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Characterization the Potential of Drinking Water Hardness Using Peanut Hull Adsorbent. (In Case of Mekelle City)

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THESIS WORK

ON

Characterization the Potential of Drinking Water Hardness Using Peanut Hull Adsorbent.

The Case of Mekelle City, Tigray Ethiopia

By: Tsegakiros Fantay

A Thesis Submitted to Addis Ababa Institute of Technology, School of Chemical and BioEngineering in Partial Fulfillment of the Requirements for the Degree of Masters ofScience in Chemical Engineering (Environmental Engineering Stream).

Advisor: Dr. Ing. Zebene Kiflie.

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Characterization the Potential of Drinking Water Hardness Using Peanut Hull Adsorbent.

By

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Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, and that all resources of materials used for this thesis have been duly acknowledged.

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Signature: ---

Date of Submission: ---------------------------------

This thesis has been submitted for examination with my approval as a university advisor.

Name: Dr. Ing. Zebene Kiflie

Signature: -------------------

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means with presence of outstanding people around me.

List of Acronyms and Abbreviations

AAS	Atomic absorption spectrophotometer
ANOVA	Analysis of variance
BIS	Bureau of Indian standards
BOD	Biochemical Oxygen Demand
CCD	Central Composite Design
COD	Chemical Oxygen Demand
C.V	Coefficient of Variation
Df	Degree of Freedom
DO	Dissolved Oxygen
DWTP	Design of Water Treatment Plant
EC	Electrical Conductivity
EDAT	Ethylene diamine tetra acetate
EPA	Environmental Protection Agency
ETB	Ethiopian Birr
EU	European Union standards
FTIR	Furrier transmitter infrared radiation
ISO	International Organization for Standardization
MCL	Maximum Contaminant Level
Nobj	Non-objectionable
NTU	Nephelometric Turbidity Unit
Obj	Objectionable
PACl	Poly Aluminum Chloride
ppm	parts per million
POU	Point of Use
RSM	Response Surface Methodology
Sp_{av}	Sample Average
TDS	Total dissolved solid
TH	Total Hardness
UNICEF	United Nations Children's Fund
Uobj	Unobjectionable
WHO	World Health Organization
XRD	X-ray diffraction

Abstract

This study focused on treatment technique using peanut hull to produce natural adsorbent for softening the tap water in Mekelle city which is hard water. Its physicochemical properties were examined. Water softening experiments were conducted to observe the changes in hardness causing Ca^{2+} and Mg^{2+} divalent ions total hardness, with varying dosages of peanut hull natural absorbent/coagulant.

Characterization study before and after the treatment process of the peanut hull natural absorbent/ coagulant was conducted using FTIR and XRD in order to control the possible hardness removal mechanisms for hardness causing divalent ions (Ca^{2+}& Mg^{2+}) by identifying its functional groups.

A total of 26 raw drinking tap water samples were collected from three different sites (Eyala, Ayder and Ayanalem) containing high concentration of hardness of the city used for domestic and other purposes.

The hardness removal efficiency was compared with Ethiopian and WHO standards. The maximum hardness removal efficiency found to be 89.5%, by taking four factors at optimum conditions were attained at initial concentration divalent of ions 1.50 mg/l, coagulant dose 2.50 g/l, pH 6.5 and settling time 120 mini.

Keywords: Physio-chemical parameters; drinking tap water; calcium; magnesium; water hardness; peanut hull adsorbent.

Table of Contents

List of Tables

List of Figure

1. INTRODUCTION

1.1. Background

Quality of water is one of the most significant natural resources of the world. It plays an energetic role in the development of communities; hence a reliable supply of water is essential. It needs to be preserved all the time for human and industrial use. As for human consumption, quantity and quality of drinking water have been standard as increasingly critical issues. Addressing the decline of water quality in developing countries, where an estimated one billion people lack access to potable quality water, is a primary encouraging factor for many community development efforts and is a key component of the Millennium Development Goals [1]. Potable water is the important need of man to sustain life. Water assists as lubricant, regulates the body temperature and provides the basis for the body fluids and metabolism [2]. Drinking water should be appropriate not only for human consumption but also for washing/ showering and domestic food preparation because chemical and other constituents of the water would give a rise to economic damage as well [3].

Water is a good solvent and picks up scums easily and thus changes its taste, color and odor and also it is a great importance in all natural and anthropogenic activities. It restores shape and oceans and seas, rivers, lakes and forests, becoming part of the identity of environments and landscapes and of principal importance for the development of ecosystems and human life. While in the past it has been measured an infinite good, but currently misuse, coupled with growing demand, has made funds of fresh and clean water decrease [4]. Because of its capability to solubilize the pure water is not found in nature. Dissolved scums include minerals, organic compounds and gases that change the physical (turbidity, color, temperature, electrical conductivity), chemical (chemical and biological demand for oxygen, pH, alkalinity, total organic carbon) and biological characteristics of water, whose effect depends on the composition, concentration and chemical reactions between pollutants [5].

Water treatment is the removal of suspended and colloidal particles, organic matter, micro-organisms and other substances that are harmful to health, seeking the lowest cost of distribution, operation and maintenance and reduced environmental impacts to the surrounding region [6]. The common systems of water treatment process involve coagulation/flocculation followed by sedimentation, filtration and disinfection. The common chemical coagulants are aluminum sulphate, polyaluminium chlorides, ferric chloride and synthetic polymers [7]. The amount of coagulant depends on numerous parameters such as type and concentration of contaminants, pH and temperature. Chemical coagulants like $FeCl_2$, Alum are used in Municipal drinking water treatment plant for purification methods. The additional use of amount of chemical coagulants can affect human health. Aluminum has also been specified to be an instrumental agent in contaminated water as the lacks of knowledge for drinking water treatment which not afford to use high cost of chemical coagulants. Some drinking water treatment plant in developing countries face a numerous of problems which are large seasonal difference in raw water quality e.g. high cost of water treatment chemicals, turbidity, under dosing of chemicals leading supply of poor drinking water [8].

It is well-known fact that when water is contaminated, its normal functioning and properties are affected. Recurrent improvement in the quality of water for purposes of domestic consumption, drinking, personal sanitation and certain medical conditions is among the top challenges of the world. The establishment of safe water to the people is a crucial development priority of any country in the world [1,2].

Impurities are substances that are dissolved in water and make it unfit for use. Some impurities can be easily recognized only by evaluating the taste, odor and turbidity of the water because pure water remains tasteless, colorless and odorless. However, most impurities cannot be easily sensed and require testing to expose whether or not water is contaminated. Physicochemical parameters of water are vital to determine the quality of drinking water affording to WHO [9]. The physical parameters that are likely to give rise to criticism from consumers are taste, color, odor and turbidity while low pH causes deterioration and high pH results in taste criticisms [9, 10].

Mekelle, the Capital of Tigray region, is placed within the Mekelle Geological outlier which is fully covered with sedimentary rocks of limestone, shale-gypsum interface, shale and dolerite sills and dykes. It is surrounded by volcanic sedimentary rock of sand stone and metamorphic rocks [11]. As a result, Mekelle outlier aspects water salinity problems due to its spatial geological formations and rock water interaction during circulation and ground-water flow. Many scholars and organizations have studied the hydrogeology of Mekelle area. All of the studies intensive on groundwater potential assessment, recharge and discharge estimation and few of these allocated with hydro geochemistry, but none on the solution of water quality on water hardness removal and treatment selections. So, present paper attempts to fill this gap and report the probable impact of water quality and propose cost-effective mechanism to decrease house hold water hardness.

Most of the water resources should be preserved for purification before consumption. In some countries, groundwater is the chief safe drinking water resource [1]. In some cases, the resource does not satisfy to the desirable levels concerning their chemical properties, such as nitrate contamination, heavy metals, hardness, soluble iron, etc. [2]. Among them, water hardness can look challenging in some cases; it can also be considered as a significant aesthetic parameter. However, because public acceptance of hardness differs unusually according to local conditions, a maximum acceptable level has not been clear. In general, water supplies with total hardness higher than 200 mg/L can be bore by consumers but are measured as poor resources; whereas values higher than 500 mg/L are not acceptable for most of the domestic consumptions [12,13]. Recently, several methods including electro membrane processes, ion exchange process, electro deionization process, capacitive deionization, membrane, fluidized pellet reactor, coagulation and adsorption have been studied for the removal of a wide variability of molecular and ionic species from several water streams, including those accountable for hardness (e.g. Ca^{+2} and Mg^{+2} cations). Among the developed processes, coagulation/absorption has been commonly studied for the uptake of numerous ionic and molecular species from water.

In a determination to decrease the proportion of people without sustainable contact to safe drinking water, there is a need to optimize the production of peanut hull from locally available wastes and apply it for water treatment in various communities. This has controlled to the development of alternative low-cost technology for the treatment of drinking water in the developing country. Drinking water situations have great influences on people's everyday life, specifically in the rural and remote areas where access to safe drinking water is very critical. Surface water frequently is the only source; so, water contaminations are difficult to avoid due to hard and uncontrolled use of surface water. Unsafe drinking water may consequence in fatal diseases.

Therefore, this research is focused on developing an efficient and cost-effective processing technique using peanut hull coagulant/absorbent to be used for drinking water treatment.

1.2. Statement of the problem

Nowadays characterizing and removing of the drinking water hardness become vital issues in the sustainable management of water. Many countries including, Ethiopia, are now suffering severe soft drinking water scarcities. Mekelle town, the capital of Tigray region state, has water distribution systems to provide tap water and curb the acute water shortages of household drinking and cooking, bathing and showering, dishwashing and clothes washing experienced by the inhabitants. But the drinking water is not comfortable for the major purposes listed here although the inhabitants are managed to use this water, which is highly concentrated with ash colored dissolved substances forming sediment at a bottom of a stand still container within hours. Thus, the possibility of the local tap water system being contaminated by physicochemical interactions from the various pits cannot be overlooked. Again, health records obtained from the nearby hospital showed that the communities experience periodic outbreaks of water-related diseases like skin diseases (irritation), dull and lifeless hair etc. The following consumer problems are also easily detectable in the current drinking water use of Mekelle city:

- ✓ Produces soap scum most noticeable on tubs and showers.
- ✓ Produces white mineral deposits on dishes more noticeable on clear glassware.
- ✓ Reduces efficiency of devices that heat water.
- ✓ Reducing the efficiency of heat transfer as hardness deposits build in thickness.

Also, hard water is said to cause serious health problems such as urolithiasis, cardiovascular disorder, kidney problems, anencephaly and cancer [14]. Because of the challenges raised by hardness in water, immediate measures to soften water are inevitable. Currently, there are various techniques that have been put in place to solve the hardness problem. Ion exchange, electro-based techniques, and membrane filtration are among the techniques having so far been applied. However, high costs in installation, operation and maintenance hinder its mass application especially in third world countries like Ethiopia. Water softening by adsorption using agricultural wastes based like peanut hull as adsorbent seems to be potential in the sense that the agricultural wastes are locally and cheaply available. Peanut hulls are agricultural wastes that mainly disposed after extraction of their inner contents. These wastes can be converted to useful adsorbent property which in turn can be used to treat water. Hard water softening by peanut hull as adsorbent is not yet reported to be done.

It is therefore significant to characterize and investigate the potential of hardness removal from drinking water and adsorbent produced from peanut hull, by examination treatment alternatives. Thus, this research was worked as a scientific information, and data input that helped to check for further treatment work and better management of the water at use attempted on to investigate the bio-absorbent performance of peanut hull for hardness removal, that can effectively remove hardness from the drinking tap water by taking real sample at different hardness levels**.**

1.3. Objective of the study

1.3.1. General Objective

- To investigate the peanut hull using adsorbent prepared for removal of hardness.

1.3.2. Specific objective

- To characterize peanut hull adsorbent for purification of drinking tap water hardness.
- To characterize the physicochemical parameters of drinking tap water.
- To investigate the effectiveness of peanut hull to adsorb hardness (Ca^{+2} and Mg^{+2}) from water.
- To study the effect of contact time duration, dose of the adsorbent, initial concentration of the hardness causing ions, and pH solution by the absorbance technique on the hardness removal.

1.4. Significance of the study

When this research is successful completion, it will play a vital role for providing substantial baseline information for treatment and purification water from its hardness by identify the areal distribution in the study areas, assess water suitability for public use and physicochemical components. Also, Farmers who grow *peanut* can generate income through selling its hulls.

1.5. Scope of the Study

This was done starting from investigating characteristics of representative drinking tap water, pretreatment and then continued by treating with peanut hull for a specific actual hard-drinking tap water and finally it was end up with determination of effect of operating conditions, which leads to high quality adsorption. Moreover, adsorbent of peanut hull waste effectiveness was checked.

2. LITERATURE REVIEW

2.1. Sources of drinking water in Mekelle city and their quality

The main source of Mekelle City's water supply is ground water from 17 boreholes that ranged from 32- 250 meters deep [14]. The distribution system depends primarily on gravity, but the network also relies on 17 pumps. Water is pumped to surface reservoirs where it is treated with chlorine. The yield of the boreholes varies from 4 to 45 liters per second. 10 of these boreholes are located in Aynalem well field, about five kilometers south of the town.

Water supply in Mekelle city does not meet demand, and sanitation coverage needs. Many households, schools and health institutions often lack water and basic sanitation facilities, which has had radical implications for the public health. The water supply system in and the treatment practices are suffering a number of design and operational problems. Consequently, the quality and quantity of distributed water do not meet the necessities of consumers and the targets set by the authorities. Mekelle city drinking tap water sources comes from different sites such as Aynalem, Lachi, Quiha, Enda Giyorgis, Ayder, Eylala and Enda Gebreil reserviors which are directly distributed to the consumers after disinfection.

2.2. Water problems in Mekelle city

In Mekelle city, water can be assorted with many contaminants. Some of them are not good for the society. In this section the problem associated with hard water is described below.

2.2.1. Hard water

Water is measured hard when it has a high concentration of dissolved minerals, specifically calcium and magnesium. Water is a good solvent and these minerals dissolved in it as it interchanges through soil and rock and are carried along, eventually up in our water supply [15].

Water hardness causes many economic problems for: beverage machines, laundry washers, water heaters, dishwashers, shower heads, faucets, fixtures, and other household units. These problems are added to the public dissatisfaction of hard water [16]. The amount of hardness minerals in water disturbs the amount of soap and detergent necessary for cleaning. Clothes laundered in hard water may be feel scratchy and harsh. Hard water may cause a film on glass shower walls, doors, sinks, bathtubs, faucets, etc. skin washed with hard water can become dry and irritated. Water flows may be reduced by deposits in shower and pipes heads. Hard water also contributes to costly operation and inefficent of water using appliances. Heated hard water forms a sacel of calcuiem and magnesium minerals that can contribute to the failuer of water or to the inefficient operation using aplliences. Pipes can become clogged with scale that decreases water flow and ultimatly requires pipe replecment.

Hard-water used for cooling water applications comprises mineral ions especially calcium ions which become insoluble when temperature rises [17]. Calcium ions react with carbonate ions existing in water to form layers of deposits on heat transfer surfaces. This reduces the efficiency of the system [18]. Polyvalent, metallic ions dissolved from soil cause water and rock to become hard. Calcium (Ca) and magnesium (Mg) are the greatest common ions even though any positively charged divalent ions, such as strontium (Sr), iron (Fe) and manganese (Mn) can cause hard water [19]. Water hardness is also enlarged in areas with increased calcium carbonate ($CaCO_3$) in the soil and high concentrations of CO_2 in the unsaturated zone [20].

Table 2.1: Environmental Protection Agency (EPA) hardness scale for concentrations of calcium carbonate in water (EPA, 1986).

Classification	Equivalent concentration of $CaCO_3$
Soft water	0-75 mg/L
Medium hard water	75-150 mg/L
Hard water	150-300 mg/L
Very hard water	> 300 mg/L

2.2.2. Sources of water hardness

Water hardness in most groundwater due to release of dissolved minerals occurring from sedimentary rock, as a result weathering of limestone and calcium bearing minerals. Hardness can also happen locally in groundwater from chemical and mining industry effluent or excessive application of lime to the soil in agricultural areas.

2.2.3. Indications of hard water

Hard water inhibits with almost every cleaning task, from laundering and dishwashing to bathing and personal grooming. The amount of hardness minerals in water disturbs the amount of soap and detergent necessary for cleaning. Soap used in hard water combines with the minerals to form tacky soap curd. Some synthetic detergents are less effective in hard water because the active ingredient is incompletely inactivated by hardness, even though it stays dissolved. Bathing with soap in hard water on the skin leaves a film of sticky soap curd. The film may prevent bacteria soil and from being removed.

2.2.4. Types of hardness

Hardness in water is caused by a diversity of divalent cations, primarily calcium and magnesium. Those cations have a tendency to associated with anions (negatively charged ions) in the water to form stable compounds known as salts. Water supply professionals do not completely agree on the descriptive terminology that should be used when categorizing the concentration of hardness in water nor what lower threshold concentration defends the investment in a water softener. Table 2.2 below shown the two common severity scales used to categorize hardness.

Table 2.2. Examples of carbonate hardness and Noncarbonate hardness compounds.

Carbonate hardness compounds	Noncarbonate hardness compounds
Calcium carbonate ($CaCO_3$)	Calcium sulfate ($CaSO_4$)
Magnesium carbonate ($MgCO_3$)	Magnesium sulfate ($MgSO_4$)
Calcium bicarbonate ($Ca\ (HCO_3)_2$)	Calcium chloride ($CaCl_2$)
Magnesium bicarbonate ($Mg\ (HCO_3)_2$)	Magnesium chloride ($MgCl_2$)
Calcium hydroxide ($Ca\ (OH)_2$)	
Magnesium hydroxide ($Mg\ (HO)_2$)	

Carbonate hardness is caused by metals combined with a form of alkalinity. While noncarbonate hardness forms when metals combine with anything other than alkalinity. Carbonate hardness is sometimes called temporary hardness because it can be removed by boiling water. Noncarbonate hardness cannot be broken down by boiling the water, so it is also known as permanent hardness.

2.2.5. Problems associated with hard water

Hard water interferes with almost every cleaning task from laundering and dishwashing to bathing and personal care [21]. The amount of hardness minerals in water affects the amount of soap and detergent necessary for cleaning. Clothes laundered in hard water may feel harsh and scratchy. Dishes and glasses may be spotted when dry. Hard water may cause a film on glass shower doors, shower walls, bathtubs, sinks, faucets, etc. Skin washed with hard water can become itchy and dry. Water flow may be reduced by deposits in pipes and shower heads. Faucets and other fixtures can have permanent deposits on them and the chrome finish can be destroyed [22]. Dealing with hard water problems in the home can be a nuisance [23]. Soap used in hard water combines with the minerals to form a sticky soap curd in washbasins and bathtubs. Hard water also contributes to inefficient and costly operation of water-using appliances [24]. Heated hard water forms a scale of calcium and magnesium minerals that can contribute to the inefficient operation or failure of water-using appliances. Pipes can become clogged with scale that reduces water flow and ultimately requires pipe replacement.

2.2.7. Health effects of hard water

Hard water has no known adverse health effects. On the contrary, very hard water can be a small contributor to the daily need of calcium and magnesium. There has been research that shows that drinking hard water can decrease the risk of heart attacks [25]. The decrease was very small, and it is still under investigation.

2.3. Physico-chemical parameters for testing of drinking tap water

Water becomes polluted with several impurities it includes hardness causing substances, heavy and toxic metals, some physical and chemical impurities. It is essential that the quality of drinking water should be checked at regular time interval, because due to use of contaminated drinking water, human population suffers from varied of water borne diseases [26]. It is very crucial and vital to test the water before it is used for drinking, domestic, agricultural or industrial purpose. Water must be tested using different physic-chemical parameters. Selection of parameters for testing of water is merely depends upon for what purpose we going to use that water and what extent we need its quality and purity. Drinking water is the mean source of disease scattering to the human being [27]. So, it is necessary to know details about different physico-chemical parameters such as hardness, color, temperature, acidity, pH, sulphate, chloride, DO, BOD, COD, alkalinity used for testing of water quality. The following different Physico-chemical parameter are tested regularly for monitoring quality of water.

Temperature: Temperature is the greatest importance environment factor with effect on plants and animals. Water has some unique thermal properties which combine to minimize temperature change. The water temperature depends on the climatic, topographic and depth of the water column changes [28]. Temperature is fundamentally important for its effect on certain chemical and biological reactions taking place in water and in organisms and inhabiting aquatic media. It depends upon season, time of sampling and ambient atmospheric temperature etc., [29]. Temperature was known to influence in the purpose of other factors like conductivity, dissolved gases, pH and various forms of alkalinity. Some of the factors that disturb water temperature are ground water movement and chemical, heat exchange on the earth surface under controlled radiation in and out, and thermonuclear processes occurring in aquifers [30].

