flows through underground aquifers, which can be accessed by digging wells. Much of the global population is hard-stricken having access to such a small percentage of freshwater on earth's surface (Perlman, 2016). It provides more than 90% of water used for domestic and industrial supply in Ethiopia, but a very small proportion of water used for irrigation, which mostly comes from surface water (MWEE, 2014). It is generally a preferred source for water supplies because of its convenient availability close to where water is required, its constant and good natural quality (which is frequently adequate for potable water supplies with minimal treatment), and relatively low capital cost of water supply system development (Nash and McGall, 1994).

Groundwater contamination has major complications on the environment and can pose serious threat to human health. Groundwater quality problems are typically associated with high

hardness, high salinity and elevated concentrations of iron, manganese, fluoride, and occasionally methane, hydrogen sulphide, and arsenic (Nash and McGall, 1994) sulphates, nitrogen compounds (such as ammonia and nitrates, petroleum products, phenols and heavy metals (UNESCO, 2004). Iron contamination is a problem in groundwater because its level ranges from 0.5 to 50 mg/L whereas World Health Organization (WHO) recommended less than 0.3 mg/L. The level higher than 0.3 mg/L, have unpleasant taste, which is apparent in drinking water. An iron limit in drinking water is based on aesthetic parameter rather than toxicity (Lemley, *et al.,* 2012). Many metals are essential for animal and plant life. However, excess concentration of trace metals in water system may be harmful due to the acute toxicity (Janardhana, 2015). Heavy metal contamination is one of the most significant environmental issues. Heavy metal ions such as copper, iron, nickel, lead, etc. in the environment are of major concern due to their toxicity to many life forms (Abbas, 2013). The content of heavy metals in the groundwater essentially increased in the areas of infiltrating acid atmospheric precipitation (Zektser, 2000). Metals pose a difficult waste-management problem. Special research is required on the chemistry, hydrogeology, and microbiology of the transport and transformation of metals in the subsurface. Remediation efforts should examine methods to modify the chemical forms of metals, to make them less mobile or to retard/sequester them in the subsurface. Metals of greatest concern include mercury, lead, cadmium, chromium, nickel, iron, manganese and arsenic (Warren and Piver, 1992).

Several methods, namely oxidation–precipitation– filtration, lime softening, ion exchange, sub-surface iron removal and membrane processes, have been employed for iron removal from groundwater. Stabilization with phosphate or silicates is applied as well to avoid the oxidation or precipitation of iron (Twort, *et al.,* 2000). Adsorption has proved to be the best (Crini, 2005 and Demirbas, 2008).

A number of researchers reported groundwater contamination by heavy metals as well as adsorptive removal of heavy metals using locally available bio-adsorbents. However, to the best of our knowledge there is no prior study of the assessment of the groundwater contamination by heavy metals in Kembata Tembaro Zone and adsorptive removal of iron, manganese, cadmium, copper and zinc using peat moss (*Sphagnum* moss). Adsorption onto low-cost media such as peat

now offer an attractive, inexpensive option for the removal of colloidal and dissolved metals (Ho and McKay, 1999). Peat has an extensive capacity to adsorb divalent metals (Brown, *et al.,* 2000). *Sphagnum* moss is widely distributed in Ethiopia, especially in southern Ethiopia. Therefore, this study was carried out to assess the groundwater contamination by iron, manganese, cadmium, copper and zinc and adsorptive removal of iron, manganese, cadmium, copper and zinc using peat moss.

1.2. Statement of the problem

Heavy metals are among the major contaminants of groundwater sources (Marcovecchio, *et al.,* 2007). A fraction of heavy metal contaminants may lead to severe poisoning if they pollute the groundwater that is used for drinking or irrigation purposes (Economou, *et al.*2014). Elevated level of iron is the most common water quality problems in groundwater. This problem occurs statewide in wells that access both shallow and deep groundwater sources. The presence of iron in groundwater is objectionable to the consumers as those contaminants could precipitate in fresh water distribution systems. When precipitated, iron may cause problems of unpleasant odour, taste in drinking water and beverages, and yellow to brown stains in plumbing and laundered clothing. Additionally, iron in distribution systems may promote growth of microorganisms, thereby forming slimy tissues several millimeters thick, which could accumulate and eventually block the distribution channels. The microorganisms could also reduce oxygen levels in the water and, where chemicals are used for disinfection; reduce the effectiveness of those chemicals (Ankrah, 2012). Iron imparts colour and a typical bitter, astringent taste to the water. The taste threshold of iron in water is 0.04-0.1 mg/L (Montgomery, 1985 and WHO, 1996). The present study mainly focuses on the assessment of the heavy metals contamination of groundwater of Kembata Tembaro Zone and adsorptive removal of iron, manganese, cadmium, copper and zinc of these areas by using locally available bio-adsorbent *Sphagnum* (peat moss) as low cost.

1.3. Objectives

1.3.1. Main objective

The aim of this study was to asses iron, manganese, copper, cadmium and zinc contamination of groundwater of Kembata Tembaro Zone and to determine the adsorptive ability of peat moss to remove iron, manganese, copper, cadmium and zinc.

1.3.2. Specific objectives

The specific objectives of this research include:

- To evaluate the physico-chemical characteristics and heavy metals (Fe^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}) contamination of the groundwater in Kembata Tembaro Zone,
- To investigate the adsorptive removal of iron, manganese, copper, zinc and cadmium using peat moss,
- To evaluate the adsorption isotherm and kinetics of adsorption process of peat moss,
- To determine the HPI, C_{deg} and HEI values of the Fe^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} in groundwater.

1.4. Research questions

In order to realize the situate objectives, the study required to answer the following research questions:

i. What are the physicochemical parameters and iron, manganese, copper, zinc and cadmium concentrations of the groundwater in Kembata Tembaro Zone?
ii. What is the adsorptive ability of peat moss to adsorb iron, manganese, copper, zinc and cadmium?
iii. What are the HPI, C_{deg} and HEI values of the metals in groundwater?
iv. What is the adsorption isotherm and kinetics of peat moss?

1.5. Scope of Study

The study focused only on five metals (Mn, Fe, Cu, Cd and Zn). These heavy metals were considered toxic in higher concentration in drinking water. The study focused on Kembata Tembaro Zone, Adilo, Kechabira, Kedida Gamela and Hadero Tunto Woredas of selected groundwater, since previously no studies have been done in these area.

1.6. Significance of the study

The result of this study will provide information about the groundwater on physico-chemical characteristics (TDS, Temperature, Conductivity, Turbidity, pH, DO) and heavy metals (Fe^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}) in Kembata Tembaro Zone and adsorptive removal of heavy metals using peat moss. The main purpose of this study was to determine the groundwater

contamination by Fe^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} in Kembata Tembaro Zone to identify and assess the area with heavy metals contamination. The present study determines whether the groundwater fit or not for the drinking purposes as well as irrigation purposes.

1.7. Limitation of the Study

The research title is more specific and it is applicable to conduct the desire scope in the study area. To conduct this research the main constraints are lack of laboratory equipments for proper scientific experiment related with this research topic. Financial issues and unavailability of the hollow cathode lamp for atomic absorption spectrometer for the most of the heavy metals are the limitation of the study. The progressive adsorption of peat moss was not seen to see the exhaustive level of adsorption. Only 500 and 1000 mg peat moss were used to observe the adsorptive ability of peat moss and one week decomposed peat was used for the experiments, this is due to equipment problems and time limitations. These problems are obstacles to assess and analyze the heavy metals and to propose planning and design solutions.

2. LITRUTURE REVIEW

2.1. Sources of groundwater contamination

Groundwater aquifers are contaminated due to natural and manmade (domestic, agricultural fertilizers and industrial wastes) disposal area based on hydraulic phenomena. Therefore, groundwater quality monitoring should be implemented and targeted on the specific groundwater quality problem caused by waste disposal area. Most often, groundwater quality is affected by saltwater intrusion into coastal aquifers, by the downward and upward influx of poor water quality from superposed and underlying aquifers into exploited aquifers or by the discharge of polluted surface water into phreatic aquifers (Vrba, 2002). The contamination of groundwater by heavy metal, originating either from natural soil sources or from anthropogenic sources is a matter of utmost concern to the public health. Remediation of contaminated groundwater is of highest priority since billions of people all over the world use it for drinking purpose (Hashim, *et al.,* 2011).

Contaminants may reach groundwater from activities on the land surface, such as releases or spills from stored industrial wastes; from sources below the land surface but above the water table, such as septic systems or leaking underground petroleum storage systems; from structures beneath the water table, such as wells; or from contaminated recharge water. In the environment, the heavy metals are generally more persistent than organic contaminants such as pesticides or petroleum byproducts. They can become mobile in soils depending on soil pH and their speciation. Therefore, a fraction of the total mass can leach to aquifer or can become bioavailable to living organisms. (Alloway, 1990 and Santona, *et al.,* 2006)

2.1.1. Natural Sources of groundwater contamination

Some substances found naturally in rocks or soils, such as iron, manganese, arsenic, chlorides, fluorides, sulfates, or radionuclides, can become dissolved in groundwater. Other naturally occurring substances, such as decaying organic matter, can move in groundwater as particles. Whether any of these substances appears in groundwater depends on local conditions. Some substances may pose a health threat if consumed in excessive quantities; others may produce an undesirable odor, taste, or color. Groundwater that contains unacceptable

concentrations of these substances are not used for drinking water or other domestic water uses unless it is treated to remove these contaminants. The inorganic compounds occur in nature in the soil (Galitskaya, *et al.*.2017).

2.1.2. Pesticide and fertilizer use

Millions of tons of fertilizers and pesticides (e.g., herbicides, insecticides, rodenticides, fungicides, avicides) are used annually for crop production (Mills, *et al.,* 2011). Heavy use of pesticides and fertilizer are causing various environmental problems. Both the surface and groundwater pollution due to toxic heavy metals has been a major concern for environment (Chhatwal, *et al.,* 1992 and Marschner,1983). In addition to farmers, homeowners, businesses (e.g., golf courses), utilities, and municipalities use these chemicals. A number of these pesticides and fertilizers (some highly toxic) have entered and contaminated groundwater following normal, registered use. Some pesticides remain in soil and water for many months to many years. Another potential source of groundwater contamination is animal wastes that percolate into the ground from farm feedlots. Feedlots should be properly sited and wastes should be removed at regular intervals (Mills, *et al.,* 2011).

In areas surrounding pumping wells, the potential for contamination increases because water from the zone of contribution, a land area larger than the original recharge area, is drawn into the well and the surrounding aquifer. Some drinking water wells actually draw water from nearby streams, lakes, or rivers. Contaminants present in these surface waters can contribute contamination to the groundwater system. Some wells rely on artificial recharge to increase the amount of water infiltrating an aquifer, often using water from storm runoff, irrigation, industrial processes, or treated sewage. In several cases, this practice has resulted in increased concentrations of nitrates, metals, microbes, or synthetic chemicals in the water. Heavy metals mobilization from soil to groundwater appears to be significantly influenced by agricultural activity (Mills, *et al.,* 2011).

2.2. Aquifer vulnerability and risks to groundwater supplies

Aquifer vulnerability is the likelihood of an aquifer being affected by a contaminant load imposed by human activities at the ground surface. The assessment of the vulnerability is based

on the estimated travel time for water to move from the ground surface to the water table. As the water moves through the ground, natural processes reduce the concentration of many contaminants. The vulnerability of aquifers to contamination from sanitation systems and other pollution sources is high in areas of high rainfall and shallow water tables. The vulnerability is also high for fractured aquifers and other permeable environments such as sandy or gravel soils. This is mainly because of high flow rates and less time and distances available for filtration, die-off and adsorption processes to take place. Proper management of groundwater and control of hazardous activities on vulnerable aquifers is essential for the protection and the sustainability of the groundwater resource. A proactive approach to protect the groundwater resources from pollution is encouraged, as it may be very difficult and costly to treat the groundwater once it has been contaminated, particularly in terms of inorganic contaminants (National Sanitation Program, 2003).

2.3. Chemical concentration of groundwater

Changes in chemical concentration occur within a dynamic groundwater system primarily due to four distinct processes:

1) Advective transport, in which dissolved chemicals are moving with the flowing groundwater;
2) Hydrodynamic dispersion, in which molecular and ionic diffusion and small-scale variations in the flow velocity through the porous media cause the paths of dissolved molecules and ions to diverge or spread from the average direction of groundwater flow;
3) Fluid sources, where water of one composition is introduced into and mixed with water of a different composition.
4) Reactions, in which some amount of a particular dissolved chemical species may be added to or removed from the groundwater as a result of chemical, biological, and physical reactions in the water or between the water and the solid aquifer materials or other separate liquid phases (Mendoza and Frind, 1990b and North, 1997)

In developing countries, only 5% of the industrial and domestic wastes produced in towns is subject to treatment and purification. The majority of two million tons of human excrement produced daily, as well as all the toxic and dangerous by-products of industrial production, are disposed into rivers and aquifers, thus contaminating them (Zektser, 2000)

2.4. Groundwater treatment

Selection of groundwater treatment depends on the contaminants to be removed. Gasoline and volatile organic compounds can be removed by air stripping and stream stripping processes. Activated carbon adsorption, biological treatment, and granular media filtration can be used for removal of gasoline and other organics. Oxidation/reduction processes remove nonvolatile organics(LETC, 1982). Inorganic chemicals and metals can be treated by coagulation/sedimentation, neutralization, dissolved air flotation, granular media filtration, ion exchange, resin adsorption, and reverse osmosis (EPA, 1994)

2.4.1. Biosorption of heavy metals

This field of remediation technology is an emerging and ever developing field but somewhat lacking in field application. Experiments with various biosorbents showed promising results. There are a number of advantages of biosorption over conventional treatment methods such as low cost, minimization of chemical or biological sludge, high efficiency, regeneration of biosorbents and possibility of metal recovery (Hashim, *et al.,* 2011).

2.4.1.1. Iron in groundwater

Iron is an essential element for all organisms. High concentrations of iron may cause color problem in water and can be slightly toxic. Iron contained water has inky flavor and bitter taste. It may cause also some health problems in humans. Prolonged consumption of drinking water containing iron at high concentration makes the teeth and nail black and weak, stickiness of hair and water and may also cause liver disease (Tunc, *et al.,* 2013). Limit value for Fe^{2+} prescribed by Ethiopia is 0.3 mg/L (EDWS, 2013). Iron is relatively abundant in the earth's crust (Rankama and Sahama,1950) so it is very common in groundwater, because water is the universal solvent, groundwater usually has some characteristics of the soil and bedrock bit flows through, which frequently contains high levels of iron 7-15 mg/L in dissolved form. Groundwater environments are generally low in oxygen near neutral pH. At higher pH iron is insoluble in water and cause the water red (Nagwa and Mohammed, 2016). Iron containing minerals in soils, rocks, and sediments dissolve more rapidly in such low-oxygen conditions. Groundwater rends to develop chemical characteristics that reflect the chemical composition of

aquifer. This is especially true if the aquifer is rich in easily soluble salts or minerals (WHO, 2012). A mineral source of iron is not the only prerequisite for having iron in groundwater reach high levels. The chemical environment within the aquifers, primarily the oxidation level and pH strongly influence iron concentrations. Common minerals that control iron concentrations include iron carbonate (siderate), iron sulphide (greigite, pyrite), and iron oxide or hydroxide (hematite, amorphous iron hydroxide). In the presence of soluble iron minerals, dissolved ferrous (reduced iron) concentrations can rise to high values of 5 mg/L. For comparison water with values above 0.3 mg/L (the recommended EPA secondary drinking water limit) contains just enough iron to begin to cause fouling problems with normal use(Joseph, *et al.,* 2001). In addition, iron can be present in surface and groundwaters at levels ranging from 0.5 to 50 mg/L (WHO, 2012). The occurrence of iron in groundwater mainly gives rise to aesthetic issues as well as additional cost for cleaning; thus, it is of interest for water treatment utilities to remove iron from groundwater (Seyedeh, 2017).