Alkalinity: Alkalinity is a chemical measurement of water's capability to neutralize acid and also a measure of a water buffering capacity or its capability to resist changes in pH upon the addition of acids or bases. Alkalinity is important in many uses and because the alkalinity of may surface water is primarily a functional hydroxide content, carbonate and bicarbonate, it is taken as an indication of the concentration of these residents. Alkalinity value reserve as an index of creative potential of water [31].

Electrical conductivity (EC): Electrical conductivity a measure of the electric current that solution transfers. Electrical conductivity used to rapidly estimate the ionic or water supplies, soluble salt concentration in soils, fertilizer solution and chemical solution. It is measured with the help of EC meter which measures the resistance presented by the water between two platinized electrodes. EC values are a good quantity of the relative difference in water quality between different aquifers [32].

Dissolved Oxygen (DO): The amount of DO in water, such as a river, lake or stream. DO is the most vital indicator of the health of water bodies and its capacity to provision a balanced aquatic ecosystem of animals and plants. Warm water released from flowages (storm sewers) and industrial outlets can also decrease DO levels. The low DO concentration detected during summer could be attributed to the higher salinity of the water and higher temperature [33].

pH: pH is one of the most common investigates in soil and water testing, is the standard measure of the intensity of acidity or alkalinity and measures the concentration of hydrogen ions. Mostly, the pH was determined by the amount of dissolved carbon dioxide which forms carbonic acid in water [34]. The pH of ground water can also be lowered by organic acids from decaying the dissolution of sulfide minerals and vegetation [35]. Usually alkaline pH is measured to be good for promoting high primary productivity. Natural water has a pH value between 6.5 – 8.5. These values are typical with small seasonal variations, and unexpected change would indicate industrial pollution. Further, highly acidic or highly alkaline waters are objectionable because of corrosion hazards and possible difficulties in treatment.

The pH does not have any adverse health consequence but it stands taste of water higher pH reduces the germicidal potentially of chloride and induces the formation of toxic trihalomethanes. Most of the natural waters are generally alkaline due to the presence of sufficient quantities of carbonate [36]. The pH scale ranges from 0-14, with 7 being neutral. pHs greater than 7 are alkaline (basic) whereas pHs less than 7 are acidic. Normal rainfall has a pH of about 5.6 somewhat acidic due to carbon dioxide gas from the atmosphere. Figure 2.1. shows the pH values and their corresponding effects living components and on the different environments.

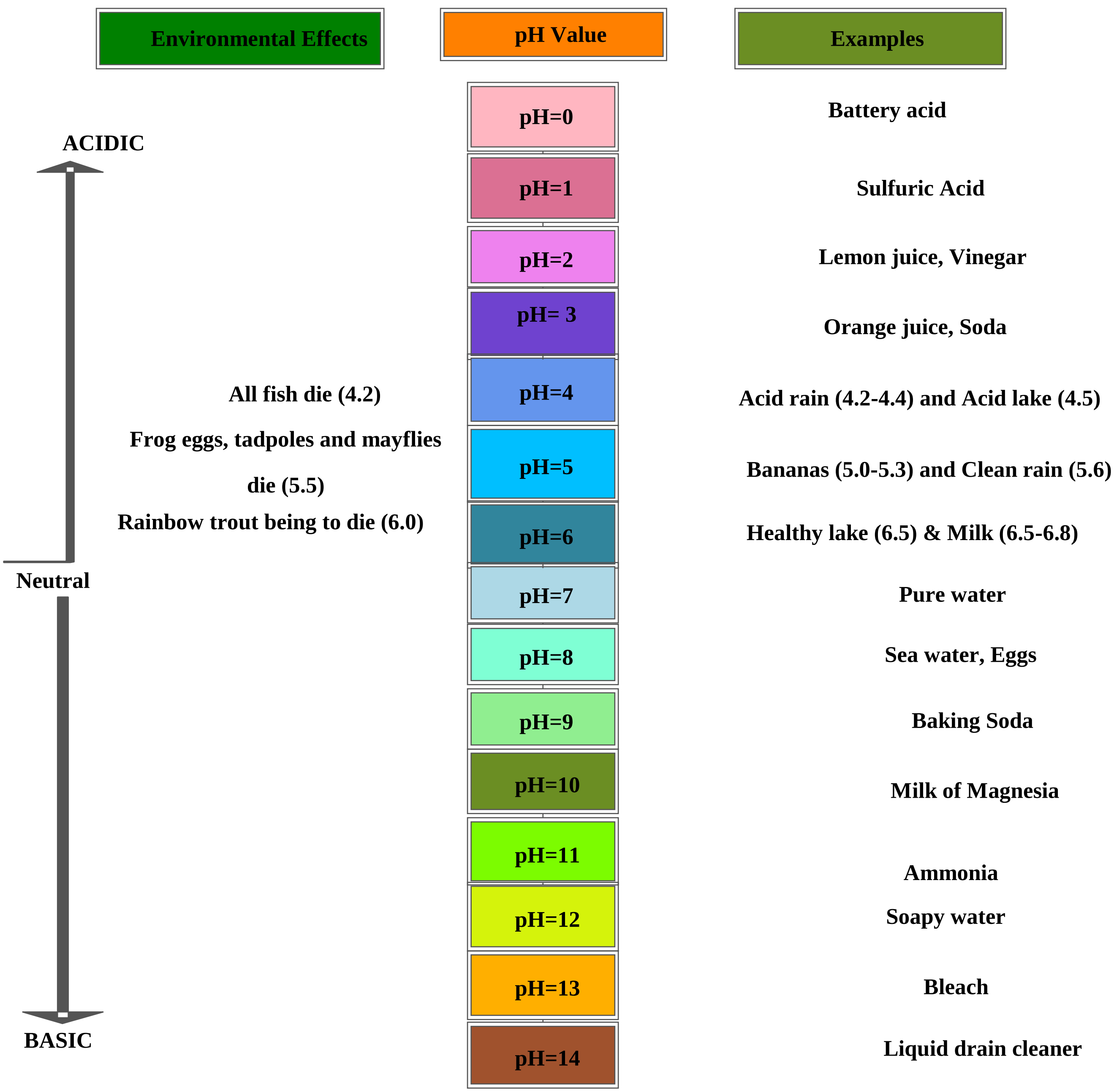


Figure 2.1. The pH scales for different environments and living components.

[Source]: Courtesy of Environment Canada (http://www.ns.es.qc.ca/).

Total Hardness (TH): Total hardness is well-defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate ($CaCO_3$) in milligrams per liter (mg/L). Drinking water hardness may cause the problem of kidney stones and heart disease [39]. The hardness is measure of polyvalent cations in the water. Hardness mostly characterizes the concentration of calcium and magnesium ions, because these are the most common polyvalent cations.

Total dissolved solid (TDS): TDS are the total amount of portable charged ions, including salts, minerals or metal dissolved in a given volume of water in mg/L. TDS is directly related to the quality and purity of water purification system and affects everything that consumes, lives in, or uses water [40, 41].

Chemical oxygen demand (COD): The COD test technique is based on the chemical decomposition of organic and inorganic contaminants, dissolved or suspended in water. COD is the oxygen essential by the organic substances in water to Oxidize then by a strong chemical oxidant.

Biochemical oxygen demand (BOD): BOD measures the amount of oxygen that microorganisms consume though decomposing organic matter, it also measures the chemical oxidation of inorganic matter.

Carbonates: It is measured with standardized hydrochloric acid by titration using phenolphthalein as indicator. Below pH 8.3, the carbonates are converted into the equivalent amount of bicarbonates.

Bicarbonates: also measured with standardized hydrochloric acid by titration using methyl orange as indicator. Methyl orange turns yellow below pH 4.0. Carbonic acid at this pH, the decomposes to give water and carbon dioxide.

Nitrate: Nitrate is naturally happening inorganic ions present in our environment. The decomposition of organic materials in soils, releases ammonia. Drinking water containing nitrates and can change normal hemoglobin to methemoglobin. Nitrate test can be distinguished through urine and blood test.

Chloride: is the ionized form of chlorine and it is one of the most abundant inorganic ions in natural water and wastewater. The potentiometric method of chloride investigation by silver nitrate titration is an effective technique of chloride level determination. The effect of chloride is discomfort on stomach, irritation on Eye/nose etc., The reality of considerable amount of chloride in river water may be due to discharge of industrial effluents into it. Industrial effluents and sewage water are rich in chloride content and the discharge of these waste waters result in greater chloride level in fresh waters [42]. But, excess of residual chlorine leads to the formation of potential cancer-causing chloro-organic compounds such as chloroform [43].

Sulphates: It is measured by the method of nephelometric in which the concentration of turbidity is measured in contradiction of known concentration of synthetically prepared sulphate solution. Barium chloride is used for making turbidity due to barium sulphate and mixture of organic substances [44] and sodium chloride is used to avoid the settling of turbidity.

Calcium and Magnesium: The calcium and magnesium contribute to the hardness of water as their carbonate. Magnesium is always significantly lower than of calcium component excessive concentration of magnesium is undesirable in domestic water because of the problems of scale formation of opposing [45].

2.4. Standards guide lines for physicochemical parameters of drinking water

Drinking water does not necessity to be absolutely pure to be safe. Because water is such a good solvent, pure water containing nothing else is almost impossible to accomplish. What is mandatory is that drinking water should be safe to drink for people in most stages of normal life, including children over six months of age and the very old. It should contain no harmful concentrations of chemicals or pathogenic microorganisms, and ideally it should be aesthetically pleasing in favor to appearance, taste and odour [46]. The Guidelines are resulting so as to take justification of the needs of an individual through a normal lifetime, including changes in sensitivity that may occur between life stages.

Drinking water quality standards defines the quality parameters set for drinking water. The main reason for not promoting the acceptance of worldwide standards for drinking water quality is the advantage provided by the use of a risk-benefit approach (qualitative or quantitative) to the formation of national standards or regulations. This approach should principal to standards and regulations that can be readily realized and enforced and which ensure the use of available national financial, technical and institutional resources for public health benefit [47]. There are no generally recognized and international accepted standards for drinking water [48]. Uniform where standards do exist and are applied. The acceptable concentration of individual constituents may differ by as much as ten times from one set of standards to another [49]. Some of the countries that functional the specific standards are World Health Organization standards (WHO), Australian standards, European Union standards (EU), Bureau of Indian standards (BIS), Ethiopia standards etc. The maximum permissible levels for the parameters used in the different project were reliable with the WHO guideline value. Some selected physicochemical parameters and their maximum limit of Ethiopian and other standards are shown in table 2.3 below.

Table 2.3. Selected physicochemical parameters and their maximum limit of Ethiopian and Other standards.

Parameters	WHO	BIS	US	Ethiopia	EU
Colour	Unobjectionable	5 Hazan units	Unobjectionable	Nonobjectionable	Unobjectionable
Odour	-	Unobjectionable	Unobjectionable	-	-
Taste	Unbjectionable	Agreable	Unbjectionable	Nonobjectionable	Unbjectionable
Turbidity	5 NTU	5 NTU	5 NTU	5 NTU	5 NTU
TDS (ppm)	1500 ppm	1500 ppm	1500 ppm	1500 ppm	1500 ppm
TH (mg/l as $CaCO_3$)	500 mg/l	300 mg/l	300 mg/l	300 mg/l	300 mg/l
pH value	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5
Calcium	75 mg/l	75 mg/l	125 mg/l	125 mg/l	75 mg/l
Magnesium	50 mg/l	50 mg/l	50 mg/l	50 mg/l	50 mg/l
Copper	1.5 mg/l	2.0 mg/l	2.0 mg/l	2.0 mg/l	2.0 mg/l
Lead	10 μg/l	10 μg/l	10 μg/l	10 μg/l	10 μg/l
Chloride	250 mg/l	250 mg/l	250 mg/l	250 mg/l	250 mg/l
Sulphate	200 mg/l	200 mg/l	200 mg/l	200 mg/l	200 mg/l
Nitrate	45 mg/l	50 mg/l	50 mg/l	50 mg/l	50 mg/l
Nitrite	3 mg/l	3 mg/l	3 mg/l	3 mg/l	3 mg/l
Alkalinity	300 mg/l	250 mg/l	250 mg/l	150 mg/l	250 mg/l
EC	2000 μS/cm	2500 μS/cm	2500 μS/cm	2000 μS/cm	2500μS/cm
Florid	1.5 mg/l	1.5 mg/l	4.0 mg/l	1.5 mg/l	1.5 mg/l

2.5. Techniques for Hardness Removal

In order to meet the standards of water quality, hardness has to be removed from water. As scientists struggle to find ways of softening hard water, some techniques are already discovered and they are in use. These methods include; cation exchange, chemical precipitation, reverse osmosis, ion exchange, electro-based techniques, membrane filtration and adsorption.

Cation exchange: is a popular option for softening domestic water supplies. The Ca and Mg ions in the hard water are exchanged with sodium (Na) or potassium (K). The cation exchange technique can remove nearly all of the Ca and Mg and even of Fe and Mn [51]. However, the cation exchange method increases the Na concentration in water which can have adverse effects on human health if consumed in large quantities.

Reverse osmosis: A reverse osmosis forces water through a filter to remove minerals and other contaminants. This technique avoids the use of salt but very hard water can clog the filter making it an expensive alternative in areas of very hard water [52].

Chemical precipitation, membrane filtration, electrolytic: Those methods have been found to be limited, since they often involve high capital and operational costs.

Ion exchange: reverse osmosis is more attractive processes method. But they do not seem to be economically attractive because of their relatively high investment and operational costs.

Adsorption: is becoming a promising approach for water treatment [53]. The reasons for its acceptance include its simplicity of design, consumption of locally available waste material, sludge production and chemical consumption free [54]. For the purpose of removing hardness ions from water, various biosorbent materials are being used. Peanut hull is one type low-cost biosorbent which is locally available in large quantities such as natural materials, agricultural waste or industrial by-products can be used as adsorbents with little processing. The sorption characteristics of the agricultural waste materials derive from their constituent polymers (approximately decreasing order of abundance): cellulose, hemicelluloses, pectin, lignin and protein [55].

2.6. Application of adsorbents in drinking water treatment

Adsorption is an effective and safe method of treating water, which rallies its quality by reducing levels of organic compounds, dissolved phosphorus, colour, iron and suspended particles. An adsorption is a small, raised reservoir that treats and stores water. It is sized to provide sufficient water for the homestead during the winter. Additional opportunity is a commercially available in-house adsorption system, which uses a tank in a batch treatment process. Adsorption of water-soluble pollutant is stimulating because of their high solubility. In addition to this and due to the development of synthesis technology, new variations of colors with different structures appear continuously, which provides difficulties for the selection of an appropriate adsorbents [57]. Due to the lack of suitable water treatment systems in these rural or underdeveloped communities, the greatest immediate option is to use simple and relatively cost-effective point-of-use (POU) technologies such as coagulation. Adsorption is crucial process in the treatment of both surface water and industrial wastewater.

2.7. Low-cost adsorption resources as drinking water purification agents

Adsorption resources are used as water purification agents, more than 2000 years ago were used in certain countries such as China, India and Africa [58]. Internationally it has become an emerging tendency among the current researchers to investigate the potential use of various low-cost adsorbent materials for water treatment purposes. Low-cost adsorbent resources for drinking water purification purposes useful to the people living in remote areas with economically disadvantaged. Figure 2.4 shows that the rapidly increasing publications using adsorbent material for drinking water treatment in indexed journals specially in past 16 years.

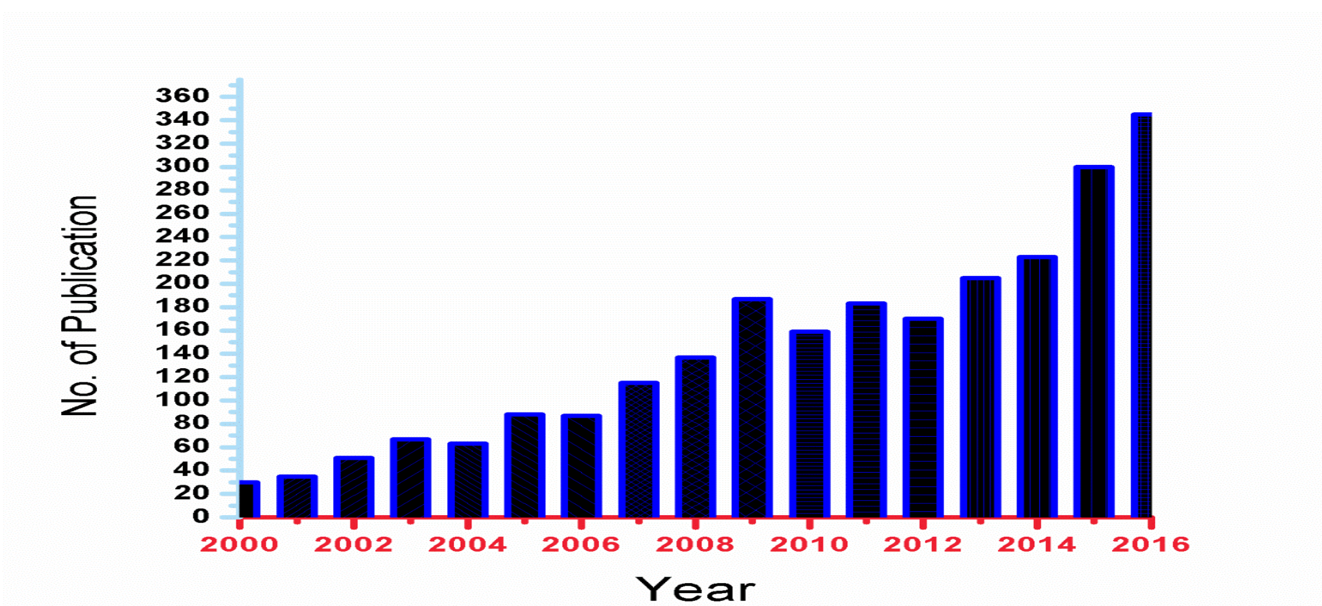


Figure 2.2: Record of the number of publications in indexed journals between 2000 and 2016 searched using natural adsorbent material for drinking water treatment.

[Source]: ScienceDirect, searched on 10 March 2017.

Water treatment processes have been studied to remove various water quality contaminants using many adsorbent resources such as; Moringa oleifera, cactus, peanut hull, Jatropha curcas, Strychnos potatorum, tannin, Solanum torvum, Cicer arietinum, banana peel, coconut's solid endosperm etc [58]. The following table 2.5 displays different countries that have studied the use of some adsorbent materials as water treatment agents.

Table 2.4: Adsorption materials used in previous researches and their countries of origin for water treatment.

Plant-based material	Countries of origin	Reference
Solanum torvum	India, Malaya, China, Philippines and tropical America	(Sivapriya & Leela, 2007)
Moringa oleifera	India, Asia, sub-Saharan Africa, Sudan and Latin America	(Yin, 2010)
Cactus	Mexico, North America	(Napacho, V. and Manyele, S. V., 2010)
Jatropha curcas	Regions of India such as Uttarakhand, Gujarat, Rajasthan, Bihar, Chhattisgarh, Punjab, Himachal Pradesh, Andhra Pradesh, Madhya Pradesh, Orissa and North-East states of India	(Bajrang Singh et al., 2013)
Peanut hull	Egypt	(Gamal O. El-Sayed, 2010)

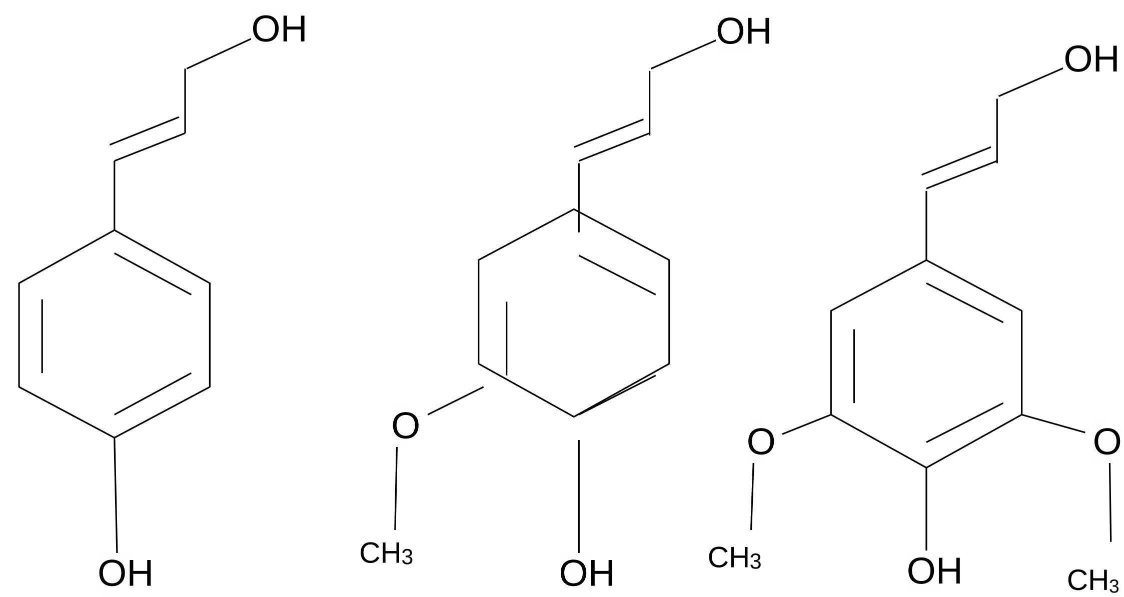
2.7.1. Peanut Hull

Peanut hull is an abundant and low-cost agricultural waste residue and is easily accessible in large quantity in southern and central Tigray, Ethiopia. Peanut in Tigray annually produced by estimation over three million kilograms. Since peanuts are grown as a plant, they are a renewable resource. As a by-product, the hulls are easy and inexpensive to obtain because industries need only the peanut as the main ingredient in their products.