The most common species of ferric iron in natural waters is ferric hydroxide, $Fe(OH)_3$ or ($Fe_2O_3.3H_2O$). It may be present in groundwater in the following five forms: i) dissolved as iron (II), ii) inorganic complexes, iii) organic complexes, iv) colloidal, and v) suspended. Its state in the water depends above all on the pH and the redox potential. Most natural waters have pH values ranging from 5.0 to 8.5 and pE values ranging from -7 to +12. Thus, iron (II) would be the predominant species in the absence of an electron acceptor such as oxygen (Hem, 1962, Faust and Aly, 1998). The concentration in natural waters is frequently limited by the solubility of its carbonate. Waters of high alkalinity often, therefore, have lower iron content than water of low alkalinity (O'Connor, 1971 and ASCE and AWWA, 1990). Its concentration in groundwater normally ranges from a few hundredths to about 50 mg/1 with the majority containing less than 5mg/1 (Hem, 1962 and Davis, 1997). At equilibrium in the pH range of 5 to 8.5, this compound is largely in the solid state, the solubility being very low (Stewart, *et al.*1962). Groundwater frequently contains significant levels of dissolved iron (Fe (II) due to more reduced redox conditions (WHO, 2008).

2.4.1.2. Manganese

Manganese is one of the most abundant metals in earth crust it present in the form of oxides and hydroxides. It is one of the common essential trace element and toxic. Suspended particulates resulting from industrial emissions, soil erosion, volcanic emissions and the burning human activities are also responsible for much of the manganese contamination in water (Lemly, 2002).Manganese solids may form deposits within pipes and break off as black particles that give water an unpleasant appearance and taste. And it increases the growth of unwanted bacteria that form a slimy coating in water pipes (Ravisankar, 2016).

2.4.1.3. Cadmium

Cadmium occurs in 0 and $^{+2}$ oxidation states. Hydroxide (Cd $(OH)_2$) and carbonate ($CdCO_3$) dominate at high pH whereas Cd^{2+} and aqueous sulphate species dominate at lower pH (< 8). It precipitates in the presence of phosphate, arsenate, chromate, sulphide, etc. It shows mobility at pH range 4.5 - 5.5. The cadmium may occur in groundwater naturally or as a contaminant from sewage sludge, fertilizers, polluted groundwater or mining and industrial effluents increase of Cd may be changes the pH of the water((Ravisankar, 2016).USEPA MCL in water: is 0.005 ppm (Smith, *et al.,* 1995 and Matthews, 1984).Very high concentration of cadmium may be carcinogenic; may cause kidney damage, lung cancer, ostemalcia or osteoporosis, anaemia, teeth discolouration (WHO, 2006).

2.4.1.4. Copper

Copper occurs in 0, +1 and $^{+2}$ oxidation states. The cupric ion (Cu^{2+}) is the most toxic species of Copper e.g. $Cu(OH)_2$ and $Cu_2(OH)_2^{2+}$.In aerobic alkaline systems, $CuCO_3$ is the dominant soluble species. In anaerobic environments, CuS(s) will form in presence of sulphur. Cu forms strong solution complexes with humic acids. Soil natural conc: 2-100 ppm. USEPA MCL in water: 1.3 ppm (Dzombak and Morel, 1990 and LaGrega, *et al.,* 1994). High levels of copper in drinking water has had been found to cause kidney and liver damage in some people (Kavitha and Elangovan, 2010). Children under one year of age are more sensitive to copper because it is not easily removed from their system. People with liver damage or Wilson's disease are highly susceptible to copper toxicity (Ravisankar, and Prasada, 2016).

2.4.1.5. Zinc

Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. The diet is normally the principal source of zinc. Although levels of zinc in surface and groundwater normally do not exceed 0.01 and 0.05 mg/L, respectively, concentrations in tap water can be much higher because of dissolution of zinc from pipes. The maximum concentration limit of Zn^{2+} in drinking water is 3 mg/L in Ethiopian drinking water standard (EDWS, 2013) and in the WHO guideline (WHO, 2008) and maximum permissible limit is 10 mg/L (Ayotte, *et al.,* 1999). However, drinking water containing zinc at levels above 3 mg/L may not be acceptable to consumers. High levels may cause stomach cramps, nausea and vomiting (WHO, 2006).

2.5. Effect of rainwater and bedrock interaction with iron and groundwater

Iron is readily found in soil and water. Rainwater while percolating through soils and rocks acquires iron in addition to other mineral constituent according to the composition of geological formation (Janardhana , 2015). As rainwater infiltrates the soil, iron can be dissolved and transported out of the soil and carried into groundwater (EMH, 2007 and WHO, 2011). The input of iron in superficial waters is due to the phenomenon of soil leaching and the input in under groundwaters is the result of the water-rock interaction. The presence of iron in natural waters can be attributed to the weathering of rocks and minerals, acid mine drainage, soils rich in organic matter, sewages or iron related industries (Janardhana, 2015 and WHO, 2008). Forestry land use often drastically changes the water quality of river systems in the treatment area. The leaching of inorganic and organic suspended solids and concentrations of dissolved organic matter and nutrients may increase as may water flow and temperature. Aluminium, iron and other metals are also leached from the soil and rinsed into river systems (Ahtiainen,1992).

2.5.1. Iron bacteria

Iron bacteria use iron in the water as an energy source and form slimy growths or gelatinous masses in plumbing. When iron bacteria invade well or plumbing, they can become a serious problem, plugging filters and pump screens or causing an unsightly mess. The slimy or

gelatinous mass of iron-bacteria colonies may also look like oil suspended in the water (Barloková and Ilavský, 2009).

2.5.1.1. Origin of iron bacteria

Iron bacteria occur naturally in the environment. Although iron bacteria can be present in groundwater, they typically exist on the top of the ground in limited numbers because of a limited food supply. The most common origin for iron bacteria in wells is their entry during well drilling or pumps installation operations (http://des.nh.gov).

2.5.1.2. Effects of iron bacteria

Iron bacteria can cause troublesome, persistent, and expensive well and related plumbing problems. These bacteria can cause the water to have an unpleasant taste or odor, corrosion of plumbing equipment, reduction of well yields (clogged screens, pipes and fixtures) and increased infestations of other types of bacteria, including coliform and sulfur reducing bacteria. They often produce an oily sheen on the surface of the water, sewage, or rotten vegetation, rusty, slime buildup in toilet tank, on filters, or the inside of the well casing, reduced well production or efficiency of point-of-use treatment devices (Pontius, 1990). Although iron bacteria can make water unsightly and cause an unpleasant taste and odor; there is no health risk associated with iron bacteria. Iron bacterial contamination can create a water quality environment suitable for disease-causing (pathogenic) bacteria, viruses, and other microbes (Barloková and Ilavský, 2009). It can sometimes be seen as reddish or brown slimy masses on stream bottoms and lakeshores. More serious problems occur when these slimy masses, called biofilms, build up in wells and water systems. The bacteria feed on iron in water and form red-brown [iron] slime in toilet tanks and can clog water systems (Barloková and Ilavský, 2009 and Tyrrel , 1998).

2.5.1.3. Preventing iron bacteria during well construction

To prevent iron bacteria of any kind into a well, the drilling process and the installation of the submersible pump assembly must be kept clean and the well must be disinfected at the completion of any construction, maintenance, or pump work (http://des.nh.gov/organization/commissioner/pip/factsheets/dwgb/index.htm). It is difficult to

totally rid a well and water system of slime-producing bacteria, prevention is the best safeguard against them and their accompanying problems. Well drillers should keep drill bits, pumps and lengths of casing pipe clean and up off the ground. All precautions should be taken during the drilling process to prevent the introduction of these bacteria or organic material that can nourish them. Prevention includes making sure that any construction tool, length of casing pipe or screen that goes into the ground is kept clean. Pump installers should also make sure that the pump, pump piping, or any other equipment to be installed in the well is free of contamination. Iron bacteria problems can often be avoided if both the licensed well driller and pump installer take adequate precautions to keep the new well clean (Yakaya, 1981).

2.5.2. Effects of high iron content

Excessive iron gives objectionable metallic taste. It can also be potentially toxic in humans. Free radicals due to iron overload can cause damage to a wide variety of cellular structures and ultimately kill the cell. Liver cirrhosis is related to drinking water contaminated mainly with high concentration of iron (EMH, 2007 and WHO, 2011). Consequently, there is the need to achieve a controlled amount of iron in water in order to produce the desired taste and color of water as well as to prevent iron overload. World Health Organization (WHO) standards stipulates a limit of general acceptability of 0.3 mg/L of iron for drinking water and an allowable limit of 1 mg/L (Yakaya, 1981). When iron is present above the maximum contaminant levels (MCL), this usually results in discolored water, laundry, and plumbing fixtures. They are seldom considered to be a health risk in drinking water. It can give water an unpleasant taste, odor and color (Mandour, 2012).

2.5.3. Adsorptive iron removal

Different alternatives for removing iron are chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis. However, some limitations in these processes can be high-energy requirement, generation of toxic sludge or other waste products that require disposal or treatment, having low efficiency, labor-intensive operation and lack of selectivity of the process. In contrast, adsorption technique is comparatively more effective and convenient due to factors like low cost, simple design, easy handling and sludge-free cleaning operations

(Njikam and Schiewer, 2012 and Kumar, *et al.,* 2012). Low-cost materials, which are found in large quantity in nature or as byproducts of industrial process or as agricultural waste, are gaining popularity as alternative sorption material (Bailey, 1999). Some of these low cost materials that are suitable for treatment of organic pollutants and metals include: nut shells, wood chips, bone, rice hulls and peat (Amuda, 2006, Robinson, *et al.,* 2001 and Nawar, 1989).

The adsorptive iron removal, however, has several potential advantages over the oxidation-floc formation mechanism, namely longer filter run, shorter filter ripening time, less backwash water use, and less sludge production. If the adsorbent (solid surface) is chosen carefully and the solution chemistry is adjusted appropriately, adsorption-based processes are generally capable of removing metals over a wider pH range and to much lower levels than processes based on precipitation. In addition to offering a more reliable and more efficient removal of uncomplexed metal ions, adsorption processes can often remove inorganically and organically complexed metals that would not be removed by conventional treatment methodology (Benjamin, 1983).

2.6. Aquifer restoration

Because each groundwater aquifer is unique, mineralization of organic and dissolved inorganic contaminants by either abiotic or biotic mechanisms is a function of the spatial heterogeneity of subsurface properties such as pore structure, hydraulic conductivity, and microorganism populations as well as carbon and energy sources (Madsen, *et al.,* 1991). This information, along with laboratory studies of degradation, sorption, and transport (as described by hydraulic conductivity and chemical dispersion), must be incorporated into plans to design and engineer the proper conditions for restoration in the field. The two approaches described below have some steps in common, but differ because biomediation methods are much more amenable to in situ operations. If in situ biomediation methods can be successfully transferred from the laboratory to the field, they have a clear economic and environmental advantage over physical-chemical methods (Raymond, *et al.*1976).

2.6.1. Physical-Chemical Methods

Physical-chemical methods of aquifer remediation/restoration usually include drilling a well into the contaminant plume to remove contaminated groundwater to the surface. Then a variety of separation methods are available such as air stripping, activated charcoal, and reverse osmosis to remove contaminants from groundwater aquifers. (Robeck and Love, 1983 and Baier, *et al.,* 1987). After separating contaminants from the aqueous phase, there is still the problem of disposal of toxic organic and inorganic chemicals, a process usually accomplished by incineration. Recently, studies have been carried out with modified clays that have demonstrated the capacity to adsorb pollutant chemicals from groundwater and then act as catalytic surfaces to decompose sorbed chemicals (Boyd, *et al.,* 1991). At the present time, this method has not been field tested. In the field, it is proposed to locate a pit upstream from the direction of groundwater flow. The pit would then be loaded with the modified clay and pollutant chemicals would be sorbed onto clay surfaces and degraded (Raymond, *et al.*1976).

2.6.2. Bioremediation

Bioremediation of contaminated aquifers include removal of contaminated groundwater to the surface and treatment in a bioreactor and in situ treatment (Thayer, 1991). Bioreactors located on the surface have the advantage that within this containment's bacterial growth can be carefully controlled and appropriate amounts of oxygen and nutrients (nitrogen, phosphorous and carbon sources) can be added to promote rapid decay to high rates of conversion (Raymond, *et al.*1976).

2.7. Iron removal by using readily available materials

Conventionally, iron is removed from groundwater by the processes of aeration and rapid filtration (O'Connor,1971 and Salvato, 1992). By this technique, impurities were precipitated and filtered out to leave clean water behind. For the purpose of oxidation, oxygen was added as an oxidant in the form of pure oxygen or by aeration with the use of cascade aerator. Operation costs and capital investments are so high for this type of treatment plant because the sand layers which work as filter were required to renew from time to time to increase the removal efficiency of iron (Hallberg and Martinell, 1988).

Different mechanisms may contribute to the iron removal in filters; flock filtration, adsorptive iron removal and biological iron removal depends on the groundwater quality and the process conditions (Lerk, 1965, Hatva, 1989, Mouchet, 1992 and Søgaard, *et al.,* 2000). In recent years, a great deal of work has been devoted at identifying suitable, low-cost, and readily available materials to be used in efficient household filters. Potential media include palm ash (Ahmad, 2007) activated alumina, agricultural by-products (e.g. rice hulls), apatite, clay minerals, granular activated carbon (GAC), industrial by-products, iron-oxide (coated sands), manganese-oxide (coated sands), metallic iron (Fe), peat and peat moss, phosphate rocks, seaweeds and their derivatives, wood chips, walnut shell, waste tea, sawdust, Bentonite, china clay and zeolites (Mohan and Pittman, 2007, Gupta and Suhas, 2009 and Malik, *et al.,* 2009).

Chemical free removal of toxic metal ions from dilute aqueous solutions by biosorbents and low cost adsorbents has been demonstrated to be a useful alternative to conventional treatment systems. Adsorption is a physical process where soluble molecules (adsorbates) are removed by attachment to the surface of a solid substrate (adsorbent) primarily by Van der Waals forces, although chemical or electrical attraction may also be important. Adsorbents must have a very high specific surface area (Wang and Peng, 2010).

2.8. Peat moss

Peat moss is a complex soil material containing lignin and cellulose. Peat moss has a large surface area and is highly porous so that it can be used to bind heavy metals. Peat moss is a good absorbent for all metals. It is widely known that peat moss exhibited a high CEC and complexities towards metals due to the presence of carboxylic, phenolic and hydroxylic functional groups (Ahmad, 2015). Decayed, dried *Sphagnum* moss has the name of peat or peat moss. This is used as a soil conditioner, which increases the soil's capacity to hold water and nutrients by increasing capillary forces and cation exchange capacity. This is often necessary when dealing with very sandy soil, or plants that need increased or steady moisture content to flourish (Hood, 1995). Peat comes from a variety of different sources and the adsorption capacity of peat in removing various types of pollutants varies a lot depending on peat origin, degree of decomposition, particle size, metal concentration, ligand concentration and competing ions. Constituents such as decomposed organic matter and mineral particles are the main build up

components of peat. It contains mainly lignin and hemicelluloses, which produces humic substances once after it has been broken down (Brady, 2002).

2.8.1. The role of humic acid in adsorptive removal of divalent metals

Humic substances are capable of interacting with metal ions to form metal-organic complexes of different stabilities and characteristics. Oxygen functional groups are involved in the formation of surface complexes with aqueous metal species and ion exchange with the displacement of protons. The capacity of humic and fulvic acids to combine with metals is usually attributed to their high contents of substituents such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O) (Piccolo and Stevenson, 1982 and Xiao and Thomas, 2004).

2.8.2. Process of adsorptive metals removal on peat moss

Bryophytes are an informal group consisting of three divisions of non-vascular land plants such as the liverworts, hornworts and mosses. They are characteristically limited in size and prefer moist habitats although they can survive in drier environments (Levetin and McMahon, 2012). Although no bryophyte seems to be restricted to substrates containing iron, photosynthesizing bryophytes have the ability to change soluble reduced metals to their insoluble oxidized form and make this molecule visible. Iron oxide completely enveloped the moss in a hard cover found that mosses *Sphagnum* play active roles in deposition of divalent metals. One of the means by which bryophytes sequester both metals and nutrients is to bind them by cation exchange to cell walls of leaves. In this process, *Sphagnum* places hydrogen ions in the water in exchange for cations (Brown, *et al.,* 2000).