2.7.1.1. Physical and chemical compositions of peanut hull

Peanut hulls have both physical and chemical compositions. The physical compositions of peanut hulls were its bulk density, porosity, solubility in water. Agricultural by-products showing high adsorption capacities for metals tend to contain lignin, cellulose, hemicellulose, pectin and protein [59]. The majority of their chemical composition is fiber counting cellulose and lignin. The high content of cellulose and lignin should make peanut hulls a good applicant for cation adsorption for water and wastewater treatment [60]. The structures of these compounds have functional groups that offer metal ion exchange and metal chelation. The structure of cellulose and lignin are shown in following figures.

Figure 2.3: Molecular structure of cellulose



Coumaryl Alcohol **Coniferyl Alcohol** **Syringyl Alcohol**

Figure 2.4: The three phenyl propane monomers of lignin.

The hulls are also rich in proteins. Table 2.5 results show that peanut hull contains protein composition can be used to purified water through a simple purification method that can be scaled up and hence encourage the use of peanut hull for large scale applications.

Table 2.5: Characteristics of peanut hull.

Characteristics	Composition	Percentage
Physical characteristic	Porosity	61.7%
	Solubility in H_2O	0.74%
	Bulk density	5-7 lb/ft^3
Chemical characteristic	Moisture	8-10%
	Protein	6-7%
	Fat	1%
	Fiber	60-67%
	Cellulose	35-33%
	Lignin	27-33%
	Ash	2-4%

[Source]: Contributed by soil adhering to peanut hull during analysis.

2.7.1.2. Peanut hulls adsorbent used in water purification

To increase awareness in the use of peanut hull application for water treatment, its availability in remote regions of the developing countries like Ethiopia. Peanut hulls are used in the production of soap, plastics, cosmetics, wallboard, linoleum, and as a replacement for synthetic food ingredients [58]. The hulls also have a few health welfares, as antioxidants are found naturally in the shell, and they contain vanillin which has potential benefits on human cancer cells [61]. Its bio-sorbent property is contributed by control of insoluble organic compounds and poly functional groups such as NH_2, –COO-, –C=O, PO_4^{-2} and OH^- [62]. The latter property brands peanut hull to be effective in removal of heavy metals and dye bleaching [63]. Similar test was showed to remove water hardness ions [64].

2.7.1.3. Selection of peanut hull adsorbent material for the study

In this study several criteria have been set prior to the selection of to be verified natural adsorbent. The selected adsorbent should be:

- Ease of preparation preceding to use in the treatment process;
- Freely accessible or native to the targeted developing countries;
- Biodegradable and cheap;
- Showed in different previous studies a capable potential in removing water quality contaminants.

3. METHODOLOGY

3.1. Study Area

This study was conducted in Mekelle city; the regional administrative capital city of Tigray region, northern Ethiopia located at 13030' North and 39028' East, with an elevation of 2000 meters above sea and 782 km from Addis Ababa. The city covers an area of 100 km^2 and population estimation for 2007 E.C based on central statically analysis was 350,000. There are about 17 bore holes used as drinking tap water sources for the city. The study used key information associated to demographic and socio-economic condition such as water use, distance, type and quality of water.

3.2. Materials

The material used for adsorption during the experimental works was peanut hull. The Reagents and Chemicals that used for this research were Sulphuric acid (H_2SO_4) used to activate peanut hull**,** Sodium hydroxide (NaOH) used to adjust the pH, Hydrochloric acid (HCl) used for titration, Sodium Chloride (NaCl) used for titration, distilled water etc., which bought from different chemical stores in Mekelle city.

The instruments and equipment used during this experimental works were Atomic Absorption Spectrophotometer (AAS nova 400plus) to measure the capacity for calcium and magnesium ions, orbital shaker (Excella E24R), pH meter, FTIR (spectrum 65 FTIR), X-ray diffraction (XRD),Jar test, electronic balance, grinder, oven, magnetic stirrer, different size conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, zipper plastic bags, filter paper whatman number 42 (150 mm Ø), different mesh size sieves and centrifuge mill.

3.3. Experimental Procedures

The procedures that were used in this research are described as follows:

3.3.1. Characterization of peanut hull adsorbent

3.3.1.1. Moisture content

A 10 g amount of the peanut hull sample was weighed in a Petri dish. The dish was placed in an electric oven kept at 105 ^{0}C for about 3 hours. The petri dish was port open or not covered during heating process. After heating petri dish was detached and cooled in a desiccator. After cooling the weight of dried sample was measured. Cooling, heating and weighing was repeated at 30 minutes between the two-consecutive balancing.

Moisture content (%) = $\frac{(X-Y)}{X}$*100 …………………………………………………..... Eq (3.1)

Where, X = Mass in grams of the absorbent taken for test.

Y = Mass in grams of the absorbent after drying.

3.3.1.2. Fourier Transform Infrared Spectroscopy (FTIR).

The FTIR analysis was carried out in order to identify the functional groups that might be involved in the binding of metal ions [66]. The functional groups of peanut hull adsorbent before and after absorption were determined using FTIR spectrometer at wave number range of 400 – 4000 cm^{-1}. The FTIR analysis was done at Addis Ababa university, College of Natural Science, Chemistry Laboratory.

3.3.1.3. X-ray diffraction (XRD)

The X-ray diffraction (XRD) technique analysis was carried out in order to characterized the structure and crystal sizes for the peanut hull adsorbent using an X-ray diffractometer. The XRD analysis also done at Addis Ababa university, College of Natural Science, Chemistry Laboratory.

3.3.2. Preparation of peanut hull adsorbent

Dry peanut hulls were obtained from Samre (Yechila) which is 35 km far away from Mekelle city. Matured hulls showing no signs of discoloration, softening or extreme desiccation were used. This raw peanut hull was washed several times with distilled water before use in order to remove any impurities. The adsorbent was then treated with 1 M solution of HCl for further purification by dissolving acid soluble components of the sample. It was then washed with deionized water to remove the excess of acid (pH= 7). Peanut hull was then dried at 45^{o}C for 24 hours to evaporate the remaining water molecules. The dried peanut hull was then milled and sieved to achieve 10-30 meshes (250 - 500 μm). In order to modify the peanut hull with sodium hydroxide, it was treated with2 M NaOH for 24 hours at room temperature. During modification, the solution was stirred at200 rpm. The modified peanut hull was then filtered with whatman filter paper number 42 (150 mm $\emptyset$) and then washed several times with deionized water to remove the excess of NaOH. Finally, the modified adsorbent was then dried at 55^{o}C for 24 hr before use.

Figure 3.1: Preparation of peanut hull adsorbent. a) before grinding b) Peanut hull after grinding

3.3.3. Jar test study

Jar test is the greatest commonly used method for determining the efficiency of peanut hull adsorbent, since it is easy to achieve. The equipment used in this study was Aqua jar test apparatus containing with 6 beakers. Each jar was filled with 500 ml of raw water with identical turbidity level, and the initial stirring rate was set to 200 rpm. For batch study, peanut hull powder was added in 1000 ml of tap water samples by varying quantity of adsorbent such as 0.5g, 1g, 1.5g, 2 g, and 2.5g. Then by rapid mixing for 2-3 minute and slow mixing for 30 minutes systematic stirring of the solution was conducted. After that 1.20 hour settling time was given. The variations in the removal of parameters were recorded. This was done mainly to test the calcium and magnesium (hardness causing ions) can be removed by using peanut hull adsorbent.

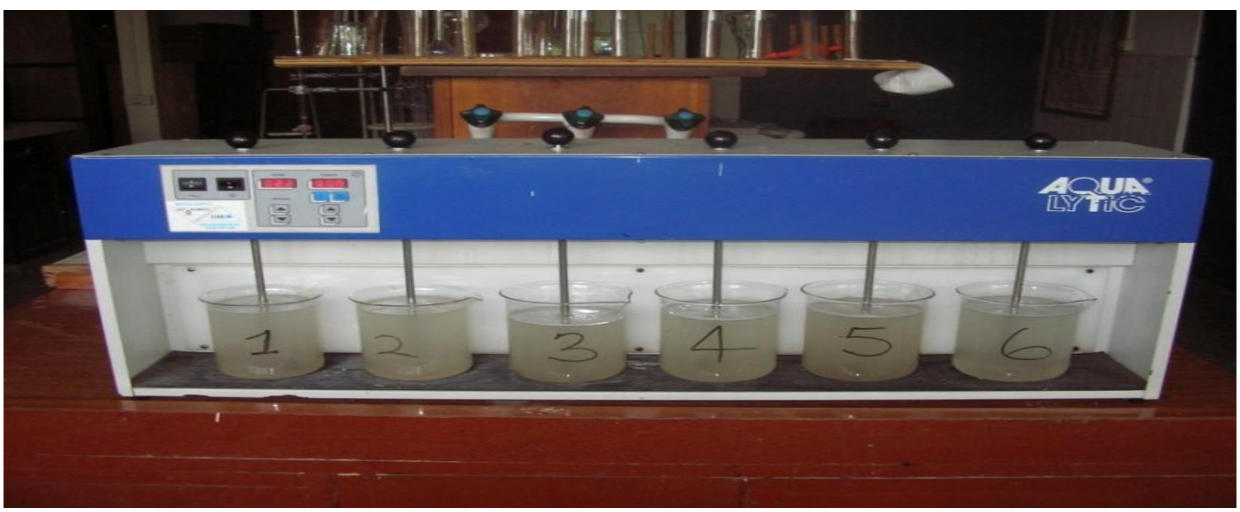


Figure 3.2: Methods of sampling using jar test equipment.

3.3.4. Treatment of sample containers

The containers were disinfected with Nitric acid (HNO_3) and finally washed with distilled water. The glass containers were also washed by soaking in Aqua Regia ratio of (3:1) concentrations HCl and HNO_3 respectively. It was then washed with tap water and finally with distilled water.

3.3.5. Storage of samples

All the samples were temporarily stored in a cold box at the time of sampling until they were finally moved into a refrigerator. Then the samples were stored at a temperature below 4 ^{0}C.

3.3.6. Physicochemical experimental works for drinking tap water

The drinking tap water quality parameters were treated using different methods. Those methods were analyzed before and after treatment of using various dosages of peanut hull adsorbent which are described as follows in table 3.1.

Table 3.1. Methods used for physicochemical study of tap water analysis.

S. No.	Parameters	Instrumentation/Method
1. Physical Parameters		
1	pH	pH meter
2	Turbidity	Nephelometer
3	TDS	Conductivity meter
4	Color	Visually
5	Electrical conductivity	Conductivity meter
6	Taste	Manually
2. Chemical parameters		
7	Calcium	AAS
8	Magnesium	AAS
9	Hardness	AAS
10	Alkalinity	Titration

3.3.6.1. Determination pH

The pH of the water samples was read using a digital Jenway 3505pH meter, which was calibrated with standard buffer solutions (pH 4 and 10.0). The water samples were measured into a clean beaker and the electrode of the instrument inserted into the water and the start button pressed, the reading was taken.

3.3.6.2. Determination of Turbidity

Turbidity was measured with turbidity meter a Model of 2100N/AN used to measure turbidity of water samples. The initial turbidity was measured 2 times on the raw water while stirring, and the average value from the three measurements was used as starting value of raw water (RW). After the sedimentation phase, the samples for turbidity measurement were collected from the supernatant using a standard pipette. The sample beaker was washed once with distilled water and twice with the supernatant before recording the turbidity. Each measurement took 2-3 minutes, washing was included. In order to remove any differences in turbidity due to different sedimentation times, samples were taken from jars 1-5 into separate beakers before measurements were taken.

3.3.6.3. Determination of Colour

The colour of water sample was determined though physical visualization comparator method in clean glassware. Then, the initial colour of water was totally removed after adding of the peanut hull adsorbent treatment method.

3.3.6.4. Determination of Taste

The taste of water sample was determined manually though a judgment based on sensory evaluation (nerve endings in papillae placed on the tongue and stimulated by chemicals) at a temperature of the experimented water 15 ^{0}C.

3.3.6.5. Total Dissolved Solids (TDS)/ Conductivity determination

The 500 ml well-mixed samples ware measured in a beaker. The water treatment TDS/Conductivity meter probe was absorbed in the sample. Then its conductivity and TDS were noted. This was done after calibration with 0.01N KC1. Conductivity of water is a property by virtue of which the current passed through it and is measured in terms of Micromho/cm (μm/cm) finally measured by sing Model 2100N/AN Laboratory turbidity meter.

3.3.6.6. Determination alkalinity

The alkalinity was measured using the methods of $CaCO_3$ scale (mg/l of $CaCO_3$). The sample was measured into a conical flask by adding two drops of methyl orange indicator. In this work the following equation was applied to determine the amount of alkalinity:

Alkalinity (mg/l as $CaCO_3$) = $(V_T - V_B) \times 50$ ………………………………………….…Eq (3.2)

Where; V_T= Volume of titrate and V_B= Volume of blank

3.3.6.7. Determination Calcium and Magnesium

Peanut hull adsorbent was prepared in a separate Erlenmeyer 0.5, 1, 1.5, 2 and 2.5 g respectively. Subsequently added the hard-raw water into Erlenmeyer. To obtain the homogeneous solution, it uses a shaker and then filtered with whatman filter paper. Finally, measure the values of calcium and magnesium in the filtrate using the equipment of an AAS.

3.3.6.8. Determination Total hardness

The total hardness of tap water samples was determined using AAS equipment. The total hardness of the tap water samples taken from sample sites were tried to be measured the following the calculation.

$$TH= \frac{((Amount\ of\ Ca\ ion\ adsorbed)}{MW\ Ca} + \frac{(Amount\ of\ Mg\ ion\ adsorbed\ ))}{MW\ Mg} \times 100 \quad \text{……...... Eq (3.3)}$$

Where, MW= the molecular weight of calcium and magnesium atoms.

3.4. Hardness removal

The raw hard-drinking water sample for this research was collected from three different sites that are used as drinking purpose in Mekelle city population. The water treatments were given directly by using peanut hull adsorbent. The hardness removal percentage (R %) is defined as the ratio of difference in metal concentration before and after adsorption (C_o – C_f) to the initial concentration of the adsorbate in aqueous solution (C_o) shown below:

$$R\ (\%) = \frac{(Co-Cf)}{Co} \times 100 \quad \text{………………………………………………...…………Eq (3.4)}$$

where; C_o = initial concentration in mg/L and C_f = final concentration in mg/L.

3.5. Experimental works using statistical design expert

The statistical operations of CCD design expert 7.0 were analyzed by characterization of the physicochemical parameters of the drinking tap water. In this experiment the jar test was used and also consisted of five identical paddles for mixing well to the hard water with adsorbent.

Table 3.2. Independent variables and CCD levels of experimental design.

Variables	Factor coding	Units	Levels	
			-1	1
Initial concentration calcium & magnesium ions	A	mg/l	150	500
Adsorbent dose	B	g/l	1.50	2.50
pH	C	-	6.5	8.5
Time	D	mini	45	120

The experimental matrix generated during this research using table 3.3 Central Composite Design Matrix as follows.

Table 3.3: Experimental matrix generated using Central Composite Design for hardness removal.

Std	Run	Factor 1 A: Concentration (mg/l)	Factor 2 B: Dosage (g/l)	Factor 3 C: pH	Factor 4 D: Settling time (mini)
1	2	150.00	1.50	6.50	45.00
2	21	500.00	1.50	6.50	45.00
3	24	150.00	2.50	6.50	45.00
4	1	500.00	2.50	6.50	45.00
5	13	150.00	1.50	8.50	45.00
6	8	500.00	1.50	8.50	45.00
7	7	150.00	2.50	8.50	45.00
8	12	500.00	2.50	8.50	45.00
9	14	150.00	1.50	6.50	120.00
10	15	500.00	1.50	6.50	120.00
11	11	150.00	2.50	6.50	120.00
12	17	500.00	2.50	6.50	120.00
13	26	150.00	1.50	6.50	120.00
14	10	500.00	1.50	8.50	120.00
15	20	150.00	2.50	8.50	120.00
16	25	500.00	2.50	8.50	120.00
17	9	237.50	2.00	7.50	82.50
18	5	412.50	2.00	7.50	82.50
19	16	325.00	1.75	7.50	82.50
20	18	325.00	2.25	7.50	82.50
21	22	325.00	2.00	7.00	82.50
22	19	325.00	2.00	8.00	82.50
23	3	325.00	2.00	7.50	63.75
24	23	325.00	2.00	7.50	101.25
25	6	325.00	2.00	7.50	82.50
26	4	325.00	2.00	7.50	82.50

4. RESULTS AND DISCUSSION

4.1. Characterization of the adsorbent

4.1.1. Moisture content

The measured moisture content of peanut hull adsorbent was obtained 7.2%. This indicated that when the hull was dried at the oven it may be holds less than10 % moisture content. This indicated that the peanut hull has a good adsorptive property. Because the amount hull content was not loss its adsorptive property by the drier.

4.1.2. FT-IR analysis for peanut hull adsorption mechanism

The FTIR technique is an important tool to identify the characteristic functional groups which are important in adsorption of hardness ions. Identified functional groups are likely to interpretation for the adsorption of hardness ions onto the adsorbent surface, hence high efficiency in water softening. Figure 4.1. shows the FTIR spectra of peanut hull. The board peaks at 3423.24 cm^{-1} is shown as stretching hydroxyl group (-OH). The peaks at 2931.13 cm^{-1} occurrence aliphatic C-H stretching. The band at 16320.97 cm^{-1}displays the variation of carbonyl group or the of carboxyl bonds. The bending at 1381.03 cm^{-1} stretch is showed alkane (C−H) group. The peaks at 1027.00 cm^{-1} show presence of alcoholic group. So, the peanut hull shows different functional groups and it predicts capable to binding Ca and Mg divalent ions.