Peat moss is a complex organic material, which is derived from the partially decomposed residue of *Sphagnum* moss, sedges and other plants in the waterlogged environment of marshes, bogs, and swamps. The precise composition of the peat formed depends on such factors as the nature of the vegetation, the regional climate, the acidity of the water, and the degree of metamorphosis. Peat is mostly composed of lignin and hemicelluloses, which partly break down to humic substances. These substances bear polar functional groups, such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides, and ethers that can be involved in chemical bonding. The polar characteristics of peat make the specific adsorption potential for dissolved

solids, such as metals and polar organic molecules quite high. This has led to the examination of the potential of peat as an agent for the purification of wastewaters contaminated with dissolved metals (Brown, *et al.,* 2000, Chaney and Hundemann, 1979 and Chauvet, 2003).

2.8.3. Factors affecting metals adsorption on peat moss

A number of factors are responsible for influencing the extent of heavy metal adsorption on peat moss. Some of these include initial pH, temperature, adsorbent dose, shaking time, initial metals concentration, adsorbent's particle size, contact time and specific surface area of adsorbent. The specific surface area of the solid adsorbent is important, as the adsorptive capacity generally increases with an increase in specific surface area. Pore structure and particle size are related factors, as the surface area of nonporous adsorbents increases considerably with a decrease in particle size. However, for highly porous adsorbents, most of the surface area resides in the internal pore structure resulting in the adsorptive capacity being independent of particle size (Faust and Aly, 1998). Under microscopic examination, peat moss exhibits a porous cellular structure (McKay and Porter, 1997). The porous characteristic of peat moss contributes to the effectiveness of physical adsorption. However, the degree and rate of chemisorptions of metals on peat moss is controlled by other factors, and surface area is only one contributor. The number of available adsorption sites on peat moss is pH dependent. The dissociation of protons from carboxylic and phenolic groups determines the charge of the peat surface. Below pH 2.5-3.0, the surface is positively charged while at pH greater than 3.0, the surface is negatively charged and favours cation adsorption (Kalmykova, *et al.,* 2006a). The optimum pH for metal removal from aqueous solution also varies, depending on the target metal. Below the pH range of 3.0 - 3.5, the removal for most metal ions from solution ceases (Ho, 1995).These conditions can influence the speed of a chemical reaction and affect the reaction's mechanism and transition states (Stum and Lee, 1961).

3. MATERIALS AND METHODS

3.1. Description of the study area and study design

The study area, shown in the Figure 3.1 is located at the SNNPR Kembata Tembaro Zone, which is located from Addis Ababa 335 km Southern Ethiopia. It is characterized by intensive agricultural and human activities. The climate of this area is temperate (*Woyna Dega in Amharic*), with a mean annual temperature and precipitation of 22℃and 1100 mm/year, respectively (https://agricultureandfoodsecurity). This is approximately lies between at latitude 7°16' 44.338"N - 7°7' 22.4412"N and longitude 37°56' 21.38"E - 37°23' 1.54"E and the elevation of 2101m above sea level. The Kembata Tembaro Zone water supply mainly concerns the borehole and shallow wells as a source of potable water. The study area covers an area of 1,355.89 km^2. There is a population of 117,170 of which male 66,818, and female 69,853. Density of population is 502.13per km^2. However, pure water supply was the main objective of the Zone. The Zone's water supply system mainly through iron pipelines.

The study was designed to conduct in Kembata Tembaro Zone particularly Hadero – Mandoye Kebele and Mugunja Kebele, Kechabira - Mesena Kebele, Kedida Gamela - Zato Shodere Kebele, Aze Dobo'o, Bezana Benara, Abonssa and Langute Chafee groundwater heavy metal impact assessment and adsorptive removal of iron, manganese, cadmium, copper and zinc using locally available material(peat moss) as low cost. It was decided to collect sample of groundwater and analyze experimentally to check the TDS, pH, turbidity, DO, iron(Fe) ,(manganese(Mn), cadmium(Cd), zinc(Zn) and copper(Cu).

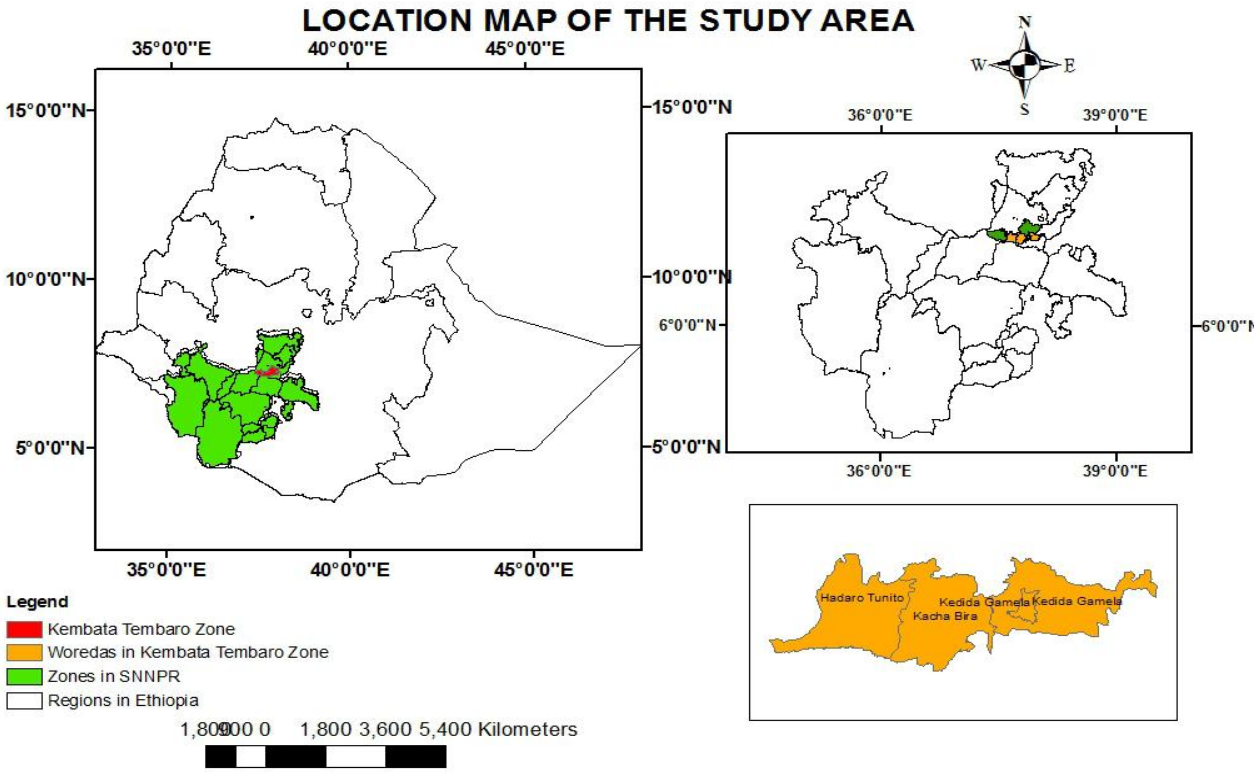

Figure 3.1: The map of the study area

3.2. Chemicals and instruments/or apparatus

Analytical grade reagents of 97% Iron(II) nitrate (FINKEM), 99% Manganese(II) nitrate (FINKEM), 99% Cadmium(II) nitrate (NICE), 95% Copper(II) nitrate (FINKEM) and zinc(II) nitrate were used to prepare the required amount of metal concentration for the adsorption experiment. Concentrated nitric acid (HNO_3) was used to rinse the apparatus to free from contamination. Analytical grade reagents of 97% sodium hydroxide (NaOH) (Central Drug House of (P) Ltd. INDIA) and 37% hydrochloric acid (HCl)(Aldrich, A.C.S. Reagent, Germany) were used to adjust pH. Deionized water was used to wash apparatus and to dissolve metal nitrates. To measure the concentration of metals in the groundwater samples, atomic absorption spectrometer was used. The pH-meter was used for the measurement of the pH values of the groundwater samples and to adjust pH for the adsorption experiments at room temperature. Turbidity was analyzed using nephelometric turbidity meter. The electrical conductivity, pH, TDS and salinity were examined using a multifunction PCD 650 water proof portable meter

(CyberScan Waterproof Portable pH/ORP/Conductivity Meter from Eutech Instruments, Metex Corporation Limited), filter material, glass, volumetric flasks and plastic transfer pipettes were used for the experiments.

All solutions used in this study were diluted with distilled water as required, and then was stored in cool dry place for later use. All glasses and other apparatus were washed with detergent and distilled water to free from any contamination.

3.3. Water sampling sites

Groundwater samples were collected from the following eight wells and boreholes (Hadero Tunto– Mandoye Kebele and Mugunja Kebele, Kechabira - Mesena Kebele, Kedida Gamela - Zato Shodere Kebele, Aze Dobo'o, Bezana Benara, Abonssa and Langute Chafee) of Kembata Tembaro Zone. The samples were collected carefully in plastic containers by avoiding floating materials. Sampling bottles were washed and cleaned with dilute nitric acid and rinsed with deionized water to avoid contamination and confusion. The stoppers of the sampling bottles were tight properly to prevent external contamination and unnecessary external reaction with the sample water.

The eight groundwater samples were collected and analyzed for TDS, PH, turbidity, dissolved oxygen, iron (II), manganese(Mn), cadmium (Cd), zinc(Zn) and copper(Cu).

Table 3.1: Sampling sites of the study area

Sampling sites	Location (GPS)	Woreda Name	Kebele Name
Site 1	7°11'58.069"N, 37°31'38.30"E	Kedida	Aze Dobo'o
Site 2	7°10'61.948"N, 37°37'26.33"E	Kachabira	Mesena
Site 3	7°13'28.223"N, 37°54'51.62"E	Kedida	Abonssa
Site 4	7°11'39.680"N, 37°51'39.35"E	Kedida	Zato Shodere
Site 5	7°7'22.4412"N, 37°23'1.54"E	Hadero-Tunto	Mandoye
Site 6	7°13'34.024"N, 37°52'46.93"E	Kedida	Bezana Benara
Site 7	7°16'44.338"N, 37°56'21.38"E	Adilo	Langute Chafee
Site 8	7°9'12.8412"N, 37°31'0.04"E	Hadero-Tunto	Mugunja

3.4. Physicochemical characteristics

The main physicochemical characteristics which water and wastewater are examined for are pH, appearances, colour, turbidity, odour, temperature (Herschdoerfer, 1986). To find physicochemical characteristics of groundwater of these areas, it was measured onsite using portable equipments. The solubility of iron and heavy metals are strongly influenced by pH and redox variations, any changes in environmental conditions during sampling can rapidly change the sample composition. Therefore, measurements of pH, conductivity, temperature and dissolved oxygen (which affect iron, manganese, cadmium, copper and zinc mobility) were carried out immediately on-site (Langenegger, 1994).

3.4.1. PH, Temperature and Dissolved Oxygen

To measure pH, temperature and dissolved oxygen a Multi-Probe was used. The Multi-Probe was submerged into a bucket filled with sample water. The measurements were done in triplicates (Muhammad *et al*., 2013).

3.4.2. Total Dissolved Solutes (TDS) and Conductivity

A total dissolved solid (TDS) is the measure of total dissolved inorganic salts and other substances that are dissolved in water. Total dissolved solids (TDS) and conductivity of the groundwater samples were measured using conductivity meter(Gaur, 2008 and Muhammad *et al*., 2013).

3.4.3. Turbidity

Turbidity is measure of the concentration or size of suspended particles (cloudiness) based on the scattering of light transmitted or reflected by the medium and the unit is nephelometric turbidity unit (NTU). Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through a water sample. Turbidity was measured by nephelometric turbidity meter(John C.*et al*,2012) .

3.4.4. Colour and odour

Colour and odour of the water was checked by observing water by field observation. Visual comparison about 20ml of the sample and 20ml of distilled water was taken in two separate wide mouthed test tubes. The results were tabulated by comparing the colour of the sample with distilled water(WHO 4thEd., 2004 and Gaur,2008).

3.5. Heavy metal assessments using pollution index methods

3.5.1. Heavy metal pollution index (HPI)

Heavy metal pollution index (HPI) is an effective method to characterize the groundwater pollution. It represents the composite influence of metals on the overall quality of water (Reza and Singh, 2010, Reza, *et al*., 2011 and Sheykhi and Moore, 2012). It is based on the weighted arithmetic quality mean method, which is developed in two basic steps (Prasad and Bose, 2001). A rating scale was developed for each of the selected parameters and a weight (Wi) was allocated to it. In this indexing, weights (Wi) between 0 and 1 were assigned for each metals. The second step is selecting the pollution parameter on which the index is to be based on. The rating can be assessed by making value inversely proportional to the recommended standard (Si) for corresponding parameter. Water quality and its suitability for drinking purpose can be examined by determining its quality index (Prasad and Mondal, 2008). The HPI was calculated using the equation 3.1:

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \qquad (3.1)$$

Where Q_i is the sub-index of ith parameter, Wi is the unit weightage defined as reciprocal value of Si where Si is the maximum permissible limit for drinking water and n is the number of parameters considered. The Q_i sub-index is calculated using the equation 3.2:

$$Q_i = \sum_{i=1}^{n} \frac{Mi}{Si} \times 100 \qquad (3.2)$$

Where M_i is i^{th} parameter monitored and S_i is the heavy metal's standard values , in ppm (µg/L). Heavy metal pollution index can be classified into three categories as low (<19), medium (19–38) and high (>38) (Kumar, *et al.,* 2012). For this index, the intended use is for drinking hence the critical pollution index value is 100. The higher HPI value causes greater damage to the health. In this study the W_i and S_i are taken as the inverse of MAC and (WHO, 2011) standard, (Table 3. 2). For this study Fe, Cd, Cu, Zn and Mn were used for the computation of the indexes.

3.5.2. Heavy metal evaluation index (HEI)

The pollution evaluation indices (HEI) of groundwater samples were assessed by employing heavy metal evaluation index (HEI) as reported in the literature (Al-Ami, *et al*., 1987 and Backman, *et al*., 1997). The heavy metal evaluation index gives an overall quality of groundwater with respect to heavy metals (Bhuiyan, *et al*., 2010, WHO, 2011 and Edet and Offiong, 2002). It was evaluated using the average values of heavy metals in the groundwater samples. It was calculated using equation 3.3:

$$HEI = \sum_{i=1}^{n} \frac{H_C}{H_{mac}} \qquad (3.3)$$

H_c is the monitored value of the i^{th} parameter and H_{mac} is the maximum admissible concentration of the i^{th} parameter (Edet and Offiong, 2002)

Table 3.2: Adopted standard for computed indices

Heavy metals	Wi	Si	I	MAC (µg/l)	MAC in mg/l
Cu	5×10^{-4}	2000	2000	2000	2.0
Fe	5×10^{-3}	300	300	300	0.3
Mn	2×10^{-2}	400	400	400	0.4
Cd	2×10^{-1}	5	5	5	0.005
Zn	3.33×10^{-4}	3000	3000	3000	3.0

MAC: maximum admissible concentration/upper permissible, W: Weightage (1/MAC)

S: Standard permissible in ppb, I: Highest permissible in ppb. The HEI index may be classified into three categories as follows: low (HEI < 10), medium (HEI = 10 – 20) and high (HEI > 20)(Yerima, *et al*., 2019).

3.5.3. Contamination index (CI)

The degree of pollution in groundwater samples were assessed by employing degree of contamination (C_{deg}) as reported in the literature (Backman, *et al.,* 1997). The degree of contamination is used as a reference of estimating the extent of metal pollution (Bhuiyan, *et al.,* 2010). The contamination factors takes into consideration both the number of parameters that exceed the upper permissible limit or guide values of potentially harmful elements and the concentration exceeding these limit values (Backman, *et al.,* 1997). To determine contamination index (CI) the following equation were used:

$$C_I = \sum_{i=1}^{n} C_{fi} \tag{3.4}$$

C_{fi} = represent the contaminant factor for the i^{th} component and is calculated from the equation

$$C_{fi} = \sum_{i=1}^{n} \frac{C_{Ai}}{C_{Ni}} - 1 \tag{3.5}$$

Where C_{Ai} = analytical value of the i^{th} component and C_{Ni} = upper permissible concentration of the i^{th} component (N denotes the normative value) (Backman, *et al.,* 1997).This index may be classified into three categories as follows: low ($C_{deg} < 1$), medium ($C_{deg} = 1–3$) and high ($C_{deg} > 3$) (Al-Ami, *et al.,* 1987, Backman, *et al.,* 1997 and Bhuiyan, *et al.,* 2010).