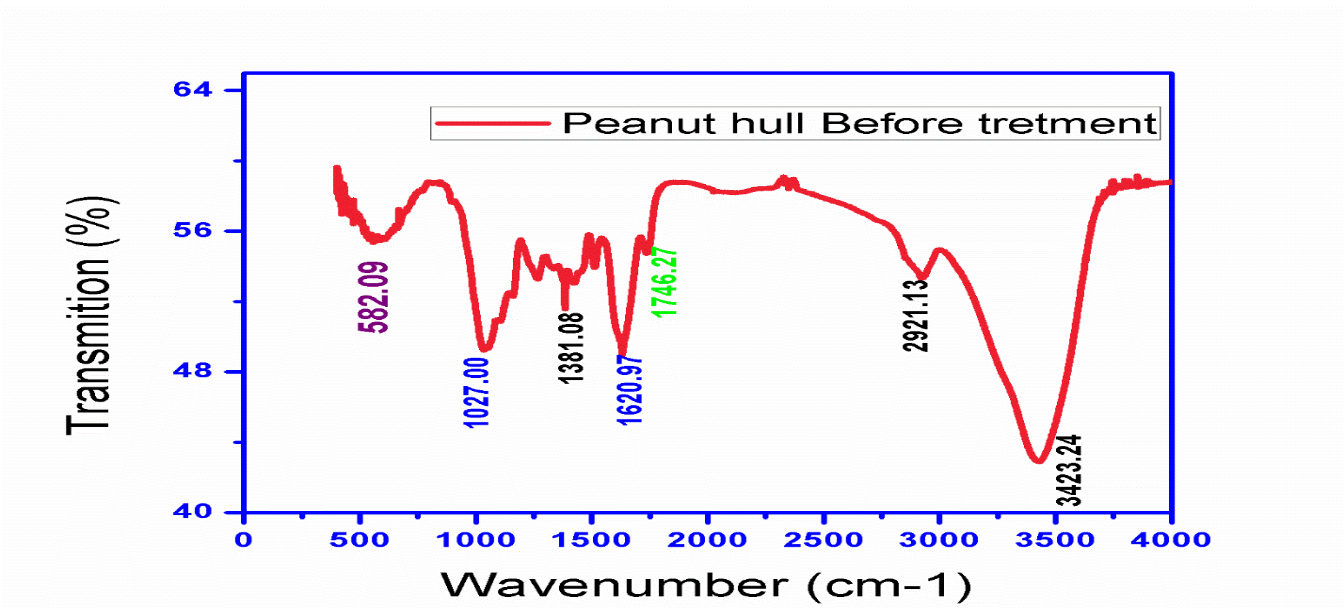


Figure 4.1: FTIR spectra for peanut hull before adsorption of Calcium and Magnesium ions.

The following table 4.1. Shows different functional groups, wave number, intensity and their types of vibrations in peanut hull adsorbent.

Table 4.1. Characteristic FTIR frequencies for peanut hull adsorbent functional groups.

Functional groups	Wave number (cm^{-1})	Intensity	Types of vibration
Hydroxyl (-OH)	3423.24	Strong, Broad	Stretch
Aliphatic (C-H)	2921.13	Medium	Stretch
Carbonyl (C-H)	1620.97	Strong	Stretch
Alkane (-C-H)	1381.03	Variable	Bending
Alcohol (C-O)	1027.00	Strong	Stretch

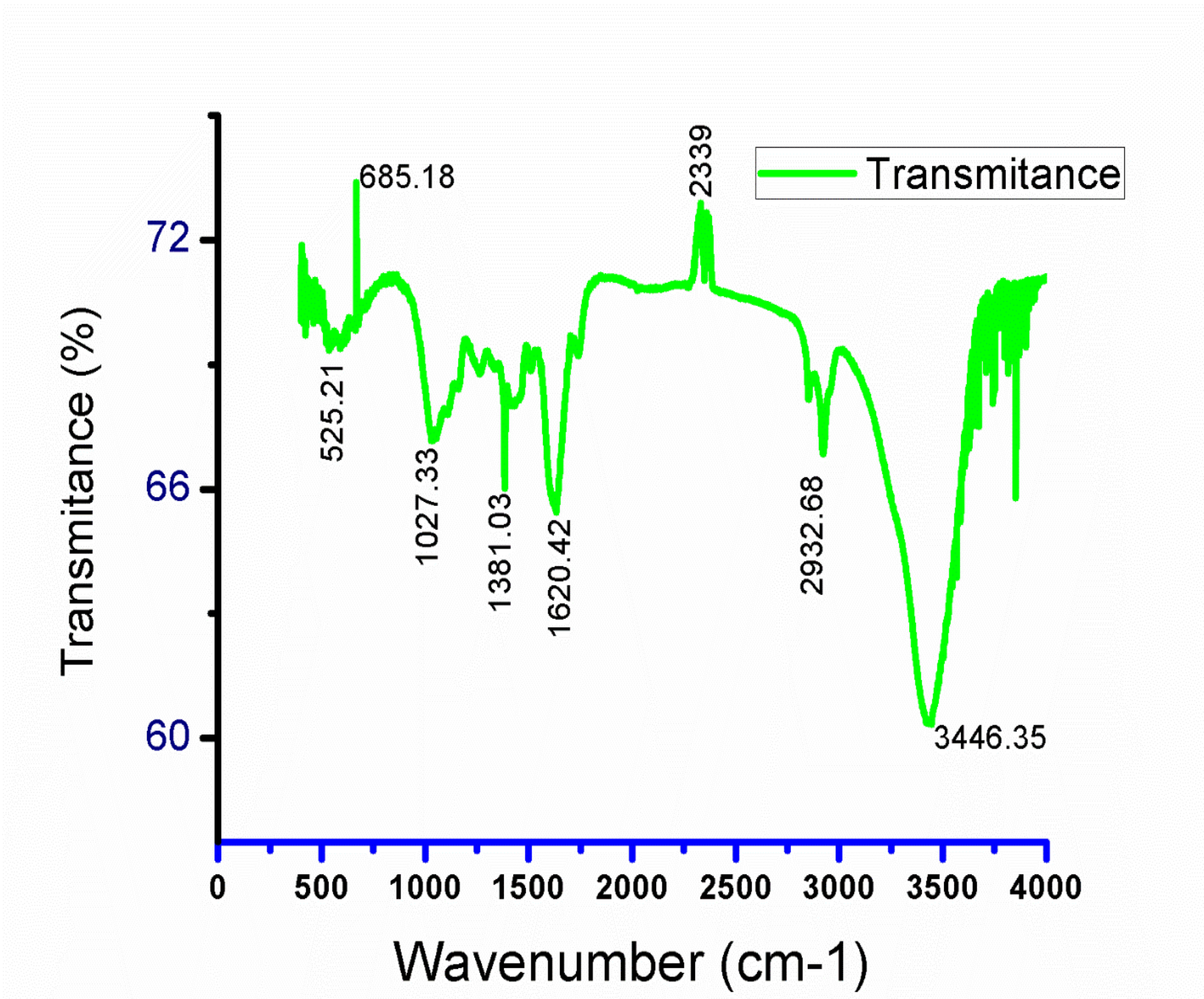


Figure 4.2: FTIR spectra for peanut hull after adsorption of Calcium and Magnesium ions.

4.1.3. XRD analysis for peanut hull adsorption mechanism

The XRD pattern of adsorbent prepared from peanut hull illustrates two characteristic broad diffraction peaks at (2θ) = 23^0 that is typical finger prints of semi-crystalline peanut hull as shown in figure 4.4. The XRD pattern of adsorbent prepared film shows peaks, this attribute a high degree of crystallinity to the prepared peanut hull. The average crystallite size of peanut hull was predictable from the strongest diffraction peak ($2\theta = 23°$) using the Debye-Scherrer equation which is expressed in Equation (4.1).

$$D = \frac{0.89\lambda}{\beta cos\theta} \qquad \text{...Eq (4.1)}$$

Where;

D= is the crystallite size,

λ= is the incident X-ray wavelength,

β= is the full width at half-maximum height and

θ= is the Bragg angle.

The peanut hull indicates crystallite sizes in the nanometer range (7-12 nm). Thus, the result tells that hardness causing ions attached to the peanut hull adsorbent surface cause a steric effect that retards the particle growth.

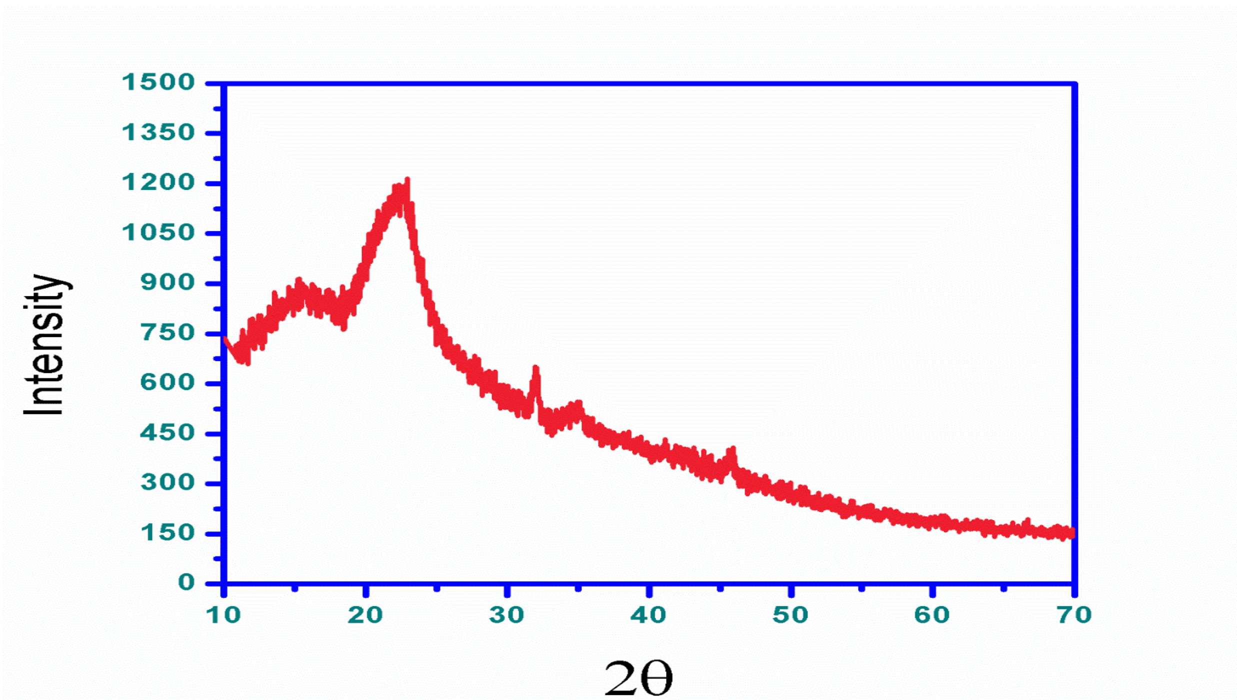


Figure 4.4: XRD pattern of the peanut hull adsorbent.

4.2. Characterization of the raw drinking tap water

Characterization of the raw water is mandatory in order to know its initial mineral compositions. Because the raw water sample covers the study area is established by determining the physical and chemical characteristics as per standard methods. In table 4.2. below shows that the physical characteristics of the drinking water under Mekelle city. The drinking tap is water sourced from ground water and it needs further study treatment using adsorption method in order to reduced its unwanted mineral compositions.

Table 4.2. Characterization of raw drinking water of Mekelle city.

Parameters of the untreated Drinking water										
	pH	Turb. (NTU)	EC (μS/cm)	TDS (ppm)	Colour	taste	Alkali. (mg/l)	Ca^{+2} (mg/l)	Mg^{+2} (mg/l)	TH (mg/l)
Average value	7.63	37.71	2355	2185.6	Brown	Obj.	285.12	420.33	46.67	1241

4.3. Analysis of Physicochemical drinking tap water using peanut hull adsorbent

In this research the very vital physiochemical water quality parameters were determined using standard analytical methods and procedures. The samples were collected using properly rinsed plastic bottles of 500 ml and kept in refrigerator until delivered to the laboratory for analysis. Some of the water quality parameters like pH, color, taste, electrical conductivity, total dissolved solid, alkalinity, calcium, magnesium and total hardness were measured. Also, to that all the reagents and distilled water were used as analytical grade and solutions respectively. The results attained with methods used for physico-chemical treatment study of drinking water in Mekelle city was as follows at table 4.3.

Table 4.3. Physicochemical parameters test results.

Parameters	Adsorbent dose(g/l)					Av.value	WHO Standard	Ethiopian Standard
	0.5	1.0	1.5	2.0	2.5			
pH	7.54	7.4	7.4	7.51	7.35	7.44	6.5-8.5	6.5-8.5
Turbidity (NTU)	24.68	15.73	12.83	11.77	8.88	11.53	5	5
Colour	Brown	colorless	colorless	colorless	colorless	colorless	colorless	colorless
Taste	Obj.	Obj.	Obj.	Obj.	Obj.	Obj.	-	Obj.
TDS (ppm)	1689.67	1062	715	529	496	898	1500	1500
EC (µS/cm)	1762.33	1346.3	862.13	710	632.66	1062.53	2000	2000
Alkalinity (mg/l)	235	170.67	145.67	122	114.67	157.20	250	150
Ca^{+2} (mg/l)	248.33	146.13	121.33	92.67	88.32	139.3	150	125
Mg^{+2} (mg/l)	36.67	30.33	18.67	10	7.0	20.54	50	50
TH (mg/l)	709.33	587.67	348.53	276.31	219.00	428.04	500	300

4.3.1. pH analysis

The pH of the tap water samples was neutral or close to it as they all range from 6.7 to 8.5 which are within the permissible limits 6.5- 8.5 given by WHO and Ethiopian Standards as given in the experimental result given above. One of the main objectives in controlling pH is to produce water that minimizes corrosion or incrustation. These processes, which can cause considerable damage to the water supply systems, result from complex interactions between pH and other parameters, such as dissolved solids, dissolved gases, hardness, alkalinity, and temperature. The variation of pH in the study samples is shown figure 4.5.

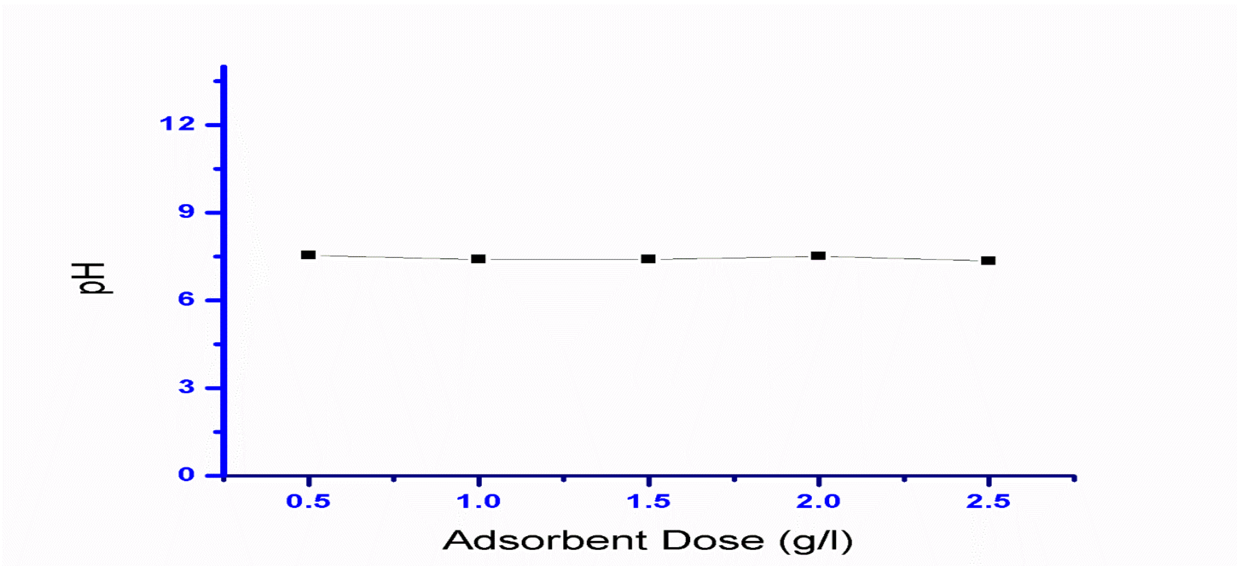


Figure 4.5: pH variations of drinking tap water being used at Mekelle city using peanut hull adsorbent.

4.3.2. Turbidity analysis

The turbidity profile shown in figure 11 below varies significantly amongst the water samples throughout the study period and ranged from 8.7 to 45.0 NTU. The turbidity values obtained from the sampling points were higher than WHO and Ethiopian standard of 5 NTU. These values disqualify the tap water for direct house hold applications. High turbidity also creates difficulty to disinfect water properly. Figure 4.6 demonstrates the turbidity reduction of the drinking tap water being used at Mekelle city.

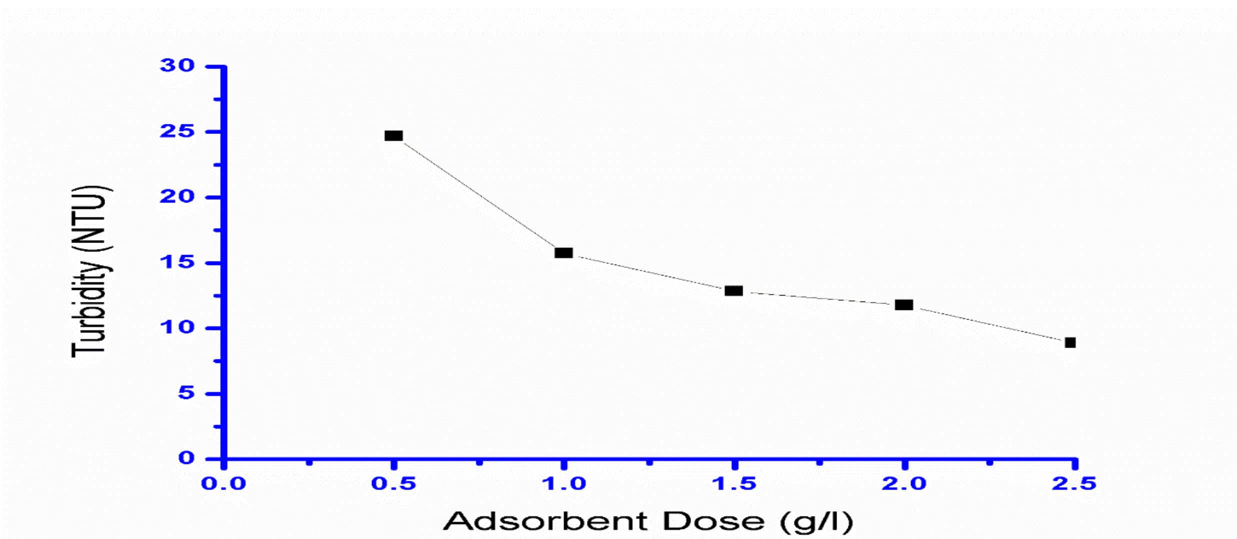


Figure 4.6: Turbidity reduction for drinking tap water being used at Mekelle city.

4.2.3. Colour analysis

The color was resolute early before biological or physical changes happened and the representative samples were collected in clean glassware. The initial colour of water was totally removed after the treatment. The peanut hull powder displays an adsorbent property. The color of samples was recognized by visuality comparator method. The visual comparison method was functional for color removed to all samples of drinking tap water, that makes water suitable for general and industrial applications. The analysis specified objectionable colorless result.

4.2.4. Taste analysis

Taste is used to regulate the acceptability of drinking water from a judgment based on sensory evaluation (nerve endings in papillae placed on the tongue and stimulated by chemicals). In this thesis work the major apprehension was with the taste rating test and not the taste threshold taste, which is used for qualitative and quantitative measurements of minimum measurable taste. The temperature of the experimented water should be around 15 ^{0}C. As this is an organoleptic test, it has not specific scientific value. Nevertheless, this parameter is significant because its effort to measure the acceptability of drinking tap water. The analysis of examination drinking tap water samples was showed objectionable taste result.

4.2.5. TDS analysis

Total dissolved solids level in the tap water is 496-1689.67 ppm which exceeds the permissible limit of 1500 ppm as per WHO and Ethiopian Standards. The term total dissolved solids refer mainly to the inorganic substances that are dissolved in water. The effects of TDS on drinking water quality depend on the levels of its individual component's excessive hardness, taste, mineral depositions and corrosion are common properties of highly mineralized water. The variation of total dissolved solids of tap water studied is shown figure 4.7 below.

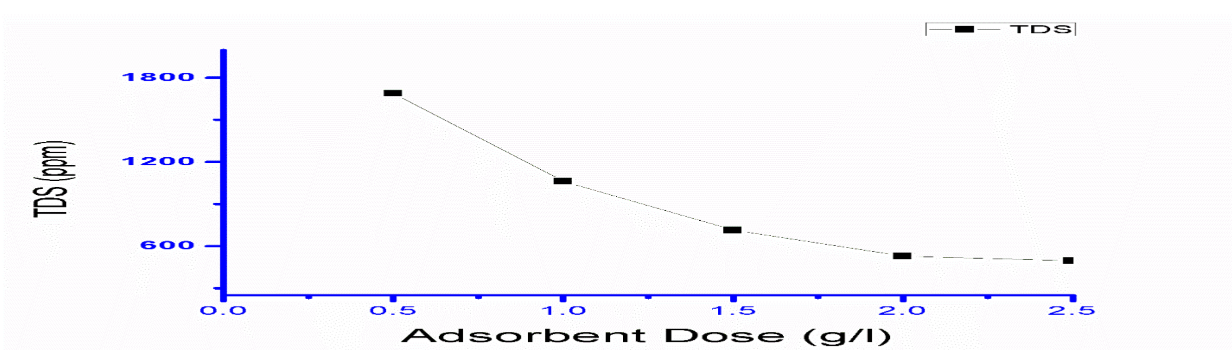


Figure 4.7: TDS variations of drinking tap water being used at Mekelle city.

4.2.6. Electrical Conductivity (EC) analysis

The Conductivity of the tap water in Mekelle town ranges from 632.67-1762.32µs/cm. Conductivity itself is not a human health concern, but because it is easily measured, it can serve as an indicator of other water quality problems. Water with high mineral content tends to have higher conductivity, which is a general indication of high dissolved solid concentration of the water. Therefore, conductivity measurements can be used as a quick way to locate potential water quality problems. The variation of Electrical conductivity in the study period is shown in figure 4.8 below.

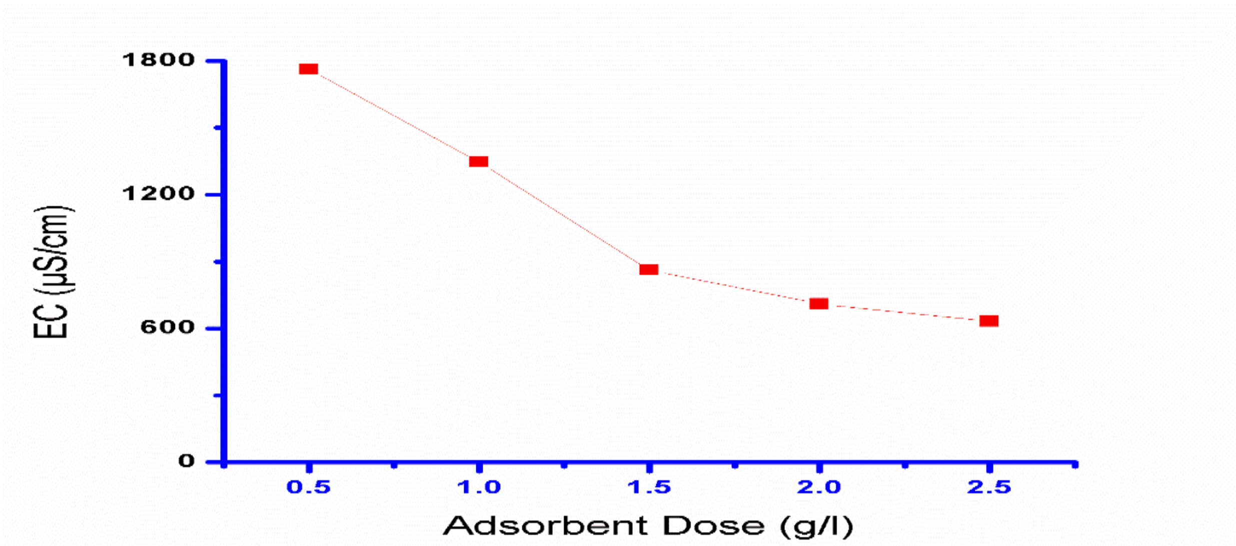


Figure 4.8: EC reduction of drinking tap water being used at Mekelle city.

4.2.7. Alkalinity analysis

During this research work before treatment the alkalinity of raw water sample was observed to be 285 mg/l as $CaCO_3$. This initial value for the different sites of the raw water samples was above permissible limit of Ethiopian standard. After adding of different dose of peanut hull adsorbent, it was observed that the alkalinity decreased from 157 mg/l as $CaCO_3$ still it is not permissible limit with the Ethiopian standards. This alkalinity value is not recommended for drinking purpose according to the Ethiopian standards. This may be causing a problem during the reaction between the peanut hull adsorbent and the hardness-causing ions due to precipitation of soluble products. Thus, the peanut hull adsorbent cannot indicate buffering capacity. The following table 4.10 indicates that alkalinity reduction for the drinking tap water being used at Mekelle city using peanut hull adsorbent.

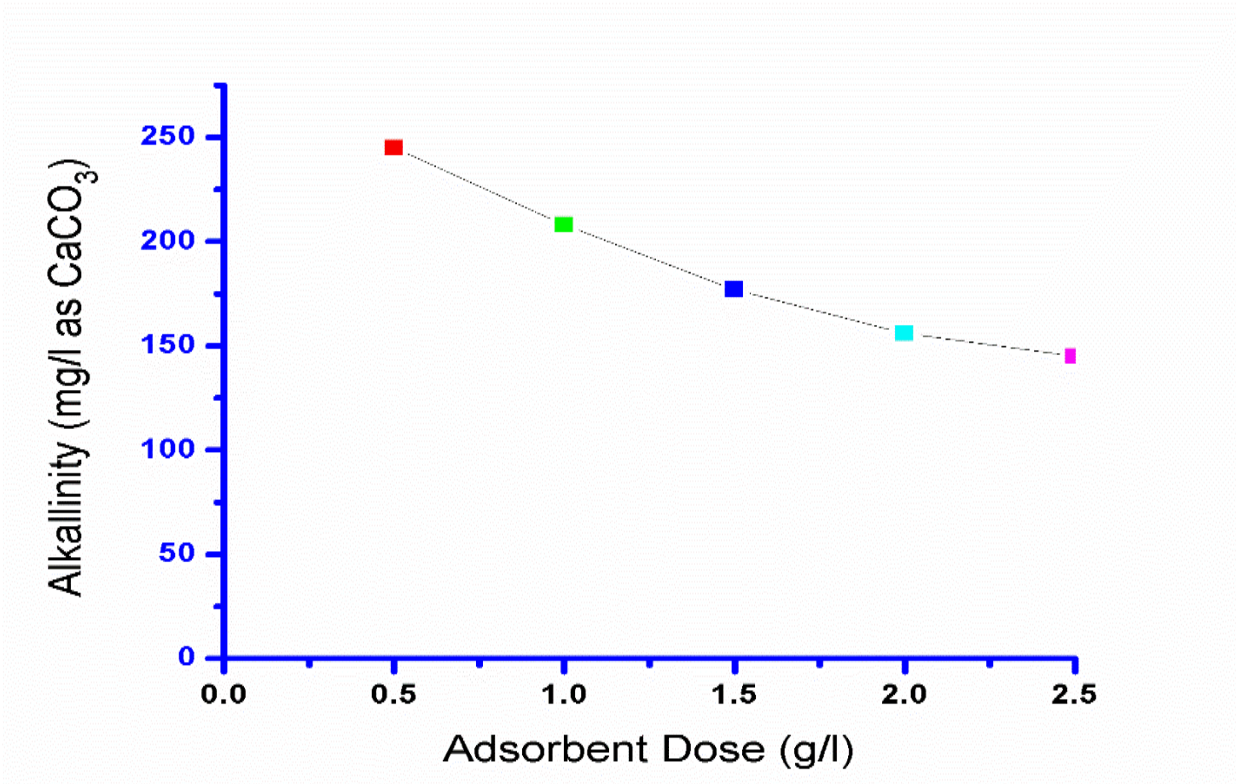


Figure 4.9: Alkalinity reduction of drinking tap water being used at Mekelle city.

4.2.8. Calcium (Ca^{2+}) analysis

Before treatment the initial calcium (Ca^{2+}) in drinking tap water for Mekelle city have an average value 420 mg/l. This calcium value sampling point was not within the range of drinking tap water standards, which was higher than the WHO and Ethiopian standard. After completion of adsorption process the amount Ca sample in the city was reduced up to the average value of 139 mg/l. This range indicates that it is accepted limits as per according to the WHO and the Ethiopian standards. This analysis result value was accepted for the treated drinking tap water as direct house hold applications. From this observation peanut hull adsorbent contains anion components that have the capacity to absorb the cations in order to reduce hardness from the hard-drinking water. So, peanut hull adsorbent is very valuable material for removal of high concentration of calcium from hard-drinking water. The following table 4.11 shows that Ca^{+2} reduction in Mekelle city of drinking water using peanut hull adsorbent.

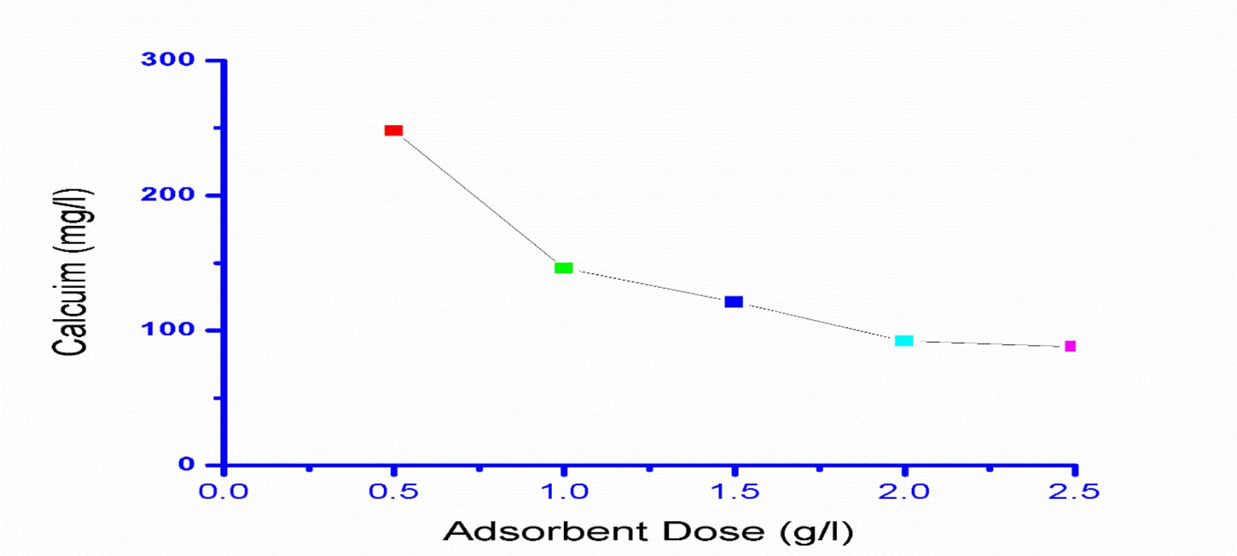


Figure 4.10: Calcium reduction of drinking water being used at Mekelle city.

4.2.9. Magnesium (Mg^{2+}) analysis

In this research work the initial magnesium the hard-drinking water sample of the Mekelle city was observed an average value of 46 mg/l. This magnesium value sampling point was within the range of permittable limit of drinking tap water standards of WHO and Ethiopian. After treatment using peanut hull adsorbent it was given hard-drinking water sample in average value of 16 mg/l, still permittable limit of WHO and Ethiopian drinking tap water standards. The following table 4.12 shows that analysis result of Mg^{+2} reduction in Mekelle city of drinking water using peanut hull as natural adsorbent.

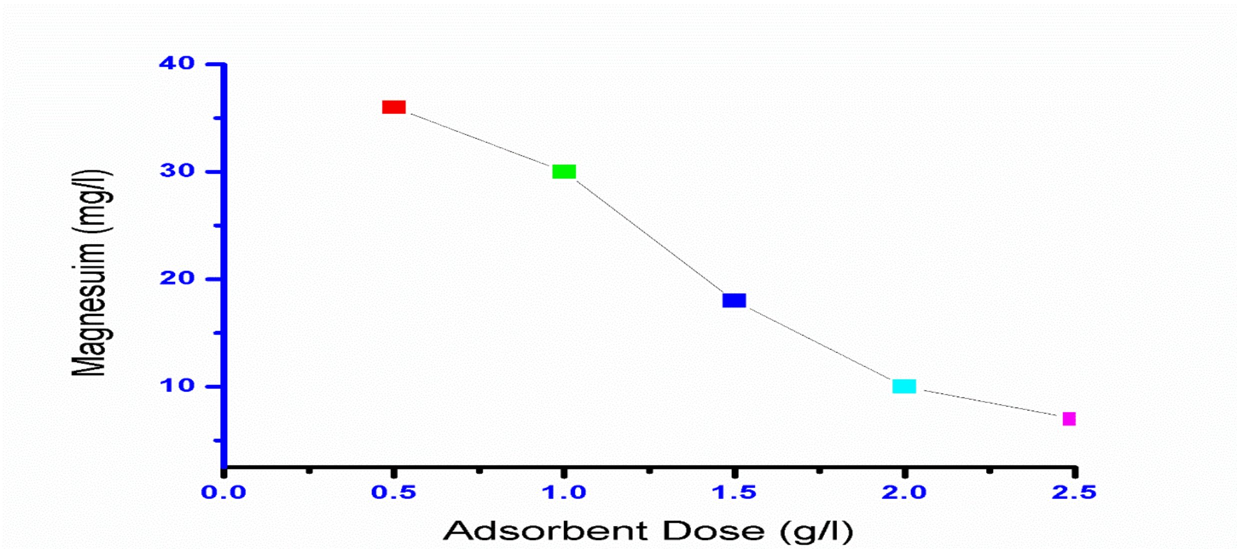


Figure 4.11: Magnesium reduction of drinking tap water being used at Mekelle city.

4.2.10. Total hardness removal analysis

In this research total hardness is the sum of calcium and magnesium divalent ions. Total Hardness of Mekelle town tap water varies from 219.9-709.33 mg/l as $CaCO_3$ having an average value greater than 428.04 mg/l as $CaCO_3$. The hardness values for the study area are found to be hard for all locations and determined to fall far from the higher edges of the desirable limit of Ethiopian standard. So, from this observation this study needs further investigation using adsorption process. Thus, peanut hull adsorbent removes hardness in water through adsorption and inter-particle bridging. The analysis result for the study area, the total hardness (TH) variation of drinking water shows in figure 4.12. below.

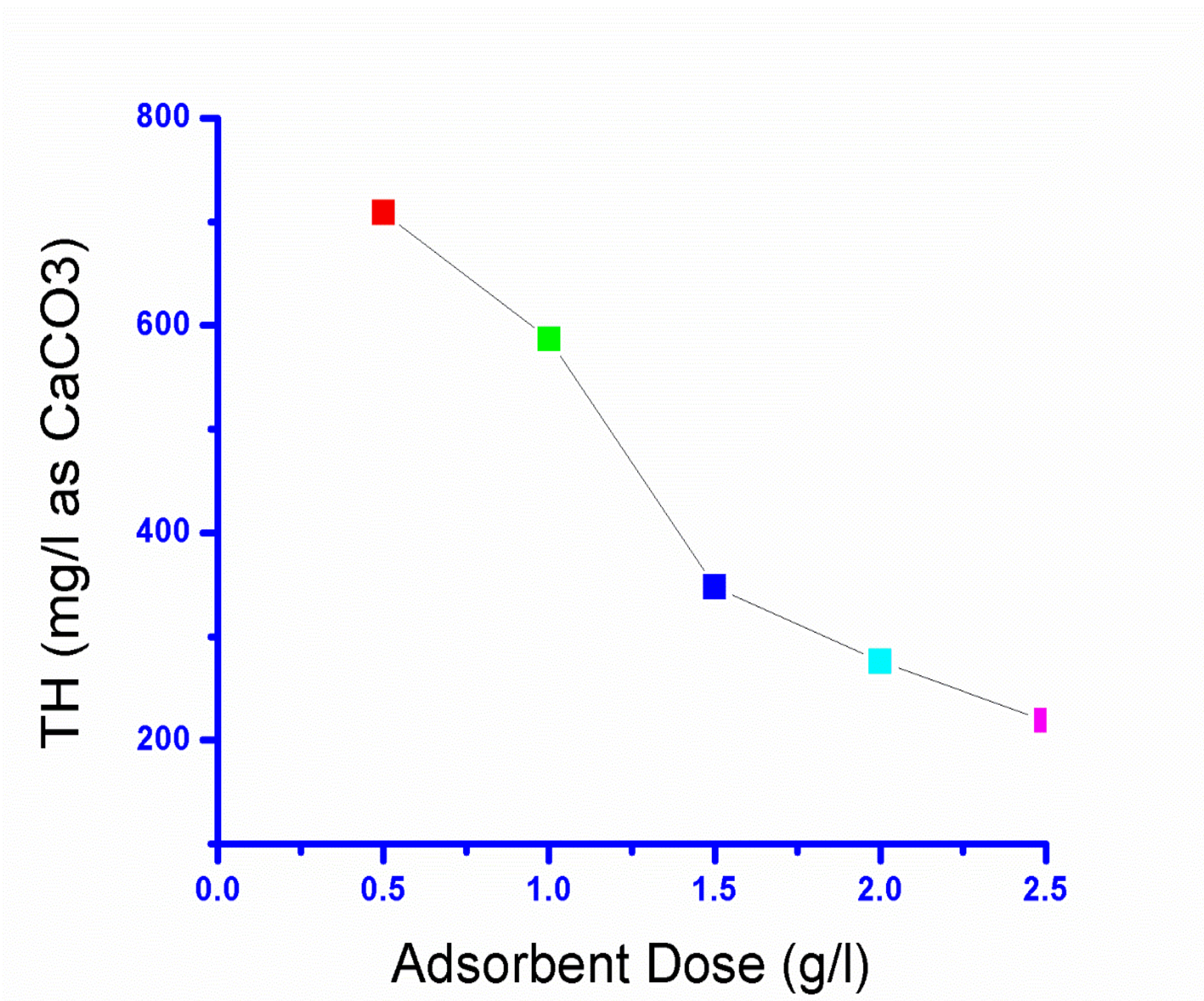


Figure 4.12: Total hardness as $CaCO_3$ removal for drinking tap water being used at Mekelle city.

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4.3. Data analysis using Design expert 7.0 software on hardness removal process

The CCD matrix can be used to express for response surface methodology (RSM), that contains four most important operating variables in the adsorption process. Table 4.4 shows the Central Composite Design Matrix of design specifications along with observed response for hardness removal.

Table 4.4: Central Composite Design Matrix of design specifications along with observed response for hardness removal.

Std	Run	Factor 1 A: Concentration (mg/l)	Factor 2 B: Dosage (g/l)	Factor3 C: pH	Factor 4 D: Settling time (mini)	Response 1 TH %
1	2	150.00	1.50	6.50	45.00	75.03
2	21	500.00	1.50	6.50	45.00	35.01
3	24	150.00	2.50	6.50	45.00	83.01
4	1	500.00	2.50	6.50	45.00	70.21
5	13	150.00	1.50	8.50	45.00	73.07
6	8	500.00	1.50	8.50	45.00	23.33
7	7	150.00	2.50	8.50	45.00	81.13
8	12	500.00	2.50	8.50	45.00	69.43
9	14	150.00	1.50	6.50	120.00	76.01
10	15	500.00	1.50	6.50	120.00	51.11
11	11	150.00	2.50	6.50	120.00	89.05
12	17	500.00	2.50	6.50	120.00	72.07
13	26	150.00	1.50	6.50	120.00	76.51
14	10	500.00	1.50	8.50	120.00	45.05
15	20	150.00	2.50	8.50	120.00	87.44
16	25	500.00	2.50	8.50	120.00	71.11
17	9	237.50	2.00	7.50	82.50	73.01
18	5	412.50	2.00	7.50	82.50	61.00
19	16	325.00	1.75	7.50	82.50	69.01
20	18	325.00	2.25	7.50	82.50	73.53
21	22	325.00	2.00	7.00	82.50	74.55
22	19	325.00	2.00	8.00	82.50	74.87
23	3	325.00	2.00	7.50	63.75	71.06
24	23	325.00	2.00	7.50	101.25	76.43
25	6	325.00	2.00	7.50	82.50	75.31
26	4	325.00	2.00	7.50	82.50	75.31

The generated ANOVA model analysis show Appendix [B], where the studied factors to influence the total hardness removal and three factors were significant that demonstrates the results discussed above at a confidence level of 95%. Three factors have values of P less than 0.05 indicate model terms are significant. The model has a large F-value and the p>F value is less than 0.05, meaning that the model is significant. The interaction effect factors between initial concentration ions and adsorbent dose are major importance for removal of hard-drinking tap water and are significant factors have p value 0.0002.