3.6. Correlation analysis

Correlation analyses were used to establish the relationships, as well as evaluating their common sources of the detected heavy metals in the groundwater samples. The Pearson correlation coefficient is widely used to measure the dependence between two quantities. It is a useful index in aerography, biology, and pollution assessment. It was selected to reveal the relationship between the heavy metal concentrations and physicochemical properties (i.e., temperature, pH, and DO) of groundwater (Pearson, 1901). The correlation coefficients (*r*) between heavy metal pollutants and physico-chemical properties were calculated using the following equation:

$$r = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sqrt{[\sum(x-\bar{x})^2][\sum(y-\bar{y})^2]}} \tag{3.6}$$

Where: r = Correlation coefficient, n = Sample size, x = Value of the independent variable, y = Value of the dependent variable. The value of correlation coefficient ‘r’ ranges from -1 to +1. If r

= +1, then the correlation between the two variables is said to be perfect and positive. If r = -1, then the correlation between the two variables is said to be perfect and negative. If r = 0, then there exists no correlation between the variables (Pearson, 1901).

3.7. *Sphagnum* peat moss (adsorbent) collection and preparation

The *Sphagnum* moss was harvested in January 2019, from Southern Ethiopia Kembata Tembaro Zone, Hambercho Mountain. This is approximately at latitude 7°33′N, longitude 37°85′ E and the elevation of 2600m above sea level. The *Sphagnum* peat moss was collected, washed, dried and decomposed under shade for one week. It was rinsed with deionized water, dried at 105°C and grinded to fine powders using a blender and sieved to 1-2mm particle size before being used.

3.8. Preparation of Fe^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}solution

The concentration of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} solutions were prepared by dissolving the required amount of metal nitrates ($Fe(NO_3)_2$ = 16.07 mg/L, $Mn(NO_3)_2$ = 16.27 mg/L, $Cd(NO_3)_2$ = 10.51 mg/L , $Zn(NO_3)_2$ = 14.47 mg/L and $Cu(NO_3)_2$ = 14.68mg/L) in distilled water to prepare 5 mg/L of each metals. The same procedure were followed to prepare 10 and 15 mg/L of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} solutions in different beakers for the experiments to test the adsorptive ability of *Sphagnum (*peat moss) in the laboratory.

3.8.1. Experimental set-up for Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} adsorption on peat moss

The adsorption of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} ions on peat moss were studied at room temperature (25℃). These tests were done in 250 mL conical flasks. The conical flasks were filled with 5-15 mg/L of Fe^{2+}, Mn^{2+}, Cd^{2+},$Zn^{2+}$and Cu^{2+} with different amount of peat moss (500 mg and 1000 mg). The required amount of peat with Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} of a known concentration were shaken with orbital shaker at 200 rpm, at constant temperature (25℃) for 3hrs at pH 3,6 and 9. Samples were withdrawn at suitable time intervals, filtered through Whatman filter paper № 1. After filtration, the adsorption of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} on peat moss were examined as a function of pH, time, peat dose and total metals concentration in the solutions.

The initial pH adjustment was carried out either by hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions and the initial adjusted pH was recorded. Finally, concentration of heavy metals were determined spectroscopically using AAS scientific model NOVA 400 (Sreenivasareddy, 2017). Effect of contact time, temperature, pH and initial concentration were also determined. Percentage removal of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} and adsorption capacity of peat were calculated using the equation 3.7 and 3.8 respectively.

$$\text{Percentage removal of metal (II) ions (\%R)} = \frac{C_i - C_f}{C_i} * 100 \quad (3.7)$$

$$\text{Adsorption capacity } (q_e) = \frac{C_i - C_f}{m} * V \quad (3.8)$$

Where, q_e (mg/g) is the amount of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} adsorbed by peat moss, C_i and C_f (mg/L) are the liquid phase concentrations of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+}at initial time and final time, respectively; V(L) is the volume of the solution (L), and m is the mass of dry mass of the peat moss (adsorbent used) in gram.

3.9. Adsorption kinetic model

The process of adsorption in dynamic conditions can be characterized by a kinetic equation according to which the rate of adsorption (or the amount of substance adsorbed in a unit time by a unit volume of the adsorbent) is directly proportional to the mass transfer coefficient, the driving force of the process and the surface area of the adsorbent by a unit depth (Pavlov, *et al.,* 1979).Kinetic models' equations assume that measured concentrations are equal to concentration or amount of adsorption sites and that in well agitated systems external film diffusion is negligible. (Ahmad, *et al.,* 2018 and Aksu, 2001).

The kinetics of adsorption of Fe^{2+}, Mn^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} onto peat moss were carried out by withdrawing and analyzing the samples at the time interval of every 5 min for the first 1hr and later at every 10 min for another 1hr until the consecutive residual of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} concentrations became closer. The adsorption kinetic experiments were carried out separately for each metal for three different initial concentrations such as 5, 10 and 15 mg/L at

25℃. The capacity of adsorption of each metal ion on peat moss at final time was calculated by using equation (3.9) (Bulut and Ozacar, 2008).

3.9.1. Pseudo First Order Kinetic Model

This model is associated with physical adsorption where the adsorption process is controlled by weak interactions between the adsorbate and the adsorbent surface (Radnia, *et al.,* 2012). The pseudo-first order rate equation by the Lagergren is given as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3.9)$$

Where q_e and q_t are the adsorption capacities at equilibrium and at time t (mg/g) respectively and K_1 is the pseudo first order adsorption rate constant (L/min). Integration at: t = 0 to t = t and $q_t = q_t$, gives the linear form of the equation as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (3.10)$$

The values of k_1 and q_e were obtained from the slope and intercept of the plot of log (q_e-q_t) versus t respectively (Ho and McKay,1998).

3.9.2. The Pseudo Second Order Kinetic Model

This model is based on the assumption that the adsorption is controlled by chemical adsorption (chemisorption) (the rate of direct adsorption/desorption process seen as a kind of chemical reaction) (Ho and Mckay, 2000). In chemisorption, the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and finds sites that maximize their coordination number with the surface (Amuda, 2006). The pseudo-second order kinetic model is given (Ho and McKay, 1999) as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3.11)$$

Integration at: t = 0 to t = t and $q_t = q_t$, the linear form of the equation was obtained as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3.12)$$

Where k_2 (g/min) is the pseudo second order rate constant. The values of model parameters, q_e, k_2 were calculated from the slope and intercepts of the linear plot of $\frac{t}{q_t}$ vs t (Ho and McKay, 1999).

3.10. Adsorption equilibrium isotherm experiments

Adsorption equilibrium isotherm can be used when the sorption process is rapid compared to the flow velocity. In these adsorption isotherm tests, the experiments were carried out by varying the initial Fe^{2+}, Mn^{2+}, Cd^{2+} , Zn^{2+} and Cu^{2+} concentrations, contact time, amount of the adsorbent, pH of the initial solution. The three conical flasks were filled with different concentrations of peat moss thoroughly mixed into 5-15 mg/L of Fe^{2+}, Mn^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} solutions. The three different tests at pH 3, 6 and 9 each used a range of initial Fe^{2+}, Mn^{2+}, Cd^{2+} , Zn^{2+} and Cu^{2+} concentrations (C_i) from 5 – 15 mg/L. The conical flask containing the adsorbent and the stock solution was placed in a orbital shaker and shaken for 3hrs at 200 rpm at room temperature (25℃) at different time periods at intervals of 5-10 minutes until equilibrium was attained (constant concentration of metal (II) ion in the filtrate). After that, the reaction mixtures were filtered using Whatman № 1 filter papers, and the metal concentrations and final pH was analyzed from the filtrate. The effect of different retention times, pH, and concentration of Fe^{2+}, Mn^{2+}, Cd^{2+} , Zn^{2+} and $Cu^{2+}$and temperature on removal of these metals by dried peat moss were considered in batch system. Blank solutions was prepared and analyzed for the Fe^{2+}, Mn^{2+}, Cd^{2+} , Zn^{2+} and Cu^{2+}concentrations, final pH and temperature were measured.

The contact time needed for adsorption equilibrium is dependent on the initial metal concentrations (Hanzlik, *et al.,* 2004). Equilibrium time can cover a wide range, 40-60 minutes for most divalent ions (Brown, *et al.,* 2000). The amounts of Fe^{2+}, Mn^{2+}, Cd^{2+} , Zn^{2+} and Cu^{2+}adsorbed on peat moss at different equilibrium concentrations were plotted. Finally, the concentration of Fe^{2+}, Mn^{2+}, Cd^{2+} , Zn^{2+} and Cu^{2+} in the supernatant was measured using AAS (Repo, *et al.,* 2011a). The performance of peat moss adsorption was evaluated in terms of its removal efficiency by using the equation (3.8) above.

3.10.1. Freundlich Isotherm Model

Freundlich's Adsorption isotherm is commonly used to describe the adsorption characteristics for the different adsorbents (Hutson and Yang, 2000 and Richard, 2009). The Freundlich model, which is an indicative of surface heterogeneity of the adsorbent. To study the validity of Freundlich adsorption isotherm, the following equation was used.

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3.13}$$

Where K = Freundlich isotherm constant (mg/g) n = adsorption intensity; C_e = the equilibrium concentration of adsorbate (mg/L), Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). The Freundlich isotherm constants K and n was calculated by linear regression. Linear equation of the Freundlich isotherm is as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3.14}$$

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process (Voudrias, *et al*., 2002). In Freundlich sorption isotherm if 1/n =0 indicate an irreversible isotherm, 0 < 1/n < 1 shows a favorable adsorption and 1/n > 1 indicates an unfavorable isotherm when 1/n becomes equal to 1 then Freundlich sorption isotherm becomes linear sorption isotherm(Areco, *et al*., 2014).

3.10.2. Langmuir Isotherm Model

The Langmuir equation is valid for monolayer adsorption on to a surface. The Langmuir model depend on the assumption of that uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir model quantifies and contrast the adsorptive capacity of various adsorbents (Elmorsi, 2011). Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered (G¨unay, *et al.,* 2007). The Langmuir isotherm is valid for monolayer adsorption onto a

surface containing a finite number of identical sites. The Langmuir model represented the following equation (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{q_m k_e} + \frac{C_e}{q_m} \quad (3.15)$$

Where C_e is concentration of adsorbate at equilibrium (mg/g),q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/g), which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity. R_L is the dimensionless constant separation factor, which is, expresses the essential characteristic of Langmuir isotherm (Weber and Chakravorti, 1974, Ayawei, *et al.,* 2015).

$$R_L = \frac{1}{1 + K_L C_0} \quad (3.16)$$

Where C_0 is the initial concentration (mg/g) and K_L is the Langmuir constant.

Equation for monolayer adsorption is given in equation 3.17

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (3.17)$$

Where q_e (mg/g) is the amount adsorbed at the equilibrium concentration C_e (mol/ L), q_m (mg/g) is the Langmuir constant representing the maximum monolayer adsorption capacity and b (L mol^{-1}) is the Langmuir constant related to energy of adsorption.

3.11. Data Analysis

After completing lab work and field tests, the results were compiled, tabulated and analyzed. As the study is aimed at assessing the heavy metal contamination's of groundwater and physicochemical parameters, data obtained were analyzed by a computer program to analyze tabulated data using WPS Spreadsheet 2019. Descriptive statistics like percentage, mean and range were used to describe the findings by means of appropriate statistical tools. WPS spreadsheet was used for the statistical analysis. The maximum admissible concentration of the WHO and Ethiopian standard values of Copper, Iron, Manganese, Cadmium and Zinc, (2.0, 0.3, 0.4, 0.005 and 3.0) mg/L respectively were used to calculate pollution indices and to compare with the findings. Different tables, graphs, charts were used for the presentation of the findings.

4. RESULT AND DISCUSSION

4.1. Results of the heavy metals distribution of the groundwater

The collected groundwater were analyzed using AAS scientific model NOVA 400 and the results were presented in Table 4.1. The groundwater samples were analyzed to assess the Cd^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} concentrations because they are characterized as unwanted heavy metals in drinking water and can infiltrate into the water system as reported in the literature (Nagarajan, *et al.,* 2012).

This study revealed that most of the groundwater wells and bore holes have higher concentration of iron (II) and manganese (II). From the tested metals, iron found the maximum average concentration (5.14 mg/L) and the next highest metal was manganese (3.47 mg/L). The maximum concentration (14.17 mg/L) of Fe^{2+} was recorded in S_8, while the lowest concentration (0.274 mg/L) was recorded in S_3. The highest amount of Mn^{2+} concentration was observed in S_1 (5.721 mg/L) and lowest concentration was observed in S_3 (0.038 mg/L). In the S_2 the maximum average concentration was observed for iron, 5.856 mg/L and the lowest concentration was measured for the cadmium 0.085 mg/L.

In the S_3 the average concentration of Mn^{2+} is 0.038 mg/L and the Fe^{2+} concentration is 0.274 mg/L. Iron in site 5 and 8 showed the highest concentrations; 9.34 and 14.17 mg/L respectively while site 1 and 8 showed the highest concentrations of Mn^{2+}; 5.721 and 5.350 mg/L respectively. Except site 8, all of the sites had the lowest concentration of cadmium. The maximum average concentration of Cd^{2+} was recorded at S_8 (0.005 mg/L) and the lowest concentration was recorded at S_2 and S_3 (0.001 mg/L). The maximum concentration of Cu^{2+} (1.493 mg/L) was recorded at S_4 and the minimum concentration was recorded in S_5 (0.006 mg/L). The maximum concentration of Zn^{2+}(0.062 mg/L) was observed at S_3 and the average lowest concentration of Zn^{2+} was measured in the water sample collected from S_8 (0.023 mg/L). Except S_3, all of the tested sites had manganese levels exceeding 0.4 mg/L, the WHO and Ethiopia guidelines. Except S_3, all of the sites had iron concentrations much exceeding 0.3 mg/L, the WHO and Ethiopia guideline values. Generally, iron and manganese concentrations of the groundwater samples were the highest. The elevated levels of metals in groundwater are likely a

wide problem. The highest concentration of these metals could cause health problems if there are no treatment and consideration. The concentration of iron and manganese in the agricultural area were significantly higher than the other groundwater samples. The presence of higher concentration of iron and manganese in the groundwater may cause health hazards to the population of these areas.

Table 4.1: The heavy metals distribution of the groundwater (S_1-S_8)

Concentration of metals (mg/L)	Sites								WHO Standard (mg/L)	Ethiopian Standard (mg/L)
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8		
Iron (Fe)	5.574	5.86	0.274	4.61	9.34	0.33	0.98	14.17	0.3	0.3
Cadmium (Cd)	0.004	0.001	0.001	0.003	0.003	0.002	0.004	0.005	0.005	0.003
Manganese (Mn)	5.721	4.32	0.038	1.64	1.56	4.75	4.45	5.35	0.4	0.5
Copper (Cu)	1.326	0.35	0.51	1.49	0.006	0.21	0.29	0.42	2.0	2.0
Zinc (Zn)	0.03	0.045	0.062	0.039	0.0012	0.045	0.051	0.023	3.0	5.0

In this study, almost all of the groundwater samples exceeding the recommended limits of WHO and Ethiopian drinking water standard values for iron and manganese.

4.1.1. Available concentration of iron (Fe)

In this study, the concentration of Fe^{2+} ranges from 0.274 to 14.17 mg/L. The Fe^{2+} concentrations of the groundwater samples collected from the site 8 contained an average value of 14.17 mg/L (Table 4.1). The result indicates that groundwater samples are higher than the recommended values of iron. The standard deviation was 4.845, which indicates that 87.5% of these groundwater are not safe for drinking as well as other purposes in respect to iron as reported in the literature (Charles, *et al.* 2018). The highest concentration of iron is occurred along with the relatively lower value of pH. Except S_3, all of the seven groundwater samples were found within the higher value of iron than the recommended limit for drinking water as well as irrigation purposes. The acceptable (WHO, 2008 and Ethiopian (EDWS, 2013) guideline value of $Fe^{2+}$is 0.30 mg/L.

4.1.2. Available concentration of manganese (Mn)

The Mn^{2+} concentration of the groundwater sample collected from the S_1 contained an average value of 5.721 mg/L (Table 4.1). The higher Mn^{2+} concentration at S_1 occurred may be due to agricultural fertilizer. The result indicates that these groundwater are higher than that of WHO and Ethiopian recommended guidelines for drinking as well as for irrigation purposes in respect of Mn^{2+} as reported (WHO, 2011). The standard deviation was 2.094, which indicates that except S_3 (0.038 mg/L) all of the seven samples were found with the higher than the recommended limit for drinking water as well as irrigation purposes. The acceptable (WHO, 2008 and Ethiopian (EDWS, 2013) guideline value of $Mn^{2+}$is 0.4 mg/L.