Final Equations in Terms of Coded Factors of Total Hardness Removal:

Total hardness removal= $+72.7-12.72*A+10.34*B-1.47*C+3.69*D+5.52*AB-O.91*AC+1.54*AD+0.87*BC-1.65*BD+0.51*CD-19.95*A^2-3.03*B^2+10.75*C^2+6.89*D^2$……..……Eq (4.2)

Final Equations in Terms of Actual Factors of Total Hardness Removal:

Total hardness removal = +633.72325 + 0.24403*Concentration ions + 42.77710*Dosage + 165.71269*pH – 0.7143*Time + 0.063057*Concentration ions*Dosage-5.17857E-003*Concentration ions*pH + 2.34476E-004*Concentration ions*Time + 1.74250*Dosage*pH - 0.087933*Dosage*Time + 0.013667*pH*Time -6.51289E-004*Concentration^2 – 12.10290*Dosage^2 + 10.75428*pH^2 + 4.90260E-033*Time^2……………………………. Eq (4.3)

The significant variables can be identified by the significant factors and the coefficients in the model equations. From Appendix [B]and Eq. (4.2) it can be seen that the total hardness removal is mostly affected by absorbent/coagulant dose. The fact that the coefficient for B in Eq. (4.2) carries a positive sign displays that the total hardness removal increases when the sample is left to absorb the cations.

It can also be seen that AB is the most significant interaction term. This indicates that the total hardness removal is positively influenced by the combination of the variation in initial concentration divalent ions and adsorbent dose. Total hardness removal also can be negatively affected by the interaction between AC, and AD. The negative sign of the AC and AD interaction relationships shows that the initial concentration divalent ions precipitate as settling time is prolonged, depending on the pH of the sample. The quadratic terms also showed the presence of curvatures. The negative signs in Eq. (4.2) tell that the quadratic curves for A^2 and $B^2$are concave. This means that total hardness removal increases with an increase in adsorbent dose up to the maximum initial concentration ions decreases.

4.3.1. Model adequacy check

The ANOVA was established the adequacy model for regression, which was found to be significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.9629, 0.9300 and 0.7448 respectively for total hardness removal. The value for the developed correlation of R-squared is 0.9629. This value indicates that experimental variables studied attributed for the total hardness removal 96.29% absorbance was achieved.

Table 4.5: The R-squared values for hardness removal.

Std. Dev.	3.99	R-Squared	0.9692
Mean	69.39	Adj R-Squared	0.9300
C.V. %	5.76	Pred R-Squared	0.7448
PRESS	1452.7	Adeq Precision	19.149

Using figures Appendix [C], result shows that the regression model equations providing a description of the experimental data, in which all the points are close to the line of perfect fit. This result shows that the agreement between the predicted and the experimental values was good. That means connection between the four factors and the removal efficiency shows a linearity. The data generated from developed model equation is close to the actual data obtained.

4.3.2. Interaction of variables

4.3.2.1. Interaction effects 3D-surface

The 3D surface graph is plotted in order to have uniform precision for the total hardness removal efficiency profile in the middle design space. The removal efficiency of total hardness was plotted as a function two factors of the interactions of the independent variables at an average value. There are six interaction factors investigated by the model equation. These interaction factors are:

- AB (initial concentration ions and adsorbent dose)
- AC (initial concentration ions and pH)
- AD (initial concentration ions and settling time)
- BC (adsorbent dose and pH)

- BD (adsorbent dose and settling time)
- CD (pH and settling time)

The 3D response surfaces, plots are shown in figures (4.13- 4.18) as a function of the interactions of two of the factors.

i. Initial concentration ions and adsorbent dose

The interaction effect between initial concentration ions and adsorbent/coagulant dose on total hardness removal efficiency is shown using 3D plot of figure 4.13. The plot of 3D can be shows that, total hardness removal increased as the adsorbent dose increased, whereas the initial concentration ions decreased. The maximum removal efficiency was found at the maximum value of the adsorbent dose as well as at the minimum value of the initial concentration ions respectively. So, the maximum total hardness removal efficiency occurred at absorbent dose= 2.50 g/l and initial concentration divalent ions=1.50 mg/l.

ii. Initial concentration ions and pH

The combined interaction effect between AC (pH and initial concentration divalent ions) factors have strong effect on hardness removal efficiency shown using 3D plot of figure 4.14. As it can be experimental from the removal plot 3D, the maximum total hardness removal efficiency was located at lower level values of both AC factors (initial concentration ions and pH range) instead of their increment values. So, the maximum total hardness removal efficiency in the saddle surface occurred at pH= 6.50 and initial concentration divalent ions=1.50 mg/l.

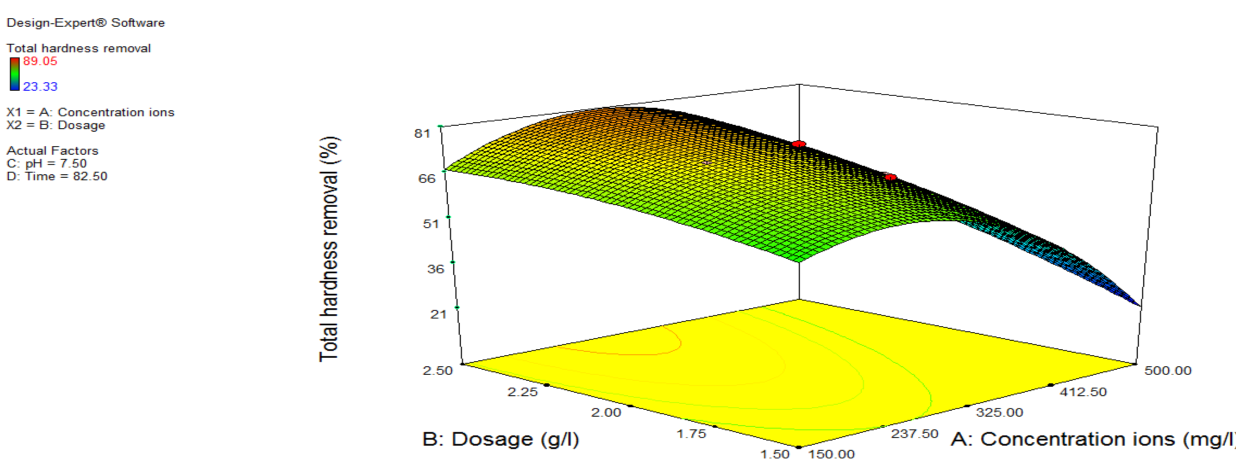


Figure 4.13: 3D plot showing the interaction effect of initial concentration divalent ions and adsorbent dose.

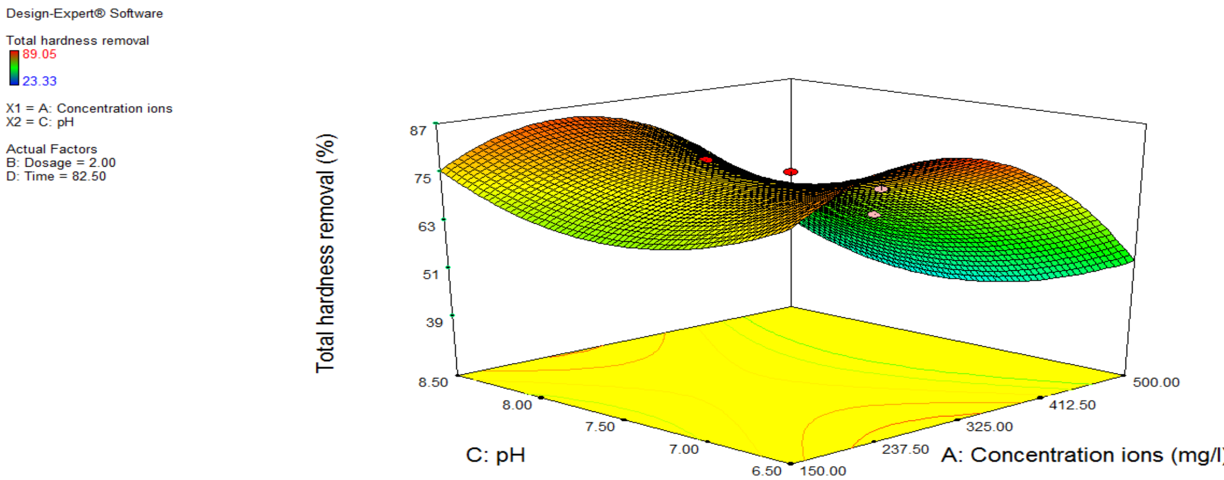


Figure 4.14: 3D plot showing the interaction effect of initial concentration divalent ions and pH.

iii. initial concentration ions and settling time

In the case of interaction effect between AD (initial concentration ions and settling time) factors on total hardness removal efficiency is also shown using 3D plot of figure 4.15. In this case, the total hardness removal has maximum value at lower level value of initial concentration ions and at higher level value of settling time. The raise level values of interval time contribute increased removal efficiency and to decreased the initial concentration of divalent ions for hardness drinking tap water treatments. So, the maximum total hardness removal efficiency in the saddle surface happened at initial concentration divalent ions=1.50 mg/l and settling time= 120 mini.

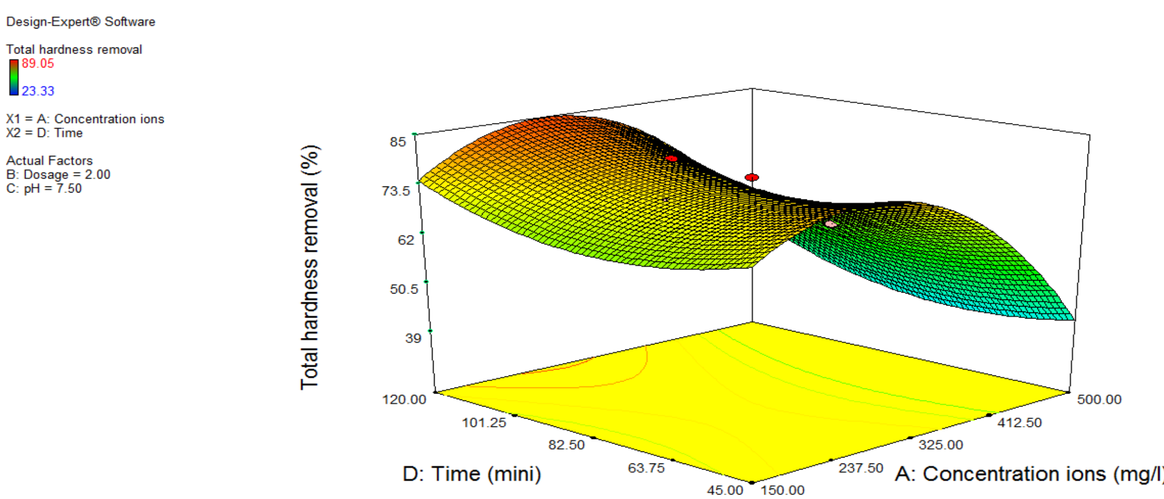


Figure 4.15: 3D plot showing the combined interaction effect of initial concentration divalent ions and settling time.

iv. Adsorbent dose and pH

Figure 4.16illustrates 3D response surface the combined interaction effect of BC (adsorbent dose and pH). The results were established the maximum point of total hardness removal efficiency on the response surface. The maximum total hardness removal efficiency was 89.05% realized for pH 6.5 and for adsorbent dose 2.50 g/l. In this case percentage removal increase with increase in adsorbent dose whereas decrease pH range.

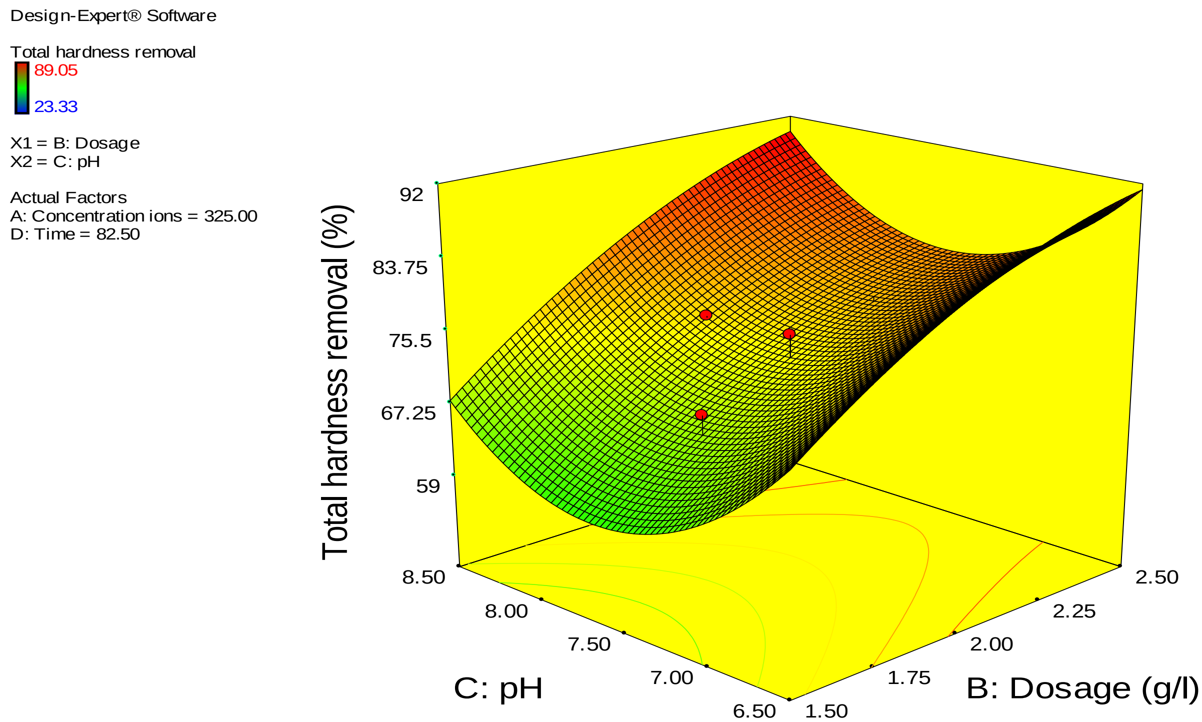


Figure 4.16: 3D plot showing the combined interaction effect of adsorbent dose and pH.

V. Adsorbent dose and settling time

The combined interaction effect BD (adsorbent dose and settling time) important factors on the response of total hardness removal. From figure 4.17, indicates that both adsorbent dose and settling time have strong effect on water hardness removal. At higher level values of both factors were further increment in removal efficiency of the hard-drinking tap water. The plot indicates that maximum hardness removal happened at adsorbent dose= 2.50 g/l and settling time= 120 mini in the batch filtration adsorption process.

VI. pH and contact time

Figure 4.18indicates 3D response surface the combined interaction effect of CD (pH and settling time) factors. The results were established the maximum point of total hardness removal efficiency on the response surface. In this case percentage removal increase with increase in absorbent/coagulant dosage whereas decrease pH range.

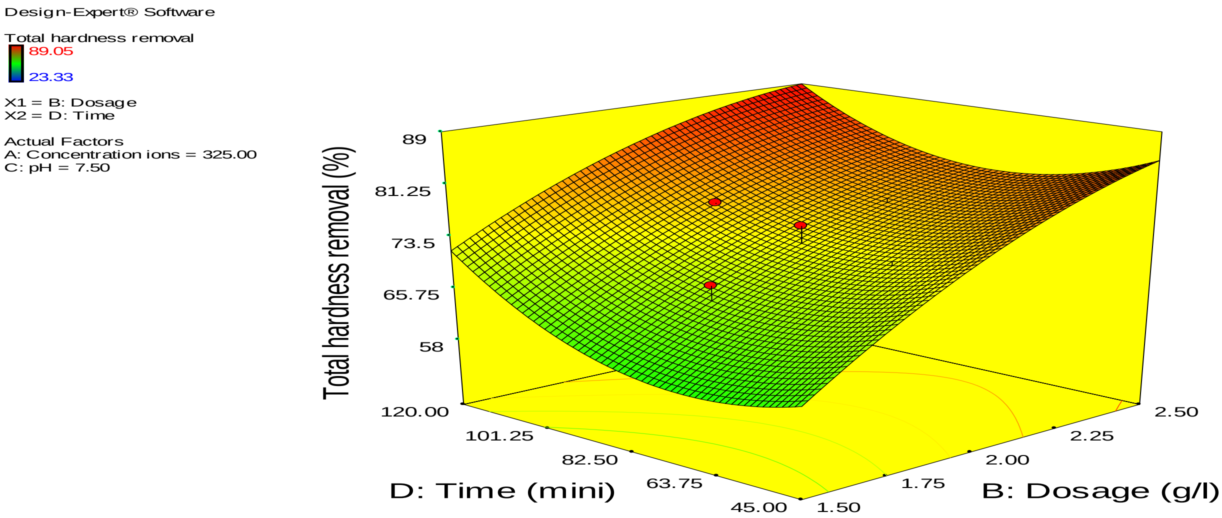


Figure 4.17: 3D plot showing the combined interaction effect between adsorbent dose and settling time.

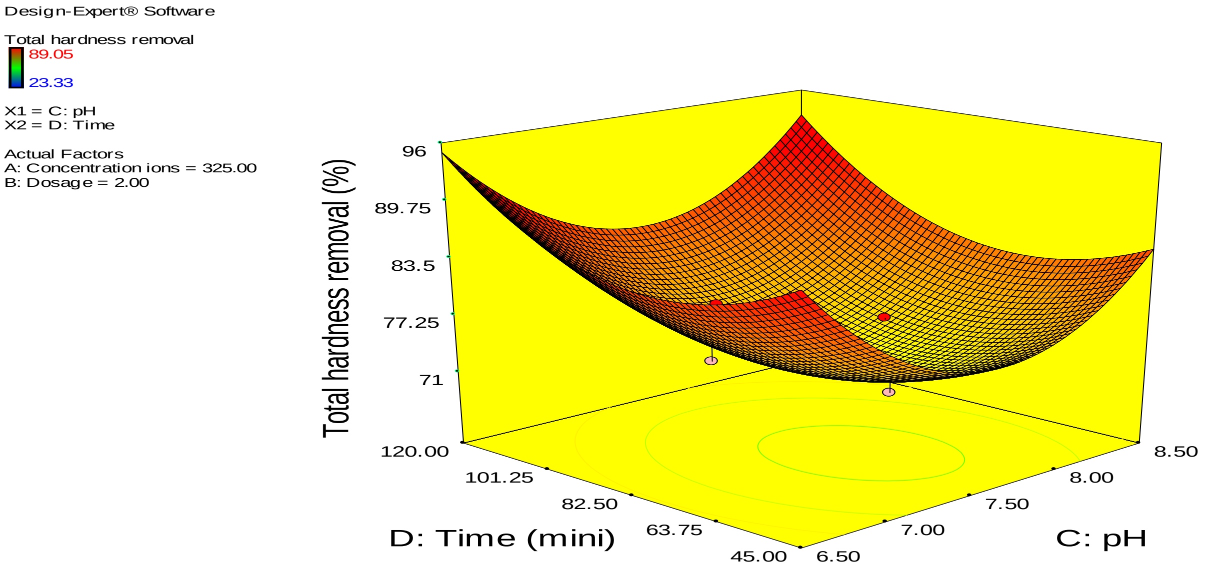


Figure 4.18: 3D plot showing the combined interaction effect between pH and settling time.

4.3.1.2. Interaction effect perturbation plot

Each variable in turn can affect the quality of peanut hull natural adsorbent for purification of hardness drinking tap water. In the region of experimental studied the efficiency of total hardness removal increase with increase of the absorbent dose and contact time variables, but it can decrease with increase of pH scale and initial concentration ions of the cations. Thus, both the adsorbent dose as well as the contact time independent variables have positive effect on the hardness removal, whereas both the pH and initial concentration ions have negative effect on the hardness removal. The effect of all four independent variables were characterized using perturbation plot. Perturbation plot is an important diagrammatic representation to compare all effects of factor at particular point in design space. The response was specified that the factor has a curvature or steeply slope i.e the response variable is sensitive to that factor. The following figure 4.19 shows the effects of each independent variable in the softening of hardness drinking tap water by peanut hull as natural adsorbent using perturbation plot.