4.1.3. Available concentration of Cadmium (Cd)

The average concentrations of Cd^{2+} was very low, which was 0.0032 mg/L as shown in Table 4.1. All samples are under the recommended values of the WHO and Ethiopian drinking water standard value. The standard deviation was 0.00146, which indicates that all of this groundwater can safely be used for irrigation as well as other purposes in respect of cadmium as reported in the literature (Charles, *et al.* 2018). The acceptable (WHO, 2008) and Ethiopia (EDWS, 2013) guideline value of Cd^{2+} is 0.005 mg/L.

4.1.4. Available concentration of Copper (Cu)

The average concentrations of Cu^{2+} was very low, which was 0.575 mg/L. The Cu^{2+} concentrations of the groundwater samples collected from the site 1 contained an average value of 1.32 mg/L as shown in Table 4.1. The average maximum Cu^{2+} concentration was recorded at S_4 (1.493 mg/L) occurred concurrently with the relatively higher value of pH. The standard deviation was 0.536, which indicates that all of this groundwater can safely be used for irrigation as well as other purposes in respect of copper (Chen, *et al*.,1999). All of the groundwater samples were found within the recommended limit for drinking water as well as irrigation where its acceptable limit is 2.0 mg/L.

4.1.5. Available concentration of zinc (Zn)

The average concentrations of Zn^{2+} was very low, which is 0.037 mg/L as shown in Table 4.1 The result indicates that these groundwater are under the recommended guideline values of WHO and Ethiopian for drinking as well as for irrigation purposes in respect to Zn^{2+}as reported in the literature (Charles, *et al.* 2018). The standard deviation was 0.01895, which indicates that all of the groundwater samples were found within the recommended limit (3.0 mg/L).

4.2. Correlation analysis

From the correlation coefficients, high correlation was observed for iron (Fe^{2+}) with correlation coefficient, r = -0.731, which is consistent with the findings (Abdel-Salam and Abu-Zuid, 2014). The Pearson correlation analysis revealed a negative correlation between Cd^{2+} (r = -0.370), Fe^{2+} (r = -0.731) and Mn^{2+} (r = -0.238) in the groundwater samples (Table 4.2) suggests that these metals are influenced by pH. In the groundwater samples, a correlation coefficient for Cu^{2+} and Zn^{2+} are positive. The correlation between copper and zinc with pH are (r = 0.219 and 0.724 respectively). This is consistent with the findings of the reported in the literature (Sappa, *et al.,* 2014). The results of the correlation coefficient indicated that there is a negative correlation between pH with Cd^{2+}, Fe^{2+} and Mn^{2+} as reported in the literature (Torre, *et al.,* 2010).

Table 4.2: Correlation coefficient with Fe^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}concentrations of the groundwater samples with pH

Sites	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	r	R^2
pH	6.3	6.5	7.1	7.4	5.9	7.6	6.9	6.3		
Fe^{2+}	5.574	5.85	0.274	4.61	9.34	0.33	0.98	14.17	-0.731	0.537
Mn^{2+}	5.721	4.32	0.038	1.64	1.56	4.75	4.45	5.35	-0.238	0.057
Cd^{2+}	0.004	0.001	0.001	0.003	0.003	0.002	0.004	0.005	-0.370	0.145
Cu^{2+}	1.326	0.35	0.51	1.49	0.006	0.21	0.29	0.42	0.2193	0.048
Zn^{2+}	0.03	0.045	0.062	0.039	0.0012	0.045	0.051	0.023	0.724	0.416

The relationship between pH and iron showed that the iron concentration decreases with increasing pH values. From the groundwater samples, site 1, 2, 5, 7 and 8 are acidic (pH 6.3, 6.5, 5.9, 6.9 and 6.3) and; iron concentrations are 5.57, 5.85, 9.34, 0.98 and 14.17 mg/L, respectively. The pH level below 6.5 tends to cause corrosion problems(Nagwa and Mohammed, 2016). In groundwater sample S_6 (pH is 7.6; iron concentration is 0.33 mg/L). The relationship between pH and manganese values displayed that the manganese concentration decreases with increasing pH values. Generally, the correlation analysis showed that the relationship between pH and Cd^{2+}, Fe^{2+} and Mn^{2+} values displayed that the concentration of Cd^{2+}, Fe^{2+} and Mn^{2+} decreases with increasing pH values. The correlation value revealed that copper and zinc concentrations increased with increasing pH values.

4.3. Heavy metals distribution assessment using pollution index methods

4.3.1. Heavy metal pollution index (HPI)

The mean HPI for groundwater samples and for each metal were calculated separately and the results are presented in Table 4.3. The HPI for the study area was determined by incorporating the mean concentration values of recorded heavy metals. In the present study, metals such as Fe^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} were considered. The mean HPI resulted in this study was 535.50 (Table 4.3).

Table 4.3 showed that iron and manganese have higher HPI than the mean value of 535.50, whereas only zinc is below the limit of high pollution by heavy metal (HPI = 0.71). The presence of higher concentrations of iron and manganese may be the effect of agricultural fertilizers on the groundwater quality in the study area. Generally, HPI for the mean concentration value was found to be 535.50, which is far higher than the critical pollution index value of 100, above which the overall pollution level should be considered unacceptable for drinking water as reported in the literature(Prasad and Mondal, 2008 and Prasad and Kumari, 2008). The HPI result indicates that the groundwater samples are highly polluted with iron and manganese.

Table 4.3: Heavy metal pollution index (HPI) calculations for the Fe^{2+}, Cd^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+}

Concentration of metals (mg/L)	Sites								Aggregates					
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	Si(mg/L)	Mi (mean)	Wi=1/Si	Qi=(Mi *100/Si)	QiWi	HPI
Iron (Fe)	5.574	5.86	0.274	4.61	9.34	0.33	0.98	14.17	0.3	5.14	3.333	1713.91	5.14	1713.91
Cadmium (Cd)	0.004	0.001	0.001	0.003	0.003	0.002	0.004	0.005	0.005	0.002875	200	64.5	12.9	57.5
Manganese(Mn)	5.721	4.32	0.038	1.64	1.56	4.75	4.45	5.35	0.4	3.47	2.5	869.65	2.6	869.65
Copper (Cu)	1.326	0.35	0.51	1.49	0.006	0.21	0.29	0.42	2	0.57	0.5	28.76	0.014	28.76
Zinc (Zn)	0.03	0.045	0.062	0.039	0.001	0.045	0.051	0.023	3	0.035	0.3333	0.71	0.0001	0.71
HPI	221.929	185.59	15.491	136.368	191.4	93.5087	101.22	350.17						

4.3.2. Pollution evaluation indices (HEI)

The estimated pollution evaluation indices for the Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, $Zn^{2+}$and Cu^{2+} of the eight sites were estimated and presented in the Table 4.4.The mean HEI indices values of iron and manganese were 137.11 and 69.57 respectively, which indicated that the water samples of these sites were contaminated by Fe^{2+} and Mn^{2+}. The mean values of HEI of Cd^{2+}, Cu^{2+} and Zn^{2+} were 5.16, 2.301 and 0.057, respectively.The mean values of the estimated pollution evaluation indices (HEI) for the eight sites observed to be 42.84. The mean HEI value for iron and manganese were greater than 20; this suggested that these sites are highly contaminated by iron and manganese as reported in the literature (Al-Ami, *et al.,* 1987, Backman, *et al.,* 1997 and Bhuiyan, *et al.,* 2010)

4.3.3. Contamination index (CI)

The quality of groundwater were evaluated by calculating contamination index (C_{deg}) and the results were presented in the Table 4.4. The results indicated that the groundwater samples are highly polluted by $Fe^{2+}$and Mn^{2+}. The mean C_{deg} value was 4.84, which is greater than 3; this suggested that these sites are highly contaminated by iron and manganese as reported in the literature (Al-Ami, *et al.,* 1987, Backman, *et al.,* 1997 and Bhuiyan, *et al.,* 2010).

Table 4.4: Heavy metals evaluation indexes for each metals collected from the site 1-8

Concentration of metals (mg/L)	Sites								MAC (mg/l)	ΣH_c	H_{Mac}	HEI
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8				
Iron(Fe)	5.574	5.86	0.274	4.61	9.34	0.33	0.98	14.17	0.3	41.138	0.3	137.11
Cadmium (Cd)	0.004	0.001	0.001	0.003	0.003	0.002	0.004	0.005	0.005	0.023	0.005	5.16
Manganese(Mn)	5.721	4.32	0.038	1.64	1.56	4.75	4.45	5.35	0.4	27.829	0.4	69.57
Copper (Cu)	1.326	0.35	0.51	1.49	0.006	0.21	0.29	0.42	2	4.602	2	2.3
Zinc	0.03	0.045	0.062	0.039	0.0012	0.045	0.051	0.023	3	0.2962	3	0.057
HEI mean	42.84											
C_{deg} Mean	4.84											

Table 4.5: Descriptive statistics of the metal concentrations in the groundwater (S_1-S_8) (in mg/L)

Metals (mg/L)	Mean	Median	SD	Variance	Range	Minimum	Maximum
Iron (Fe)	5.141	5.090	4.845	23.474	13.90	0.270	14.17
Cadmium (Cd)	0.0028	0.003	0.0014	0.000002.1	0.004	0.001	0.005
Manganese (Mn)	3.478	4.385	2.094	4.385	5.683	0.038	5.721
Copper (Cu)	0.575	0.385	0.536	0.288	1.484	0.006	1.49
Zinc (Zn)	0.037	0.042	0.018	0.00036	0.061	0.001	0.062

4.4. Result of physicochemical characteristics of the groundwater

The present study showed that the pH, conductivity, turbidity, TDS, colour and odour of the groundwater are relatively higher than the recommended values of Ethiopia(EDWS, 2013) and WHO standards (WHO, 2011). The results are presented in the Table 4.6.

Table 4.6: Physicochemical characteristics of the groundwater (S_1-S_8)

Parameters	Sites								Ethiopia standards	WHO standards
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8		
pH	6.3±0.09	6.5±0.03	7.1±0.06	7.4±0.03	5.9±0.06	7.6±0.13	6.9±0.13	6.3±0.17	6.5–8.5	6.5–9.5
Conductivity (µS/cm)	940±0.032	1164±1.23	960±1.44	1240±2.53	1186±2.11	983±2.53	1255±0.046	1568±2.66	1000	1000
Temperature (℃)	14.5±1.54	20.7±0.76	19.3±1.33	22.6±1.67	21.6±1.56	18.9±0.43	22.7±0.75	22.7±0.63	12-25	12-25
Dissolved oxygen (mg/L)	3.37±0.06	6.71±0.65	5.38±0.07	6.45±0.45	1.39±0.32	5.37±1.03	5.58±1.22	5.25±1.02		
TDS (mg/L)	127±0.57	112±1.23	127±3.13	119±1.03	102±3.27	134±0.30	155±1.07	1124±2.77	1000	1000
Turbidity (NTU)	25 ±1.03	13±0.43	4.8±0.38	13±0.58	13±0.72	26±0.78	18±0.71	22±1.38	5	5
Colour	Yel.	Sl. Yel.	Sl. Yel.	Sl. Yel.	Yel.	Sl. Yel.	Yel.	Yel.		
Odour	meta	meta	-	-	-	meta	-	meta		

NB: "Yel." Yellowish, "Sl. Yel." slightly yellowish, "-"odorless, "meta" Metallic

4.4.1. pH, Temperature and Dissolved Oxygen

The highest values of temperature were recorded for sample site S_7 (22.7 ℃) and the lowest value observed for groundwater sample site S_1 (14.5 ℃). All of the groundwater samples are under the recommended values of WHO and Ethiopia drinking water standards for the temperature. The pH value of the groundwater of site S_6 measured was the highest (7.6), the lowest pH was measured in the site S_5 (5.9). The groundwater samples S_1, S_5 and S_8 are not under the recommended values for pH. Dissolved oxygen was the highest in the site S_2 (6.71) and lowest in the site S_5 (1.39) (Table 4.6**)**.

4.4.2. Total Dissolved Solutes (TDS) and conductivity

The total dissolved solid was measured, the value were recorded in the Table 4.6. The result revealed that the highest concentration of TDS were recorded at site S_8 and lowest was measured at the site S_5. The highest conductivity was observed at the site S_8 and lowest one was obtained at the site S_1.

4.4.3. Turbidity

Turbidity was measured by nephelometric turbidity meter and the results were recorded in the Table 4.6. The highest turbidity were observed at the site S_8 and the lowest one was obtained at the site S_3. Except S_3, all of the groundwater samples are not under the recommend values for turbidity.

4.4.4. Colour and odour

Colour and odour of the water was checked by observing water by field observation. The results were presented in the Table 4.6. The water was yellowish or slightly yellowish in all locations of the study area. The tested water were with some metallic like odour. The yellowish color of water generally indicated the presence of iron (Fe) in the groundwater as reported in the literature (Ankrah, 2012). The result at the S_1, S_2, S_5, S_6 and S_8 showed yellowish colour and the rest-tested sites showed comparable colors and odors.

4.5. The result of the adsorptive ability of peat moss on each metals

The Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+}concentrations were measured after adsorption in triplicates at different concentration of adsorbent, contact time, temperature and pH using AAS scientific model NOVA 400 at Hawassa University Agriculture College Soil Laboratory. The results were presented in the Table 4.7.

Table 4.7: Adsorptive ability of peat moss: (Metals concentration = 5 mg/L, pH = 3, 6 and 9, adsorbent dose = 1000 mg, Temperature = 25 ℃ and Contact time = 12 hr).

	C_e = Concentration of metals after adsorption at equilibrium (mg/L)					Q_e = Concentration of metals adsorbed at equilibrium (mg/g)				
pH	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
3	0.38	0.27	0.65	0.27	0.36	4.62	4.73	4.35	4.73	4.64
6	0.18	0.26	0.49	0.2	0.29	4.82	4.74	4.51	4.80	4.71
9	0.46	0.37	0.95	0.39	0.43	4.54	4.63	4.05	4.61	4.57

Table 4.8: Adsorptive ability of peat moss: (Peat moss dose = 500mg, Metals concentration = 5 mg/L, pH = 3, 6 and 9, Temperature = 25 ℃ and Contact time = 12hr)

pH	Concentration of metals after adsorption at equilibrium (mg/L)				
	Fe^{2+}	Mn^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}
3	0.587	0.489	0.745	0.589	0.547
6	0.346	0.294	0.683	0.348	0.464
9	0.699	0.676	0.983	0.798	0.637

Table 4.9: Adsorptive ability of peat moss: (Peat moss dose = 1000 mg, Metals concentration = 10 mg/L, pH = 3, 6 and 9, Temperature = 25℃ and Contact time = 12hr)

pH	Concentration of metals after adsorption at equilibrium (mg/L)				
	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
3	6.351	6.066	7.153	5.114	5.495
6	4.243	3.859	5.134	2.669	3.477
9	3.874	3.821	4.853	2.625	3.398

Table 4.10: Adsorptive ability of peat moss: (Peat moss dose = 1000 mg, Metals concentration = 15 mg/L, pH = 3, 6 and 9, Temperature = 25℃ and Contact time = 12hr)

pH	Concentration of metals after adsorption at equilibrium (mg/L)				
	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
3	13.35	13.06	13.86	13.24	13.16
6	12.66	12.07	13.02	12.55	12.32
9	11.88	12.04	12.88	11.87	12.05

The 5, 10 and 15 mg/L of 50 ml of heavy metal solutions were mixed with 500 and 1000 mg adsorbent (peat moss) for 12 hours at pH 3, 6 and 9. After 1hour of treatment, about 90.80 %, 96.3%, 96.0%, 94.5% and 94.8% of Cd^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} respectively were adsorbed onto the peat moss at pH 6. Generally, Cd^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} were highly adsorbed at pH 6.0 and at higher adsorbent dose (1000 mg), then absorption were decreased at higher pH(9.0) as shown in Table 4.7 and Table 4.13.

The peat moss (adsorbent) was active to adsorb Cd^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}. The most highly adsorbed metal was iron (96.3%); the next metal highly adsorbed on the peat moss was copper (96.0%). Table 4.7 - 4.10 showed that peat moss was active at pH 6 and at high adsorbent dose (1000 mg). Most of the Cd^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} concentrations were adsorbed at pH 6, then adsorption were dropped to 48-73% after the addition of 10 mg/L Cd^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} concentrations and pH increment from pH 6 to pH 9. The decrease in adsorption percentage suggests that peat moss is approaching its saturation point with regards to additional adsorption of metal concentrations. This may be taken as an indicator that the peat moss may not have vacant sites to adsorb metals when concentration of metals increases as reported in the literature (Jenny, 2006).

4.5.1. Adsorption Kinetics

The kinetic experiments at two different peat doses, 500 and 1000 mg were shown typical adsorption curves for effect of peat moss dose on the adsorption kinetics of iron, manganese, cadmium, copper and zinc. The plot of the pseudo first order rate (log ($q_e - q_t$) versus t) and pseudo second order rate (t/q_t vs t) of the experimental data are shown in Figure 4.1 and Figure

4.2 respectively. The amounts adsorbed at the equilibrium (q_e) and calculated values for the two models are given in Appendix 3 and Appendix 4. The plot of the pseudo second order models gives a straight line with correlation coefficient $R^2 \geq 0.8884$ as shown in Figure 4.2. Therefore, these results showed that pseudo second order model was reliable and accurate in correlating the experiment. Hence, a pseudo second order kinetic model can represent the adsorption of iron, manganese, cadmium, copper and zinc onto peat moss. In this study, adsorption of iron, manganese, cadmium, copper and zinc onto peat moss showed the reaction is chemical sorption or chemisorption as reported in the literature (Ho *et al.*, 1994). The adsorption of iron, manganese, cadmium, copper and zinc by peat moss is consistent with the reported literature (Robinson, *et al.,* 2001).The plot of the pseudo first order models worse than a straight line, then correlation coefficient R^2 of 0.157. This model does not follow the trend of the experimental data, so fits worse than a horizontal as shown in Figure 4.1.

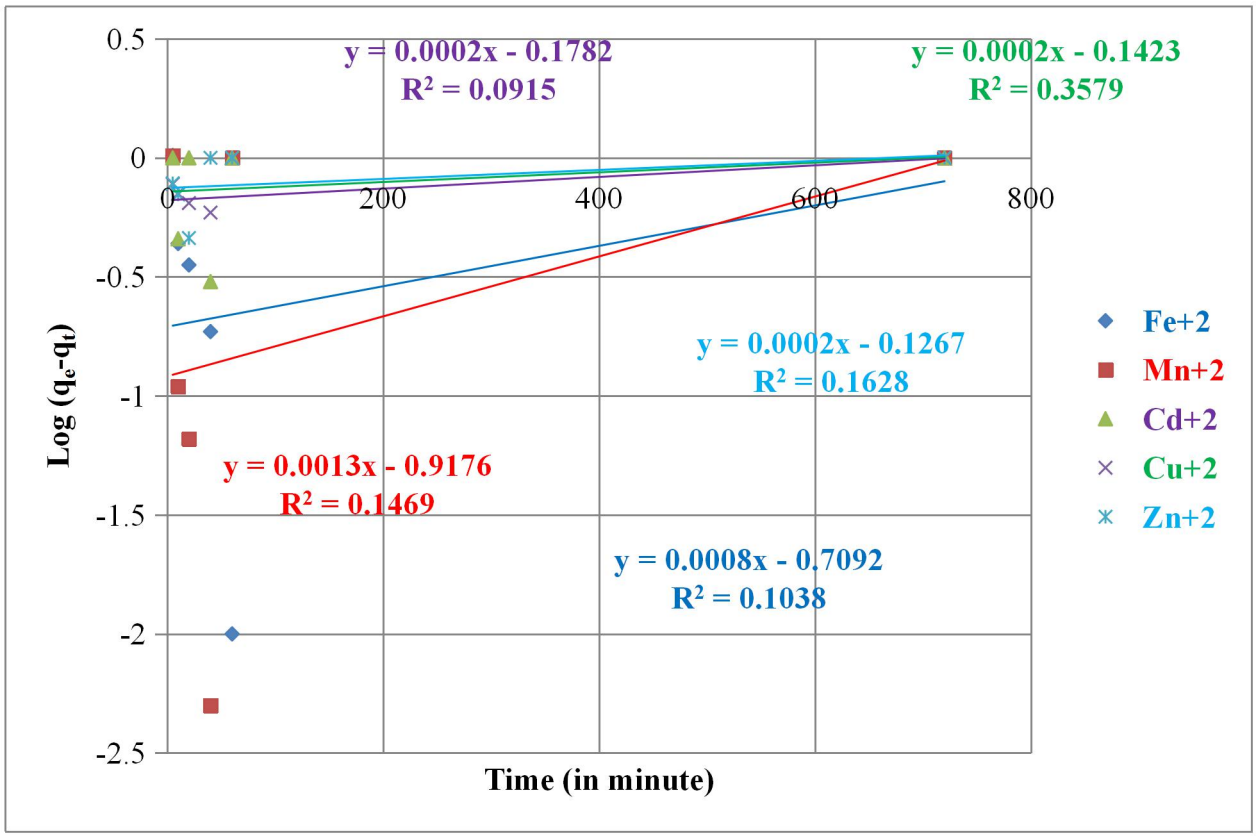

Figure 4.1: The plot of the pseudo first order rate (log (qe− qt) versus t)

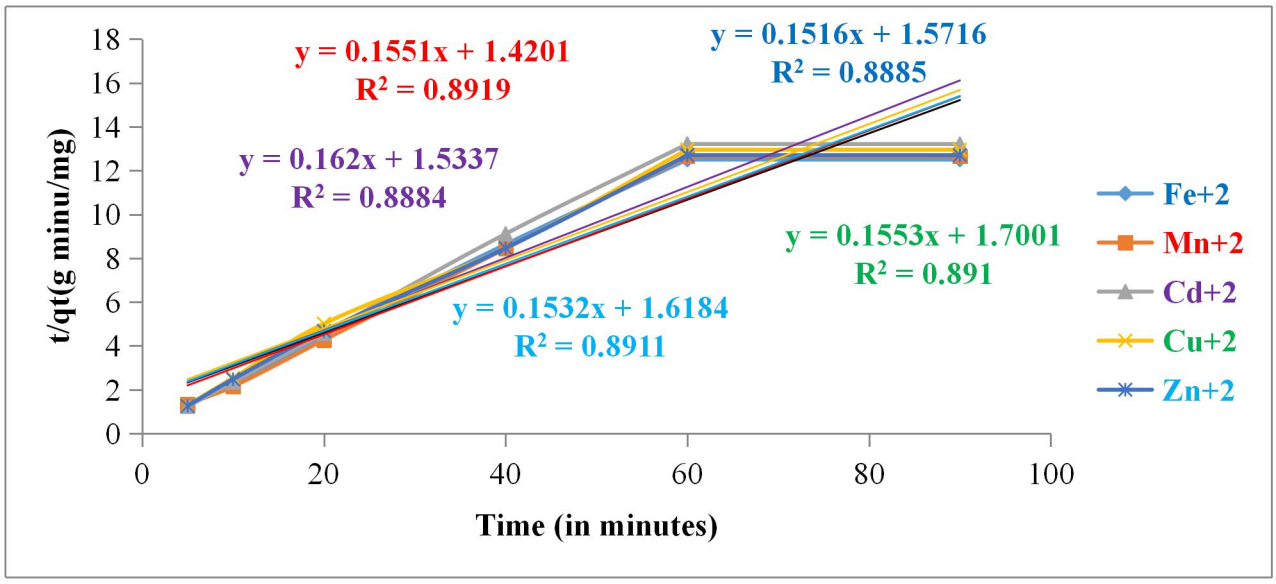

Figure 4.2: The plot of the pseudo second order rate (t/q_t vs t)

4.5.2. Adsorption equilibrium isotherm experiments

The adsorption equilibrium data were analyzed into two well-known isotherm models via Freundlich and Langmuir models.

4.5.2.1. Freundlich model

The plots between log q_e and log C_e for the adsorption of metal ions were drawn in Figure 4.3. It was found that correlation coefficient values were more than 0.98 at different temperatures and pH. The adsorption of iron (Fe^{2+}), Cadmium (Cd^{2+}), manganese (Mn^{2+}), copper (Cu^{2+}) and Zinc (Zn^{2+}) data for the peat moss fitted well the Freundlich isotherm at pH 3, 6 and 9. Peat moss exhibited the highest metals adsorption capacity at pH 6 than that of at higher pH (pH 9).

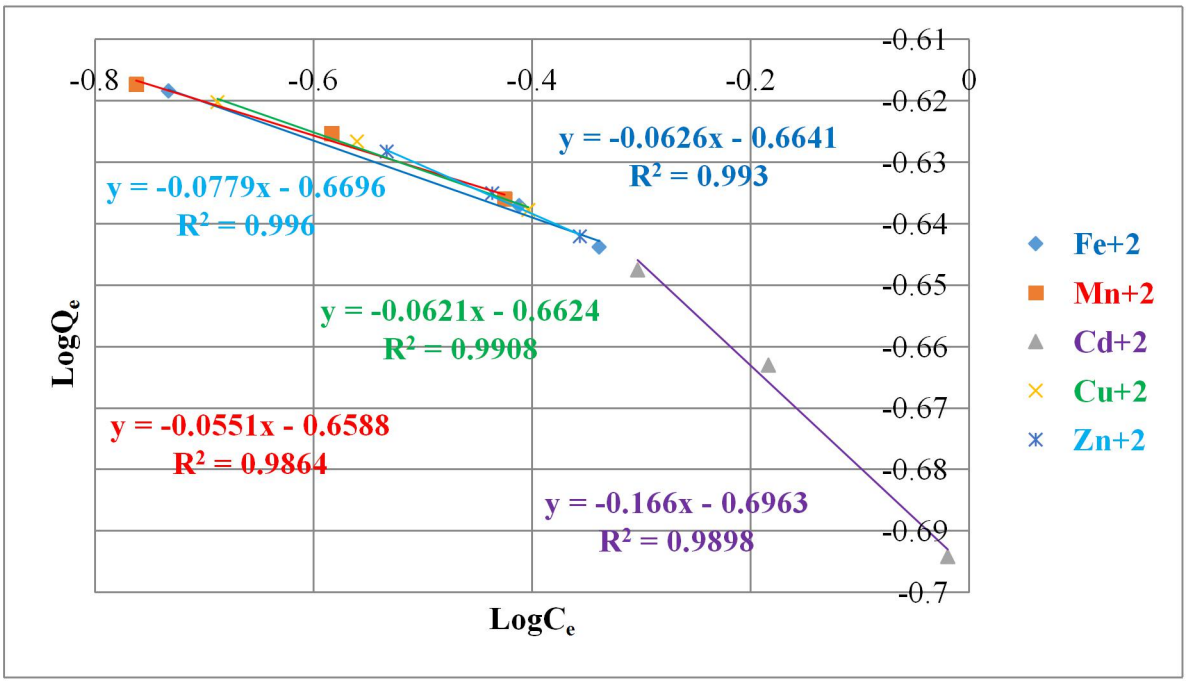

Figure 4.3: The plot of Freundlich adsorption model: volume of the solution = 50 mL, initial concentration of metals = 5 mg/L, pH = 3, 6 and 9, adsorbent dose =1000 mg and contact time = 60 minutes.

4.5.2.2. Langmuir Isotherm

The metals adsorption at different concentration gave different adsorption patterns. The data obtained were fitted well the Langmuir isotherm under increasing metals adsorption when the adsorbent concentration increases. The adsorption for Cd^{2+} and Zn^{2+} are comparable to the maximum adsorption obtained from the adsorption isotherms. These facts suggest that $Cd^{2+}$and Zn^{2+} are adsorbed in the form of mono-layer coverage on the surface of the prepared adsorbent as reported in the literature (Singh, I.B. and Singh, D.R. 2001). The Langmuir model best fits to the adsorption of Cd^{2+} and Zn^{2+}on peat moss (adsorbent). Higher adsorption was observed at pH 6. Peat moss showed very low adsorption capacity especially at pH 9. The adsorption capacities of the peat moss increased with an increase in pH from 3 - 6, then adsorption capacity of the peat moss slightly decreased at pH 9.

Table 4.11: The adsorption capacity and concentration of metal ion in the filtrate at equilibrium: Metal = 5 mg/L, Time = 60 min, Temp. = 25 ℃ and Adsorbent =1000 mg.

Metal ions	C_e	$1/C_e$	$Q_e = (C_i - C_f)*0.05$	$1/Q_e$	log C_e	log Q_e
Fe^{+2}	0.387596	2.580005986	0.23062	4.336134	-0.411619	-0.63710274
	0.185185	5.4000054	0.24074	4.153846	-0.732393	-0.6184504
	0.458715	2.180002834	0.227064	4.40404	-0.338456	-0.64385129
Mn^{+2}	0.261096	3.830008886	0.236945	4.220385	-0.583198	-0.62535214
	0.17301	5.780012716	0.241349	4.143369	-0.761927	-0.61735363
	0.375939	2.660006012	0.231203	4.325203	-0.424881	-0.63600652
Cd^{+2}	0.655307	1.526002316	0.217234	4.603318	-0.183554	-0.663071
	0.497512	2.010001769	0.225124	4.441988	-0.303196	-0.64757747
	0.956022	1.046001033	0.202198	4.945626	-0.019531	-0.69422131
Cu^{+2}	0.275482	3.630001234	0.236225	4.233236	-0.559902	-0.62667249
	0.205338	4.870019188	0.239733	4.171306	-0.687528	-0.62027207
	0.395256	2.53000587	0.230237	4.343347	-0.40312	-0.63782459
Zn^{+2}	0.293255	3.410001535	0.235337	4.249221	-0.532754	-0.62830933
	0.3663	2.73000273	0.231684	4.316205	-0.436162	-0.63510211
	0.440528	2.270003269	0.227973	4.386473	-0.356025	-0.6421155

4.6. The result of the factors affecting metals adsorption on peat moss

4.6.1. Effect of pH

The effects of pH were carried out at three different pH levels: pH 3, pH 6 and pH 9. The results obtained from the experiments are presented in Table 4.7 - 4.10. Regression coefficients were calculated for each pH level. The peat moss powder proved to be effective adsorbent for the removal of iron, manganese, cadmium, copper and zinc from aqueous solution at pH 6. With increasing in pH, adsorptions were increased up to pH 6, then adsorptions were decreased at higher pH (9). This may be due to decrease in negative charge on the adsorbent as the pH of the solution increases. At lower pH values, the surface charge on the adsorbent is positive and

because of this, the H^+ ions compete with metal ions for active sites in adsorbent as reported in the literature (Patnukao, *et al.,* 2008). Increase in pH result in the electrostatic repulsion between the cations and surface sites, there by the competing effect of the H^+ ions decreases and the positively charged metal ions are adsorbed on the free binding sites, resulting an increase in the total metal uptake as reported in the literature (Sposito, 1989). This indicates that peat moss mainly contains humic acid as reported in the literature (Jenny, 2006).

4.6.2. Effect of adsorbent dose

The results of the effect of peat dose was carried out by varying the peat dose range from 500 to 1000 mg by fixing parameters like initial metal concentration (5 mg/L), temperature of 25 ℃ and pH 6 as shown in Table 4.12. It was found that the removal of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, $Zn^{2+}$and Cu^{2+} ions increases up to certain limit and then remains almost constant. This is because the number of available active sites increased by increasing the adsorbent dose from 500 mg to 1000 mg, resulting in the higher removal of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, $Zn^{2+}$and Cu^{2+} ions and it reaches the maximum removal of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} ions at an optimum dose of 1000 mg for the adsorbent as reported in the literature (Ademiluyi and Nze, 2011).

Table 4.12: The effect of peat dose on metal ion adsorption: Metal ion concentration = 5 mg/L, Contact time = 60 min, pH = 6, Temp 25 ℃ and Adsorbent dose =500 and 1000 mg.