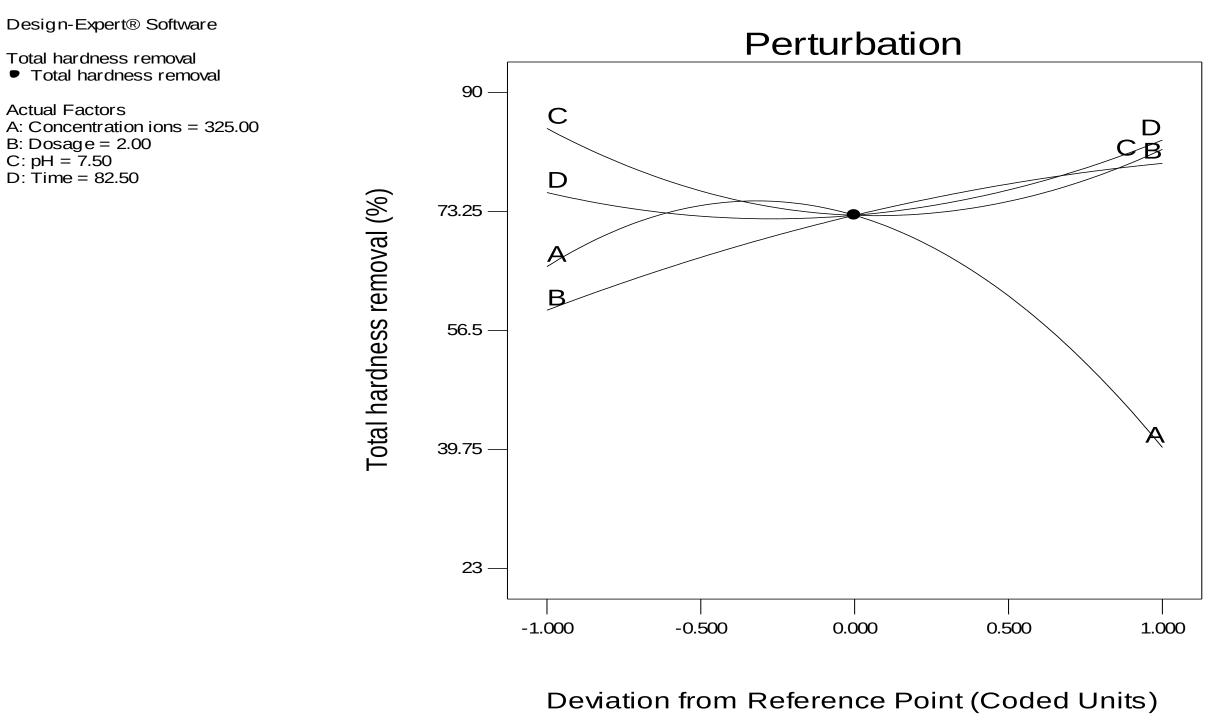


Figure 4.19: Perturbation plot depicting the effect of operational parameters for purification of hardness from drinking tap water.

4.4. Factors affecting hardness removal using natural adsorbent

In this research, throughout the adsorption process different factors were influenced the adsorption capacity of potential adsorbents. The efficiency of any adsorbent is powerfully influenced by the characteristics various parameters such as, initial concentration ions, adsorbent dose, pH and contact time. The effects those four factors are discussed below based on the results gained in the adsorption process using ANOVA design expert 7.0.

4.4.1. Effect of the initial hardness concentration ions

The higher adsorption was takes place at lower concentrations, due to the interaction of calcium and magnesium ions existing in the drinking tap water with binding sites. At higher concentrations of the hard-drinking tap water, there were more calcium and magnesium ions were left unabsorbed due to saturation of adsorption sites. The removal efficiency was increased by decreased the initial concentration of calcium and magnesium ions**.** This were upgraded by increasing both the contact time as well as dose of the adsorbent. The peanut hull natural adsorbent was upgraded the adsorption capacity for calcium and magnesium cations. The effects of the initial calcium and magnesium concentrations was demonstrated in the following figure 4.20 when the total hardness removal efficiency was increased with decreased in concentration of the divalent ions.

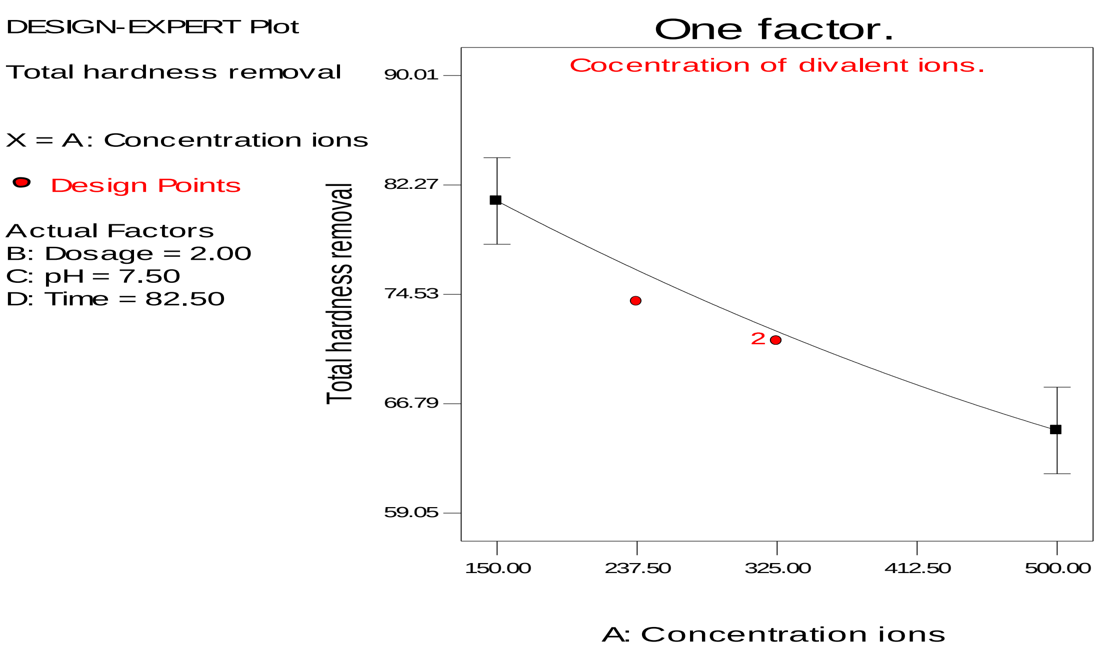


Figure 4.20. Effect of initial concentration ions on hardness removal efficiency.

4.4.2. Effect of peanut hull adsorbent dose

The effect of adsorbent dose on the removal of drinking tap water hardness causing residents by different dose of the peanut hull adsorbent to examine for the concentration of hardness ions (Ca^{+2} and Mg^{+2}). The percentage removal of total hardness (Ca and Mg ions) increases from 23.33% to 89.05% with an increase in the peanut hull as natural adsorbent amounts from 1.5 to 2.5 g. So, the peanut hull adsorbent is low cost as well as suitable for the removing of hardness divalent ions from drinking tap water. The following figure 4.21 indicated that the availability of low-cost peanut hull natural adsorbent to adsorb hardness ions (calcium and magnesium ions) and increase of the adsorption capacity.

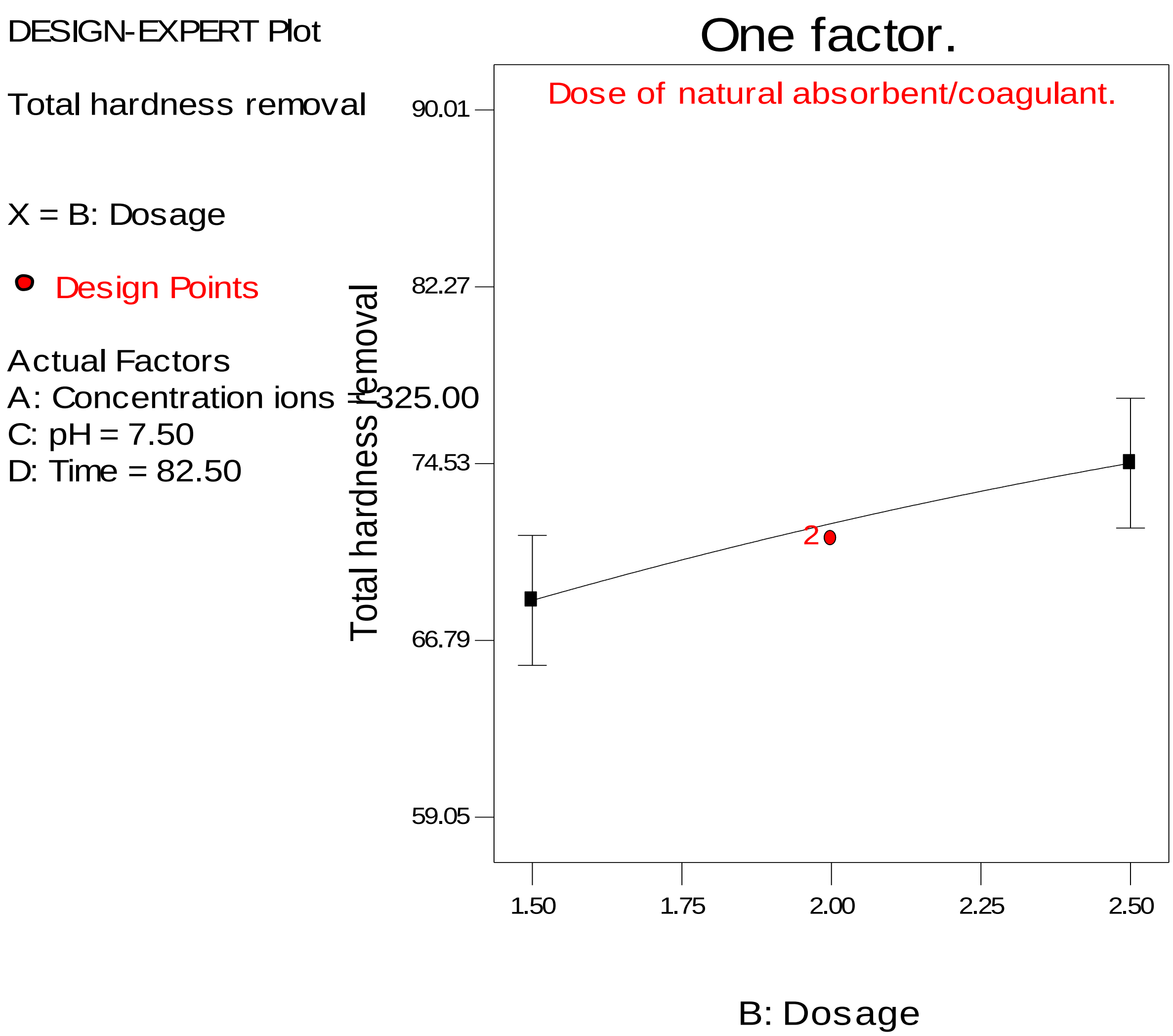


Figure 4.21. Effect adsorbent dose on hardness removal efficiency

4.4.3. Effect of pH

The pH of divalent metal ions for hard drinking tap water is the most significant parameter that can affecting the absorption behavior of cations due to its impact on the degree of ionization of metal specie and the surface charge of the adsorbent. The number of calcium and magnesium ions binding sites on the adsorbent surface due to the difference of hydrogen ion concentration affects. The effect of pH on the adsorption efficiency at different doses was observed in order to optimize the adsorbent dose and the pH. In this research the results for total hardness removal at pH 6.5 was the highest removal efficiency and at pH 8.5 the lowest removal efficiency towards Ca^{+2} and Mg^{+2} ions was attained for peanut hull tested dosages. The determined total hardness removal efficiency at different pH values are demonstrated in the following figure 4.22.

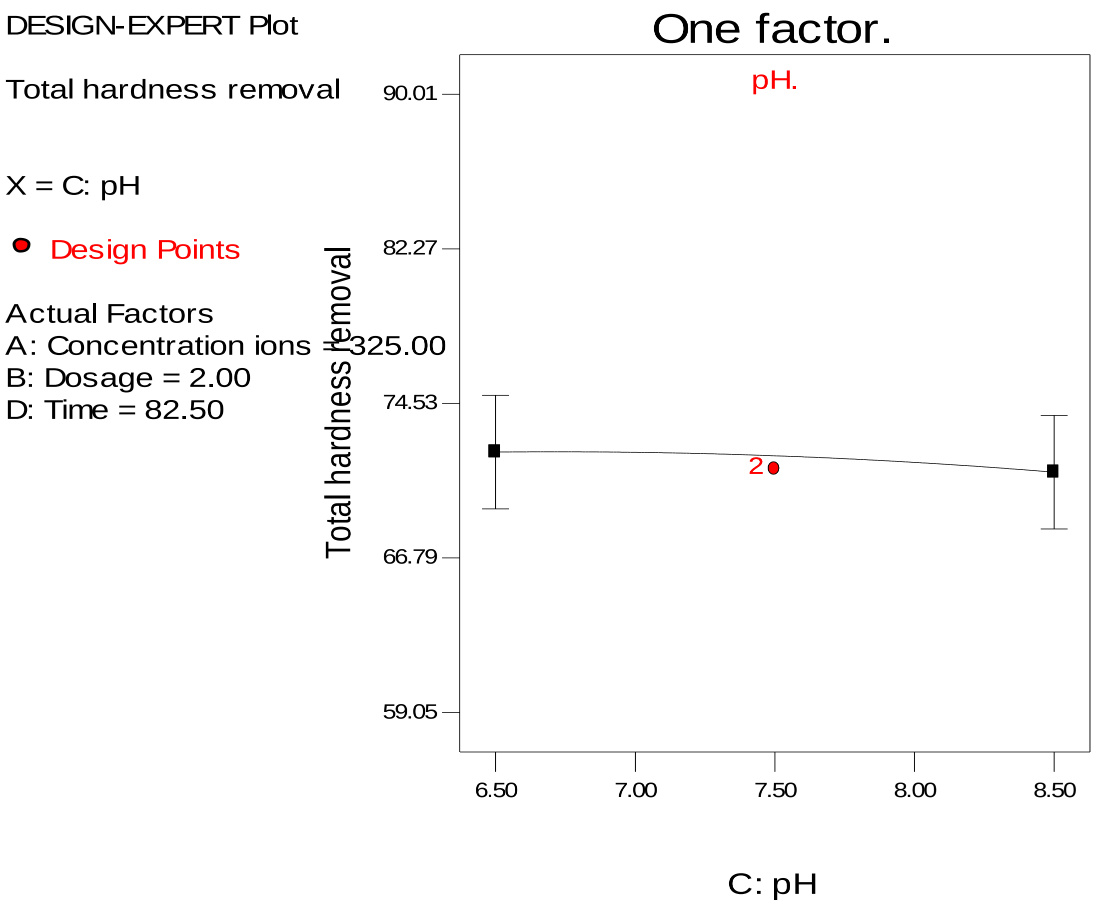


Figure 4.22. Effect pH on hardness removal efficiency.

4.4.4. Effect of the settling time

The effects of the settling time on the drinking tap water hardness removal efficiency is demonstrated in the following figure 4.33. It shows the adsorption efficiency was upgraded by increasing the settling time. The calcium and magnesium parameters were decreased by increased the effects of settling time that were vary from 45-120 mini. So, the hardness of drinking tap water in case of Mekelle city its softening efficiency was increased with increased of settling time. The following figure 4.23 shows hard-drinking tap water removal efficiency with an increased settling time.

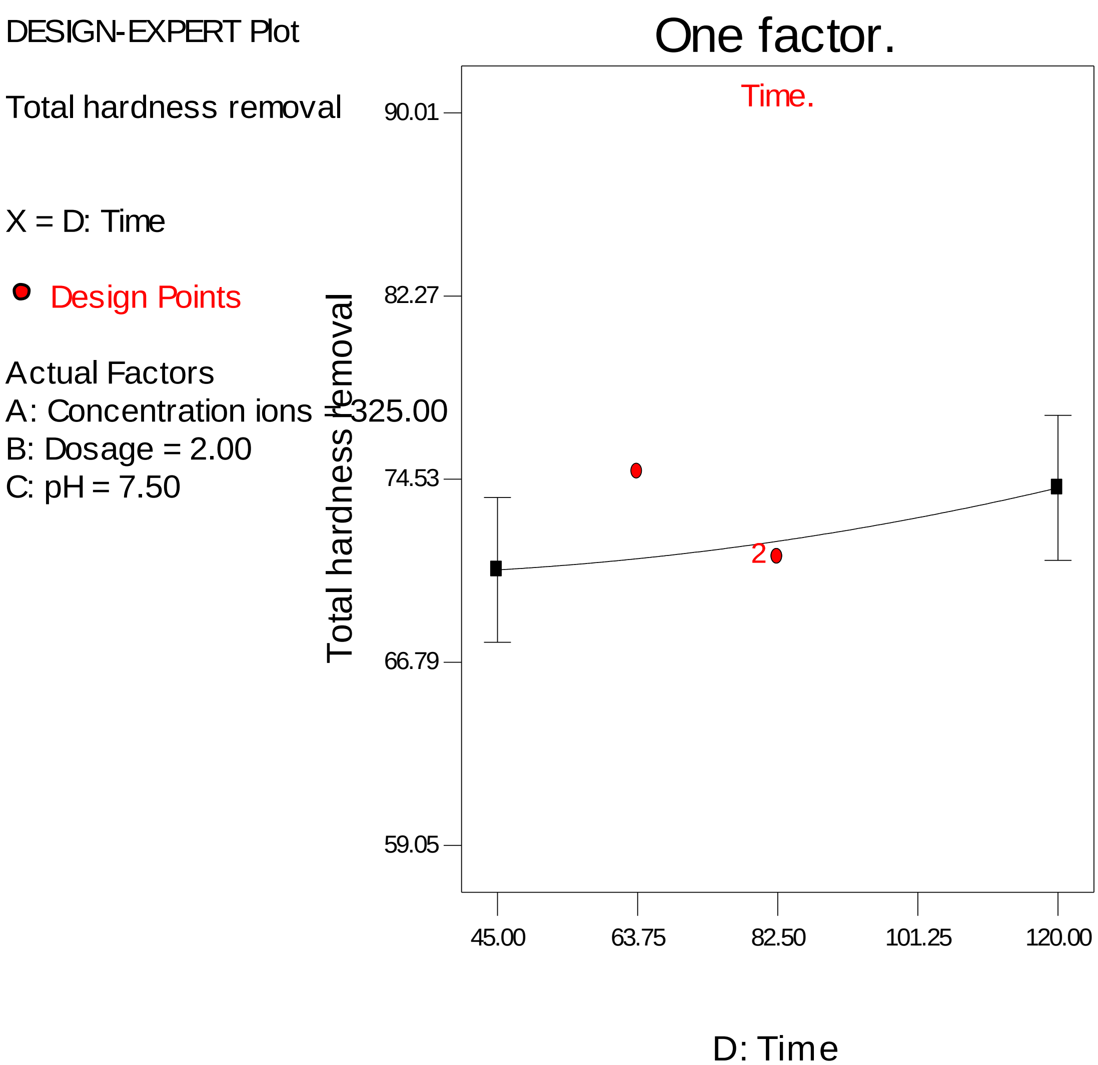


Figure 4.23. Effect settling time on hardness removal efficiency.

5. CONCLUSION AND RECOMMENDATION

6.1. Conclusion

The careful analysis, interpretation and discussions of the physicochemical parameters of tap water of Mekelle city revealed that the current water quality problem is beyond the limit and needs serious treatment. Peanut hull contains different functional groups, such as hydroxyl group (-OH), carbonyl group (C=O), alkane (C−H) group and alcoholic group (O-H). It can be concluded that peanut hull talented to binding Ca and Mg divalent ions. The optimum peanut hull doses of 2.50 g/L gave the maximum removal of calcium and magnesium from drinking tap water to meet the WHO drinking water quality standards. Generally, the results proposed that the peanut hull was capable of treating the real drinking tap water samples to meet the severe WHO standards.

The capacity of locally available plant-based by-product to remove hardness from drinking tap water was investigated. The result tells that the low-cost locally available peanut hull waste material generated from peanut plant has vital practical implications for removal of hardness causing ions from drinking tap water. Hardness removal efficiency of peanut hull was found to increase with increasing dosage.

The physiochemical parameters of drinking tap water in Mekelle city, 26 total samples were studied based on the Ethiopian and WHO standard guideline. The quality of drinking water available in the city in turn reproduces the extent that concerned authorities should strictly monitor the quality of drinking water being supplied to the consumers.

The adsorption of metal ions Ca^{+2} and Mg^{+2} on peanut hull was successfully achieved and confirmed for development a highly effective adsorbent. The adsorption efficiency of the adsorbent for removal of Ca^{+2} and Mg^{+2} ions from drinking tap was studied by using the batch process under influence of different parameters. The maximum adsorption capacity values of metal ions were identified at pH 6.5. So, this application of the method for natural tap water-softening and treatment was successfully accomplished.

6.2. Recommendation

Water resource management programs will be vital for economic growth, poverty reduction, food security and conservation of natural systems. The requirement for better community participation in water management of Mekelle city should not be overlooked and the water quality problems are recommendable to be improved as soon as possible.