Mass of adsorbent	500 mg					1000 mg				
Heavy metal ions	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
C_e = concentration of metals after adsorption(mg/L)	0.346	0.294	0.683	0.348	0.464	0.18	0.26	0.49	0.2	0.29
Amount of metal adsorbed (mg/L)	4.654	4.706	4.317	4.652	4.536	4.82	4.74	4.51	4.8	4.71
% Removal	93.08	94.12	86.34	93.04	92.8	96.4	94.8	90.2	96	94.21

4.6.3. Effect of initial concentration

The effect of initial metal concentration was analyzed by varying initial metal ions concentration from 5-10 mg/L as shown in Table 4.7 - 4.10. The decrease in the removal of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} ions may be due to the saturation of the available active sites because only the fixed quantity of adsorbent was used for all the initial Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+}

ion concentrations. The rate of adsorption dropped from 96.3% - 48% as the concentration of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} ions increased from 5 mg/L to 10 mg/L within 12hr of adsorption. The fixed amount of adsorbent can be able to remove only the fixed amount of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} ions present in the solution as reported in the literature (Emeka, *et al.,* 2014, Emmanuela, *et al.,* 2015 and Kamari, *et al.,* 2014).

4.6.4. Effect of contact time

The effect of contact time on adsorption of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} ions at different time were determined by keeping adsorbent dosage, initial concentration, temperature and pH constant as shown in Table 4.13. The rate of adsorption was fast at the early stage, this is due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the adsorbent surface. The attainment of equilibrium adsorption might have been due to reduction in the available active adsorption sites on the adsorbent with time resulting to limited mass transfer of the adsorbate molecules as reported in the literature (Patnukao, *et al*., 2008). After 5 minutes of adsorption, 77.20 % average concentration of Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} were removed. The maximum time required for adsorption was 60 minutes for 93.72% average adsorption, after which the amount adsorbed remains virtually constant. After 12-hours of treatment, 94.36% Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} were adsorbed by peat moss.

Table 4.13: The effect of contact time on metal adsorption: Metal ion = 5 mg/L, Adsorbent dose = 1000 mg, pH = 6 and Temp 25 ℃

Time (min.)	Q_t (mg/g)				
	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
5	3.77	3.71	4.01	3.87	3.94
10	4.38	4.63	4.24	3.93	4.02
20	4.46	4.67	4.37	3.99	4.26
40	4.63	4.73	4.39	4.05	4.72
60	4.81	4.74	4.54	4.63	4.72
90	4.81	4.74	4.69	4.63	4.72
180	4.81	4.74	4.69	4.63	4.72
720	4.81	4.74	4.69	4.63	4.72

4.6.5. Effect of temperature

The adsorption of Fe^{2+}, Mn^{2+}, Cd^{2+}, $Zn^{2+}$and Cu^{2+} were carried out at different temperatures. The results of adsorption at different temperature were presented in the Table 4.14. The metal adsorption capacities of peat moss increased with increasing temperature up to 318K, then adsorption was slightly decreased at 328K as reported in the literature (Rungrodnimitchai and Kotatha, 2015).

Table 4.14: The effect of temperature on the metal adsorption: Adsorbate =1000 mg, Metal ion concentration = 5 mg/L, Contact time = 40 minutes and pH 6

Temp. (K)	Concentration of metals adsorbed (mg/L)				
	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
298	4.53	4.62	4.04	4.6	4.56
308	4.61	4.73	4.34	4.72	4.63
318	4.72	4.82	4.50	4.79	4.70
328	4.55	4.71	4.58	4.66	4.43

The correlation coefficient computed from the sample data (Appendix 7) showed that temperature and adsorption of metals have good relationship between each other. The removal efficiency of peat was higher at 318K, then slightly decreased in higher temperature (328K). In these studies, peat moss has the ability to removal up to 94.12% average Fe^{2+}, Mn^{2+}, $Cd^{2+,}$, Zn^{2+} and Cu^{2+} concentrations from the sample solution at higher temperature (318 K), contact time (60 minutes) and at pH 6. The removal efficiency of peat mos was slightly decreased (93.28%) at 328K at contact time 40 minutes.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

Groundwater movements in the aquifers and contamination of aquifers can be governed by solute transport. The rates of degradation of heavy metals in many soil environments are slow. Because of these, heavy metals travel great distances from their point of entry without much attenuation in initial entry concentration (Thayer, 1991). Bioremediation of contaminated groundwater by a bioreactor is a best method to remove heavy metals.

The physico-chemical analysis result showed that the average groundwater pH (5.9±0.06 to 7.6 ± 0.13), Total dissolved solids (102 ± 3.27 to 1124 ± 2.77 mg/L), Electrical conductivity (940 ± 0.032 to 1255 ± 0.046 μS/cm), Dissolved oxygen (1.39 ± 0.32 to 6.71±0.65 mg/L), Temperature (14.5 ± 1.54 - 22.7 ± 0.75 0C), Turbidity (4.8 ± 0.38 to 25 ± 1.03 NTU).

The average metal concentration in groundwater samples analyzed is in order of Fe^{2+} (5.14175) > Mn^{2+} (3.478625) > Cu^{2+} (0.57525) > Zn^{2+} (0.0359) > Cd^{2+} (0.003225). Presences of iron in groundwater are relatively higher. The S_8 groundwater possessed the highest iron contamination (14.17 mg/L). The sampled wells had iron content much greater than the Ethiopia and WHO recommended value (0.3 mg/L). Except S_3, manganese levels much exceeded the WHO health-based guideline of 0.4 mg/L. The S_1, S_2, S_5 and S_8 are not under the recommended values for pH. A linear multiple regression showed significant correlation between the concentrations of iron in well water with pH. The zinc concentration showed significant positive correlation with pH. Generally, agricultural chemicals might cause the high concentration of parameters at the sites. From the tested groundwater resources, waste disposal areas and agricultural areas have high metals concentrations. The HPI, C_{deg} and HEI indices were greater than their critical values near the agricultural and waste disposal sites, indicating groundwater pollution by iron and manganese. The result showed that Fe^{2+} and Mn^{2+} are the major groundwater contaminants in the study area. The Groundwater from these areas required treatment to reduce the level of iron, manganese, cadmium, copper and zinc concentrations in drinking water before to supply to the consumer.

In this study, bio-adsorbent (peat moss) was presented to remove iron, manganese, cadmium, copper and zinc. The effects of different parameters like pH, adsorbent dosage, concentration, contact time and temperature on removal of iron (II), manganese (II), copper (II), zinc (II) and cadmium (II) ions were studied. The average (94.12%) adsorptive result indicated that there was a reduction of iron, manganese, cadmium, copper and zinc concentration in the water samples at pH 6, adsorbent dose 1000 mg and at 60 minutes. At pH 6, 1000 mg peat moss was effective to remove 96.30% of iron with the contact time 60 minutes. The adsorptions were found to increase with increase in adsorbent dose, contact time up to 60 minutes and temperature up to 318K. Langmuir isotherm model was found to be best fit with high correlation coefficient for Cd^{2+} and Zn^{2+}. From linear regression values, all of the tested metals best fit Freundlich adsorption isotherm model. The kinetic study data indicates that the adsorption of all tested metals on adsorbent followed the second order kinetics. Maximum adsorption capacity was found to be 1000 mg of peat moss at 318 K. Adsorption equilibrium was attained after 60 minutes of contact time and it was described by kinetics studies. Finally, it can be concluded from the study that peat moss is a suitable adsorbent for adsorption of iron (II), cadmium (II), copper (II), manganese (II) and zinc (II) ions.

5.2. Recommendations

- This is the only preliminary study of physicochemical and adsorptive removal of iron, manganese, cadmium, copper and zinc from contaminated groundwater; further studies should be carried out to obtain method of using this bio-adsorbent (peat moss).
- Method of installation of *Sphagnum* (peat moss) to remove iron, manganese, cadmium, copper and zinc in situ from groundwater should be carried out to provide this resource for large-scale treatment.
- The scientific information obtained from this study should be placed in systematic and accessible database in an appropriate institution to follow the trend.
- Installing water treatment plant using locally available bio-adsorbent works well to minimize the chemical costs and health effects of chemicals.
- Protecting iron contamination during well drilling minimizes iron problems.

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Appendix 1: The photos of *Sphagnum* moss (peat moss)

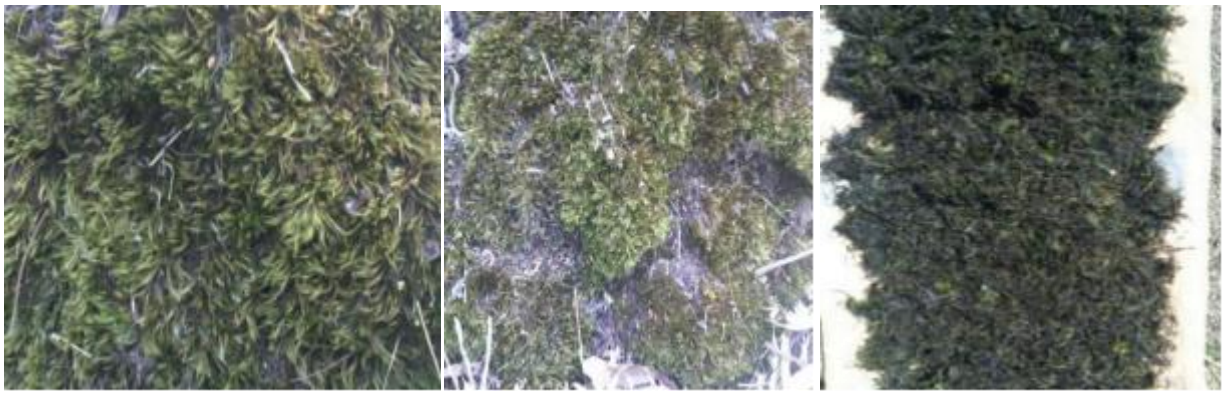


Figure (a-c): Aerial part of *Sphagnum* moss*,* Photo by Natnael S., January 2019

Appendix 2: Experiment photographs

Appendix 3: Measured and calculated adsorption constants for pseudo-first and pseudo-second order reaction.

Metal ions adsorbed	Calculated values for the pseudo-first order				Metal ions adsorbed	Calculated values for the pseudo-second order				
	Slope	R^2	K_1 (L/min)	Intercept		Slope	R^2	K_2(g/min)	Q_e (mg/g)	Intercept
Fe^{2+}	0.0008	0.103	-0.102	-0.707	Fe^{2+}	0.207	1	0.00571	0.2405	0.243
Mn^{2+}	0.0013	0.146	-0.025	-0.917	Mn^{2+}	0.209	1	0.00588	0.237	0.278
Cd^{2+}	0.0001	0.0313	-0.0564	-0.106	Cd^{2+}	0.212	1	0.00601	0.2345	0.348
Cu^{2+}	0.0002	0.357	-0.016	-0.142	Cu^{2+}	0.215	1	0.00617	0.2315	0.2336
Zn^{2+}	0.0002	0.162	-0.034	-0.126	Zn^{2+}	0.211	1	0.00593	0.236	0.213

Appendix 4: Measured and calculated adsorption constants for pseudo-first & second order reaction

Time (min.)	q_t (mg/g)					q_e (mg/g)					C_t (mg/L)				
	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
5	3.77	3.71	4.01	3.87	3.94	4.81	4.74	4.69	4.63	4.72	1.23	1.29	0.99	1.13	1.06
10	4.38	4.63	4.24	3.93	4.02						0.62	0.37	0.76	1.07	0.98
20	4.46	4.67	4.37	3.99	4.26						0.54	0.33	0.63	1.01	0.74
40	4.63	4.73	4.39	4.05	4.72						0.37	0.27	0.61	0.95	0.28
60	4.80	4.74	4.54	4.63	4.72						0.20	0.26	0.46	0.37	0.28
720	4.81	4.74	4.69	4.63	4.72						0.19	0.26	0.31	0.37	0.28

Appendix 5: The metal ions adsorption data of the pseudo first order kinetic model

$q_e = C_o - C_e$	$t_b - a_b$	Log $t_b - a_b$	$q_e = C_o - C_e$	$t_b - a_b$	Log $t_b - a_b$	$q_e = C_o - C_e$	$t_b - a_b$	Log $t_b - a_b$	$q_e = C_o - C_e$	$t_b - a_b$	Log $t_b - a_b$	$q_e = C_o - C_e$	$t_b - a_b$	Log $t_b - a_b$
Fe^{+2}			Mn^{+2}			Cd^{+2}			Cu^{+2}			Zn^{+2}		
4.81	1.03	0.01	4.74	1.02	0.01	4.69	0.68	-0.16	4.63	0.76	-0.11	4.72	0.78	-0.107
	0.42	-0.36		0.1	-0.96		0.45	-0.34		0.7	-0.15		0.7	-0.154
	0.35	-0.45		0.065	-1.18		0.32	-0.49		0.64	-0.19		0.46	-0.337
	0.18	-0.73		0.005	-2.3		0.3	-0.52		0.58	-0.23		0	
	0.01	-2		0			0.15	-0.8		0			0	
	0			0			0			0			0	

Appendix 6: The metal ions adsorption data of the pseudo second order kinetic model

Time(in minutes)	t/q_t (g min/mg)				
	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
5	1.32	1.34	1.24	1.29	1.26
10	2.27	2.15	2.35	2.54	2.48
20	4.48	4.27	4.57	5.01	4.68
40	8.63	8.44	9.11	8.46	8.46
60	12.5	12.65	13.21	12.95	12.70
180	149.53	12.65	153.51	12.95	12.70
720	149.53	12.65	153.51	12.95	12.70

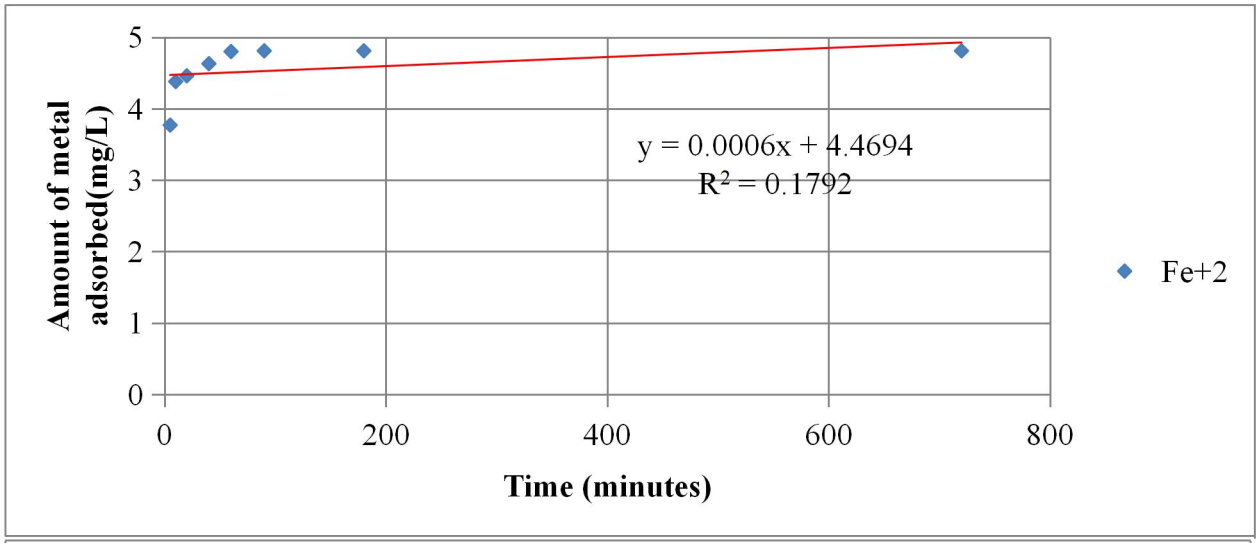
Appendix 7: Correlation coefficients between heavy metals adsorption and temperature

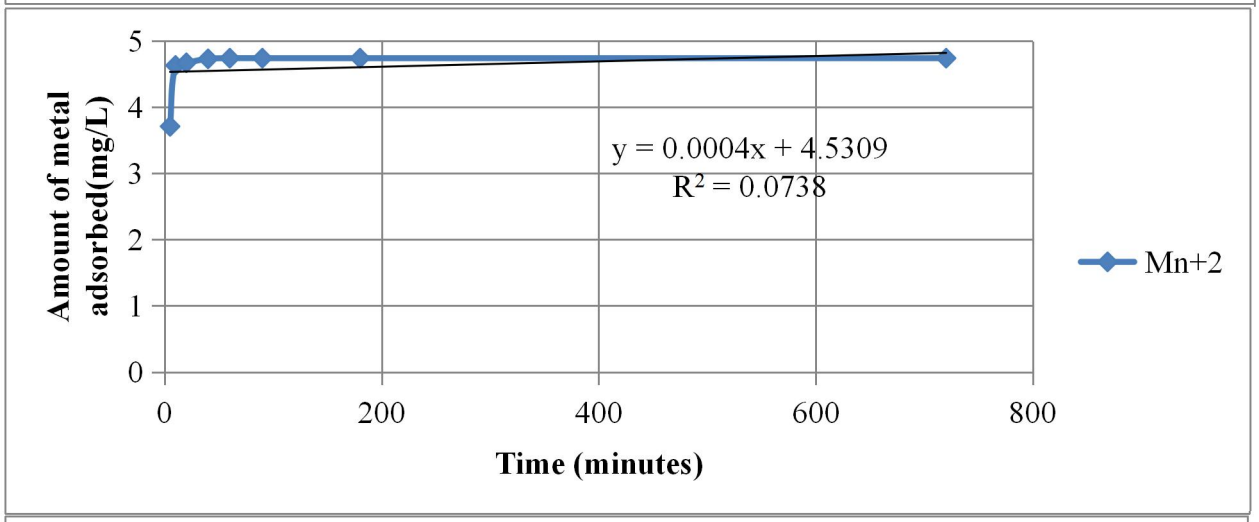
Temp(K)	Concentration of metals adsorbed (mg/L)				
	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
298	4.53	4.62	4.04	4.6	4.56
308	4.61	4.73	4.34	4.72	4.63
318	4.72	4.82	4.5	4.79	4.7
328	4.69	4.74	4.5	4.71	4.68
r	0.89162	0.70639	0.916	0.657	0.889
R^2	0.795	0.499	0.840	0.432	0.791

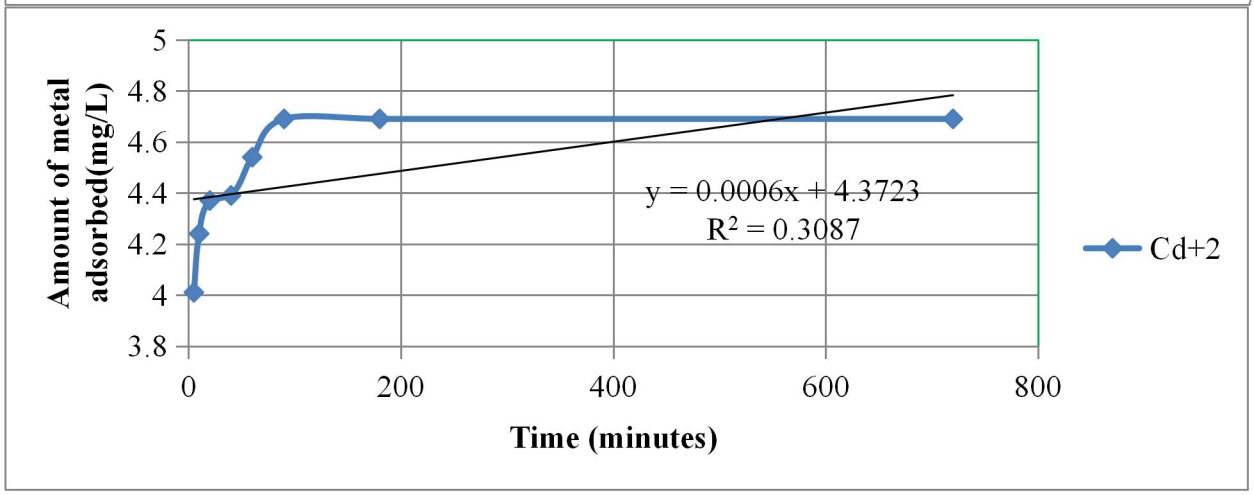
Appendix 8: Correlation coefficients between heavy metals adsorption with pH: (Metals concentration = 5 mg/L, pH = 3, 6 and 9, peat moss dose = 1000 mg, Temperature = 25 ℃ and Contact time = 12 hr).

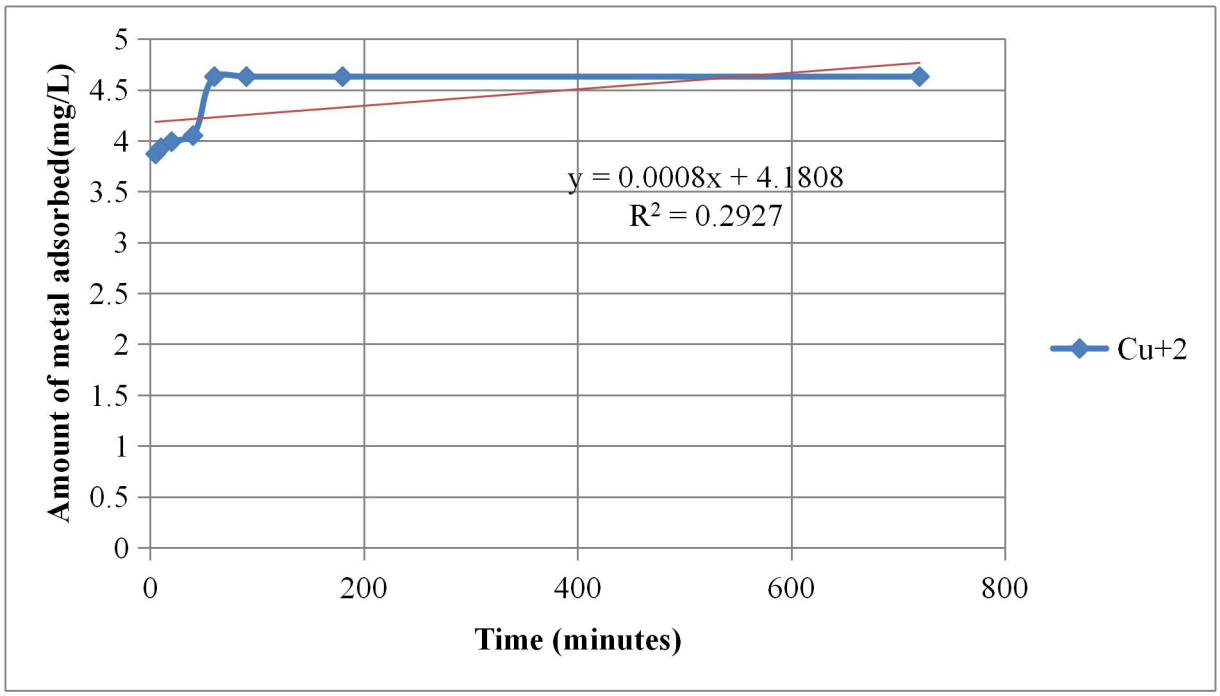
	C_e = Concentration of metals after adsorption (mg/L)				
pH	Fe^{+2}	Mn^{+2}	Cd^{+2}	Cu^{+2}	Zn^{+2}
3	0.38	0.27	0.65	0.27	0.36
6	0.18	0.26	0.49	0.20	0.29
9	0.46	0.37	0.95	0.39	0.43
r	0.275	0.821	0.641	0.623	0.50
R^2	0.076	0.675	0.412	0.389	0.25

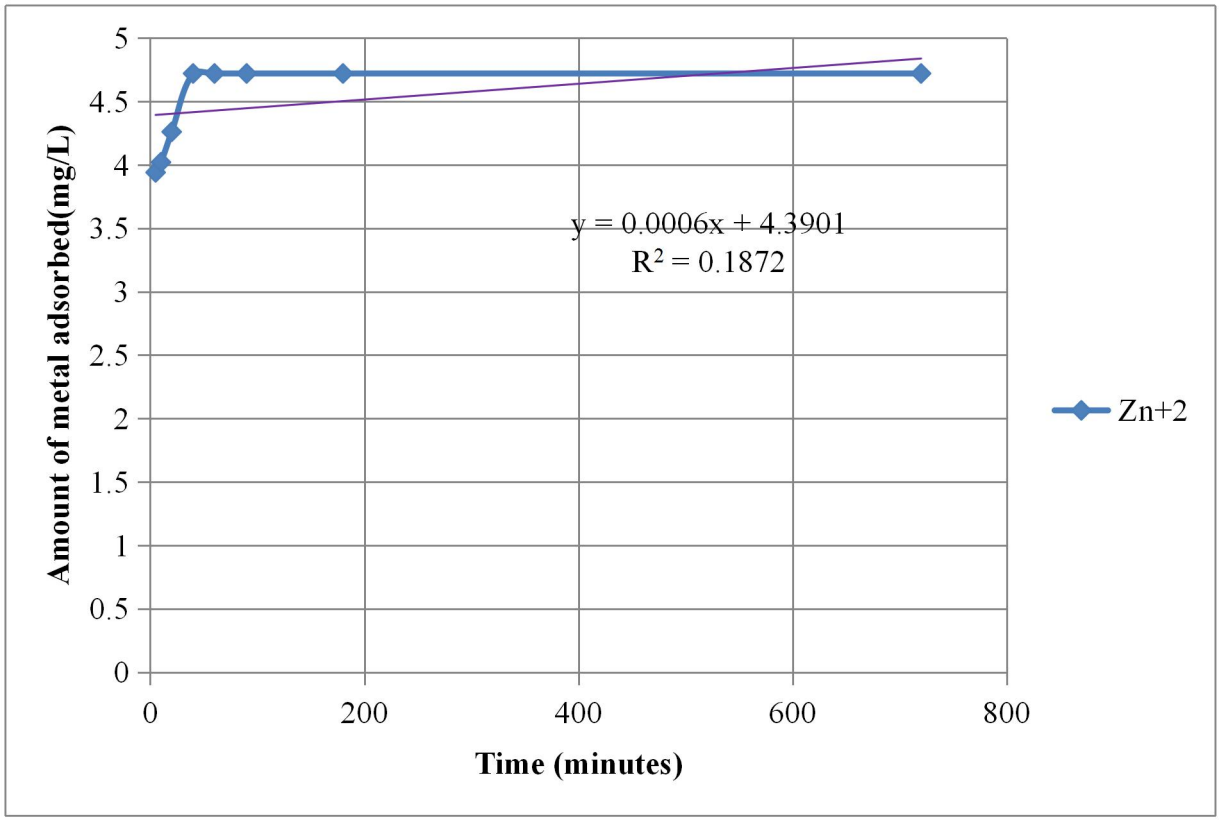
Appendix 9: The plot of metal adsorption versus contact time: Metal ion concentration = 5 mg/L, pH = 6 and Temp 25 ℃



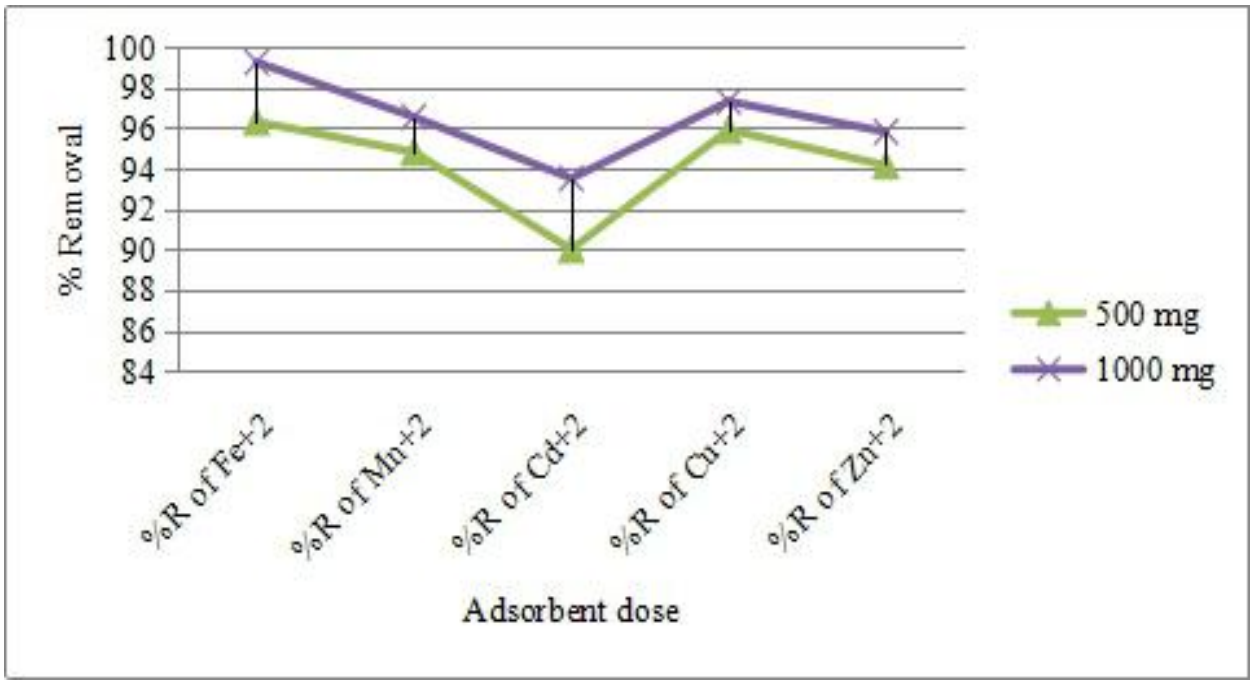




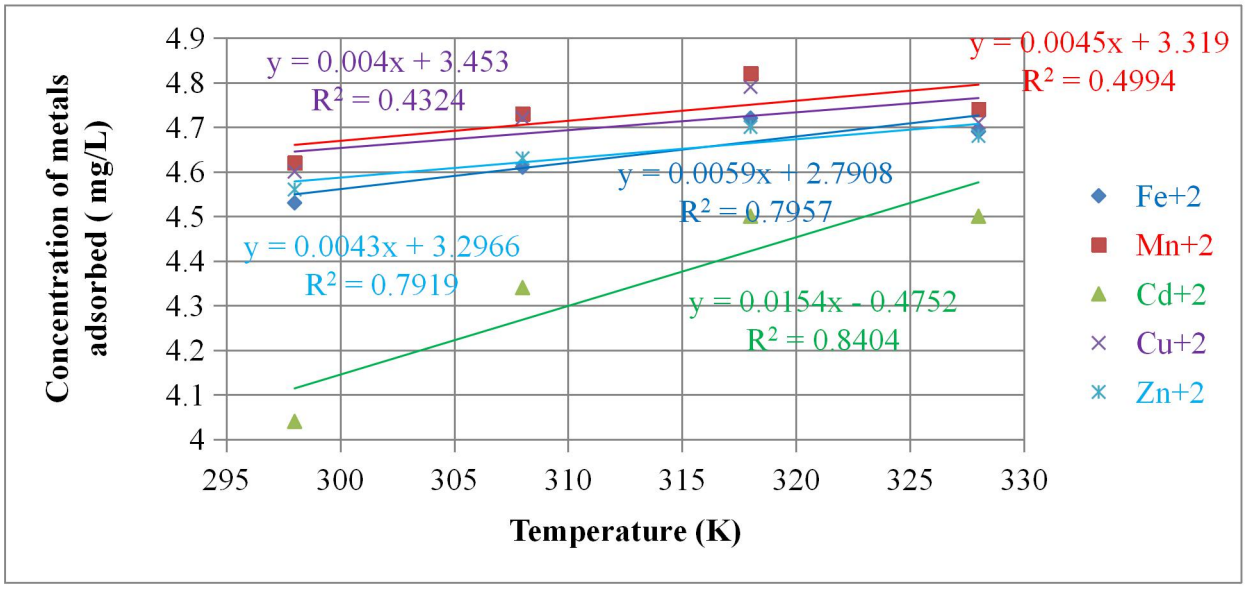

Amount of metal adsorbed(mg/L)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
200
400
600
800
Time (minutes)
y = 0.0008x + 4.1808
R² = 0.2927
Cu+2


Amount of metal adsorbed(mg/L)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
200
400
600
800
Time (minutes)
y = 0.0006x + 4.3901
R² = 0.1872
Zn+2

Appendix 10: The plot of adsorbent dosage versus percentage metal ions removal: Metal ion concentration = 5 mg/L, Contact time = 60 min, pH = 6 and Temp 25 ℃



Appendix 11: Plot of Temperature in (K) vs Concentration of metals adsorbed (mg/L)



Appendix 12: The plot of pH versus Concentration of metal ions in the filtrate when equilibrium was attained