The following recommendations are suggested to attendant future research:

- A suitable water purification method for purifying water from the hard-drinking tap water source needs to be established for Mekelle city as soon as possible.
- Domestic treatment such as boiling should be stimulated before the tap water is used for drinking purposes until well developed treatment mechanism is applied.
- Thorough study it was mandatory to identify the active adsorption site in the protein. If it is desired to create the minimum number of scums required for its activity as well as to reduce the cost and simplify the procedure.
- Investigations on the effectiveness of peanut hull could be also extended to other types of water quality contaminants that can be act as antimicrobial agent in water treatment.
- The characteristics the physiochemical of hard-drinking tap water samples taken from these sites could be different tests should be to validate the applicability of the future treatment methods.

REFERENCES

[1]. Joshi, D.M., Kumar, A. and Agrawal, N. 2009. Studies on physico-chemical parameters to assess the water quality of river ganga for drinking purpose in Haridwar district. Rasayan journal of chemistry. 21(1): 195-203.

[2]. Biadglegne, F., Tessema, B., Kibret, M., Abera, B., Huruy, K., Anagaw, B. and Mulu, A. 2009. Physico-chemical and bacteriological quality of bottled drinking water in three sites of Amhara Regional State, Ethiopia. Ethiop Med J.47(4): 277-84.

[3]. Boxall, J.B., Sent mittionekipworth, P.J., Saul, A.J., (2003). Aggressive flushing for discoloration event mitigation in water distribution networks. Water Sci. Technol-Water Supply3 (1/2), 179-186.

[4]. Venkateswara Rao. B, (2011). Physiochemical analysis of selected ground water samples of Vijayawada rural and urban in Krishna district, Andhra Pradesh, India, International Journal of environmental sciences Volume 2, No 2, pp 710-714.

[5]. Meena, K.S., Gunsaria, R.K., Meena, K., Kumar, N., Meena, P.L. 2012. The problem of hardness in ground water of Deoli Tehsil (Tonk District) Rajasthan. Journal of Current Chemical and Pharmaceutical Sciences: 2(1). pp 50-54.ISN 2277-2871.

[6]. Atkinson, T.C. 1977. Carbon dioxide in the atmosphere of the unsaturated zone: an important control of groundwater hardness in limestones. Journal of Hydrology, 35(1977)111-123.

[7]. Evens, E., Yanick, S., Osnick, J. 2013. Characterization of hardness in the groundwater of Port-Au-Prince. An overview on the significance of magnesium in the drinking water. Aqua-LAC. vol 5. pp 35-43.

[8]. Nerbrand, C., Agreus, L., Lenner, R.A., Nyberg, P., Svardsudd, K. 2003. The influence of calcium and magnesium in drinking water and diet on cardiovascular risk factors in individuals living in hard and soft water areas with differences in cardiovascular mortality. BMC Public Health 2003, 3:21.

[9]. Anne, K. 2011. Magnesium and calcium in drinking water and heart diseases. Geological Survey of Finland. Accessed on Elsevier February 18, 2015.

[10]. Rosanoff, A. 2013. The high heart health value of drinking-water magnesium. Elsevier. Medical Hypotheses 81. pp 1063-1065.

[11]. World Health Organization (WHO). Guidelines for Drinking Water Quality. Health criteria and other supporting information (2nd ed.Vol.2) AITBS publishers, New Delhi. 1999. (Pg.119 -382)

[12]. ASTM International, 2003a, D1889–00 Standard test method for turbidity of water, in ASTM International, Annual Book of ASTM Standards, Water and Environmental Technology, West Conshohocken, Pennsylvania 2003, v. 11.01.

[13]. Singh Vijender, Assessment of the Quality of Drinking Water in Outer Rural Delhi. Physico- Chemical Characteristics. Research Journal of Chemistry and Environment, (3), (2006).

[14]. Subramani, A., Jacangelo, J.G., 2015. Emerging Desalination Technologies for Water Treatment: A Critical Review. Water Res. doi: 10.1016/j.watres.2015.02.032.

[15]. Kahan R., and Siddique I. (2000). “Urban water management problems in developing countries with particular reference to Bangladesh”, Journal of Water Resource Development, 16(1), 21-33.

[16]. Hallberg, G.R. and Keeney, D.R., (1993), Nitrate, Alley, William A., ed., Reginal 55 Ground-water Quality, Van Nostrand Reinhold, New York, p.297-322.

[17]. Cool Today Resource Library. Water softening vs. reverse osmosis. Accessed February 19, 2015. http://www.cooltoday.com/library/article/water-softening-vs.-reverse-osmosis-whats-the-diference.

[18]. Saeed, A. M. and Hamzah, M. J., 2013. New Approach for Removal of total Hardness (Ca^{+2}, Mg^{+2}) from Ware Using Commercial Polyacrylic Acid Hydrogel Beads, Study and Application. International Journal of Advanced Biological and Biomedical Research, 1 (9): 1142-1156.

[19]. Meena, K.S., Gunsaria, R.K., Meena, K., Kumar, N., Meena, P.L. 2012. The problem of hardness in ground water of Deoli Tehsil (Tonk District) Rajasthan. Journal of Current Chemical and Pharmaceutical Sciences: 2(1). pp 50-54.ISN 2277-2871.

[20]. Atkinson, T.C. 1977. Carbon dioxide in the atmosphere of the unsaturated zone: an important control of groundwater hardness in limestones. Journal of Hydrology, 35(1977)111-123.

[21]. Evens, E., Yanick, S., Osnick, J. 2013. Characterization of hardness in the groundwater of Port-Au-Prince. An overview on the significance of magnesium in the drinking water. Aqua-LAC. vol 5. pp 35-43.

[22]. Nerbrand, C., Agreus, L., Lenner, R.A., Nyberg, P., Svardsudd, K. 2003. The influence of calcium and magnesium in drinking water and diet on cardiovascular risk factors in individuals living in hard and soft water areas with differences in cardiovascular mortality. BMC Public Health 2003, 3:21.

[23]. Anne, K. 2011. Magnesium and calcium in drinking water and heart diseases. Geological Survey of Finland. Accessed on Elsevier February 18, 2015.

[24]. Rosanoff, A. 2013. The high heart health value of drinking-water magnesium. Elsevier. Medical Hypotheses 81. pp 1063-1065.

[25]. Patil P.N, Sawant D.V, Deshmukh R.N, Physico-chemical parameters for testing of water A review, International Journal of Environmental Sciences Volume 3, No 1, 2012.

[26]. Riordan, O', E. G., Dodd, V. A., Tunney, H., Fleming, G. A, 1983. The chemical composition of sewage sludges. Ireland Journal of Agriculture Research, 25, 239-49.

[27]. Degremant, J. Water Treatment Handbook (6th) Edition, Lavoisier, Paris, pg. 10-15. (1991).

[28]. Water Quality Assessment (WQA), A guide to use of biota, sediments and water in environmental monitoring, 2nd Edition,1992, UNESCO/WHO/UNEP.

[29]. Pillai, Mathevan M, 1994. Hydrobiological investigations on the inter-tidal diatoms of the Cuddalore- Uppanar estuary (India), Ph.D. Thesis, Annamalai University, India, P.86.

[30]. Govindasamy, C. and L. Kannan, 1991: Rotifers of Pichavaram mangroves, South east coast of India. A Hydrobiology approach, Mahasagar. Bull.Natl. Inst. Oceangr. 24: 39-45.

[31]. Pandey, A.K. 2006. Histopathological alterations in the gill and kidney of an esturine mullet, Liza parsia (Hamilton-Buchanan) caused by sub-lethal exposure to lead (Pb). Indian, J. Fish, 44 (2): 171-180.

[32]. Mariappan, P., V. Yegnaraman and T. Vasudevan, 2000. Ground water fluctuation with water table level in Thiruppathur block of Sivagangai (T.N.). Pollution Research., 19(2): 225-229.

[33]. Dezuane, J. 1979. Handbook drinking water quality. Indian University Press.

[34]. Ketchum, B.H. 1951. The exchange of fresh water and salt water in tidal estuaries. J. Mar. Res., 10: 19-38.

[35]. Jayaraman, R. 1954. Seasonal variations in alkalinity, dissolved oxygen and nutrient salts in the inshore waters of the Gulf of Mannar and PalkBay near Mandapam. Ind. J. Fisher., 1(1&2): 345-364.

[36]. Palanichamy S. and A. Rajendran, 2000. Heavy metal concentration in seawater and sediments of Gulf of Mannar and Palk Bay, southeast coast of India. Ind. J.Mar.Sci., 29: 116-119.

[37]. Sudaramanickam, A., T., Sivakumar, R., Kumaran, V., Ammaiappan, and R. Velappan, 2008. A comparative study of Physico-chemical investigation along Parangipettai and Cuddalore coast. J.Environ.Sci. Tech., 1(1): 1-10.

[38]. Soundarapandian, P., T. Premkumar, and G.K. Dinakaran, 2009. Studies on the Physico-chemical Characteristic and Nutrients in the Uppanar Estuary of Cuddalore, South East Coast of India. Curr. Res. J. Biol. Sci., 1(3): 102-105.

[39]. Trivedy, R.K. and P.K. Goel, 1984. Physicochemical analysis of water. In Chemical and Biological methods of water pollution studies, Environmental Publications, Karad, India, 35-96.

[40]. RMC. 1990. A manual of freshwater aquaculture Oxford and IBH Publishing Co. Pvt. Ltd., India.

[41]. Kemmers, R.H. 1986. Calcium as hydro chemical characteristics for ecological states, Tech. Bull. No.47, Institute for Land water management Research (ICW), Wageningen, The Netherlands, pp.13.

[42]. Jain, R. 1996. Individual and combined effects of heavy metals on behaviour and respiratory responses of Oreochromis mossambicus. Indian. J. Fish., 37 (2): 129-143.

[43]. UPSH, 1983. Manual of drinking water standards comparable to the official. Journal of European Communities. 229:16-21.

[44]. Gupta, D. P., Sunita and J. P. Saharan, (2009), Physiochemical Analysis of Ground Water of Selected Area of Kaithal City (Haryana) India, Researcher, 1(2), pp 1-5.

[45]. Ashok Prabu, V., M. Rajkumar and P. Perumal: 2008 Seasonal variations in Physico – chemical characteristics of pichavaram mangroves, Southeast coast of India. J. Environ, Biol., 29, 945 – 950.

[46]. P. Mahesh Kumar and C. Prabhahar, Physico – Chemical Parameters of River Water: A Review, International Journal of Pharmaceutical & Biological Archives 2012; 3(6): 1304-1312.

[47]. ANZECC/ARMCANZ (2000) Australian Guidelines for Monitoring and Reporting, National Water Quality Management Strategy Paper no.7. Australia and New Zealand Environment and Conservation Council/Agricultural and Management Council of Australia and New Zealand.

[48]. http://www.se.gov.sk.ca/environment/protection/water/Drinking Water Standardt.pdf

[49]. World Health Organization (WHO). Guidelines for Drinking Water Quality. Health criteria and other supporting information (2nd ed.Vol.2) AITBS publishers, New Delhi. 1999. (Pg.119 -382).

[50]. WHO (1984) Guidelines for Drinking Water Quality: Vol. I; Recommendations. World Health Organisation, Geneva.

[51]. Asma et al., 2005; Ferda and Selen, 2012; Kishore et al., 2008; Nuria et al., 2010.

[52]. Graham N, Gang F, Fowler J, Watts M. Characterisation and coagulation performance of a tannin-based cationic polymer: a preliminary assessment. 2008; 327:9–16.

[53]. Sarah, M. M., Ezekiel, J. F., Vinka, Oyanedel, C., James, A. S., and Julie, B. Z.: Toward understanding the efficacy and mechanism of Opuntia spp. as a natural coagulant for potential application in Water treatment. Environmental Science and Technology, 42, 4274–4279, (2008).

[54]. Asrafuzzaman, M., Fakhruddin, A. N. M., & Hossain, M. A. Reduction of Turbidity of Water Using Locally Available Natural Coagulants. International Scholarly Research Network (ISRN) (2011).

[55]. Muyibi Suleyman A. and Evison Lilian M., Wat. Res., Vol. 29, No. 4, pp. 1099-1105, 1994.

[56]. Kumar, U. Agricultural Products and by-Products as a Low-Cost Adsorbent for Heavy Metal Removal from Water and Wastewater: A Review. Sci. Res. Essay 2006, 1, 33–37.

[57]. Davis, K. O. Adsorption of Aqueous Copper on Peanut Hulls; Western Carolina University: Cullowhee, NC, 2014.

[58]. Geetha, K.; Ramarao, N.; Kiran, R. S.; Srilatha, K.; Mamatha, P.; Umamheswar Rao, V. An Overview on Arachis Hypogaea Plant. Pharmaceutical Sciences and Research 2013, 4, 4508-4518.

[59]. Albrecht, W. J. Peanut Hulls: Their Properties and Potential Uses. Agricultural Reviews and Manuals, ARM-S-1, 1-5, 1979.

[60]. Ilyas, M., Ahmad, A., & Saeed, M., Removal of Cr (VI) from Aqueous Solutions using Peanut shell as Adsorbent. Journal of the chemical society of Pakistan, 35(3): 760-768, 2013.

[61]. Ugwekar, R. P. and Lakhawat, G. P., 2012. Recovery of Heavy Metal by Adsorption using Peanut Hull. International Journal of Advanced Engineering Technology, E-ISSN 0976-3945

[62]. Hassanein, M.M.M, El-Shami, S. M. and Taha, F. S., 2011. Evaluation of Peanut Hulls as an Alternative to Bleaching Clays. Grasas Y Aceites, 62 (3): 299-307.

[63]. El-Sayed, G. O., 2010. Removal of Water Hardness by Adsorption on Peanut Hull. Journal of International Environmental Application & Science, 5(1): 47-55.

[64]. U. Kumar. Agricultural products and by-products as a low-cost adsorbent for heavy metal removal from water and wastewater: A review. Sci. Res. Essay 2 (2006) 33–37.

[65]. Albrecht, W. J. Peanut Hulls: Their Properties and Potential Uses. Agric. Rev. Manuals 1979, 1, 1–5.

[66]. PerkinElmer Life and Analytical Sciences. FT-IR Spectroscopy Attenuated Total Reflectance (ATR) http://www.utsc.utoronto.ca/~traceslab/ATR_FTIR.pdf (accessed Apr 5, 2014).

APPENDIXES

Appendix A. Experimental Results for Physicochemical Parameters.

S.no	Sp. Aver.	Colour	Taste	pH	Turb. (NTU)	TDS ppm	EC µS/cm	Alkal. (mg/l)	Ca^{+2} mg/l	Mg^{+2} mg/l	TH mg/l
1	Sp_{av1}	colorless	Obj.	7.66	27.37	1540	1890	257	315	43	967
2	Sp_{av4}	colorless	Obj.	7.38	19.70	983	1247	213	234	35	732
3	Sp_{av7}	colorless	Obj.	7.73	17.20	632	879	183	149	21	460
4	Sp_{av10}	colorless	Obj.	7.71	15.61	594	812	179	141	17	412
5	Sp_{av13}	colorless	Obj.	7.27	13.52	483	684	168	113	12	333
6	Sp_{av16}	colorless	Obj.	7.43	11.92	451	654	154	108	11	316
7	Sp_{av19}	colorless	Obj.	7.32	10.30	447	637	149	103	8	291
8	Sp_{av22}	colorless	Obj.	7.20	9.12	442	597	141	89	7	252
10	Sp_{av2}	colorless	Obj..	7.55	222.34	1633	1768	237	278	39	861
11	Sp_{av5}	colorless	Obj..	7.51	13.30	960	1356	204	216	32	663
12	Sp_{av8}	colorless	Obj..	7.47	12.48	650	912	172	168	12	465
13	Sp_{av11}	colorless	Obj.	7.32	11.01	613	798	167	134	11	363
14	Sp_{av14}	colorless	Obj.	7.49	10.20	456	696	158	105	9	324
15	Sp_{av17}	colorless	Obj.	7.41	9.57	453	687	152	104	8	293
16	Sp_{av20}	colorless	Obj.	7.37	8.40	447	684	146	101	7	282
17	Sp_{av23}	colorless	Obj.	7.24	7.51	439	629	142	93	6	258
18	Sp_{av3}	colorless	Obj.	7.43	24.33	1896	1432	241	302	35	900
19	Sp_{av6}	colorless	Obj.	7.31	14.20	1243	924	209	227	24	668
20	Sp_{av9}	colorless	Obj..	7.51	12.50	863	596	178	146	13	419
21	Sp_{av12}	colorless	Obj.	7.48	11.01	663	516	178	123	11	353
22	Sp_{av15}	colorless	Obj..	7.60	11.60	634	426	161	117	9	330
23	Sp_{av18}	colorless	Obj.	7.54	9.47	591	415	152	110	8	308
24	Sp_{av21}	colorless	Obj.	7.50	8.78	549	353	146	101	7	279
25	Sp_{av24}	colorless	Obj.	7.44	7.25	426	313	137	94	6	260
Overall Average samples				7.42	10.69	949	1116	167	147	16	448
Standards		WHO		6.50-8.50	5	1500	2000	250	150	50	500
		Ethiopian			5	1500	1500	250	150	50	300

Appendix B: Data analysis by design expert 7.0.0 software.

Source	Sum of squares	df	Mean Squares	F value	p-value probe > F
Model	5518.37	14	394.17	24.73	< 0.0001
A-Concentration ions	2669.55	1	2669.55	167.49	< 0.0001
B-Dosage	1762.97	1	1762.97	110.61	< 0.0001
C-pH	35.61	1	35.61	2.23	0.1631
D-Time	224.37	1	224.37	14.08	0.0032
AB	487.08	1	487.08	30.56	0.0002
AC	13.14	1	13.14	0.82	0.3833
AD	37.88	1	37.88	2.38	0.1514
BC	12.15	1	12.15	0.76	0.4014
BD	43.49	1	43.49	2.73	0.1268
CD	4.20	1	4.20	0.26	0.6178
A^2	66.18	1	66.18	4.15	0.0664
B^2	1.52	1	1.52	0.096	0.7630
C^2	19.24	1	19.24	1.21	0.2954
D^2	7.91	1	7.91	0.50	0.4959
Residual	175.3211	15.94			
Lack of Fit	175.3210	17.53			
Pure Error	0.000	1	0.000		
Cor Total	5693.70	25			

Appendix C: Analysis of variance (ANOVA) for hardness removal using Model adequacy check

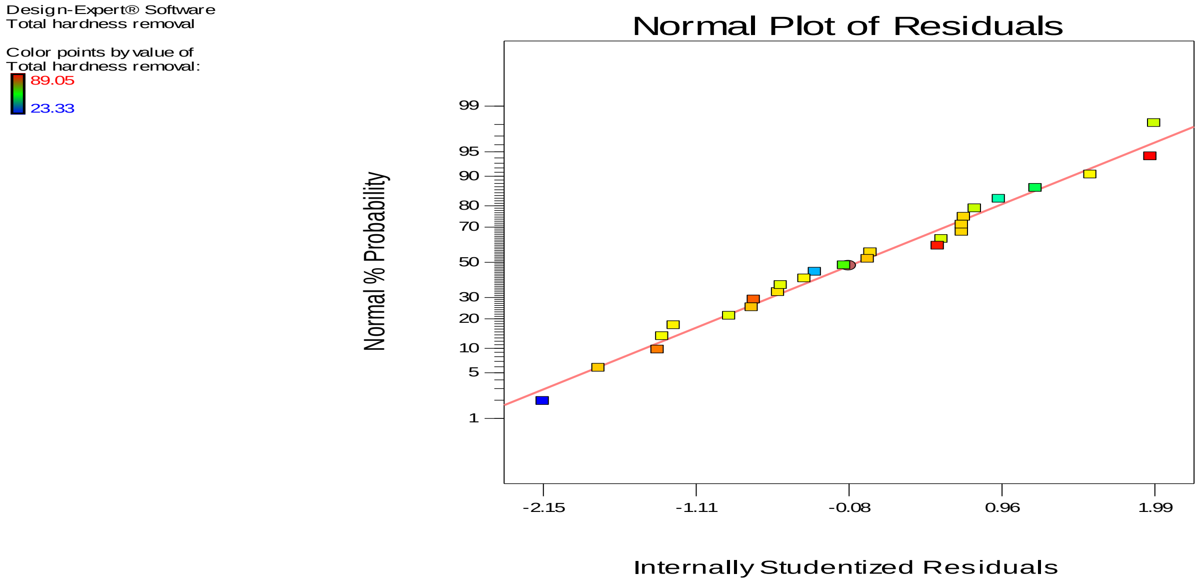


Figure C1: Normal plot of residuals experimental value for absorption hardness removal.

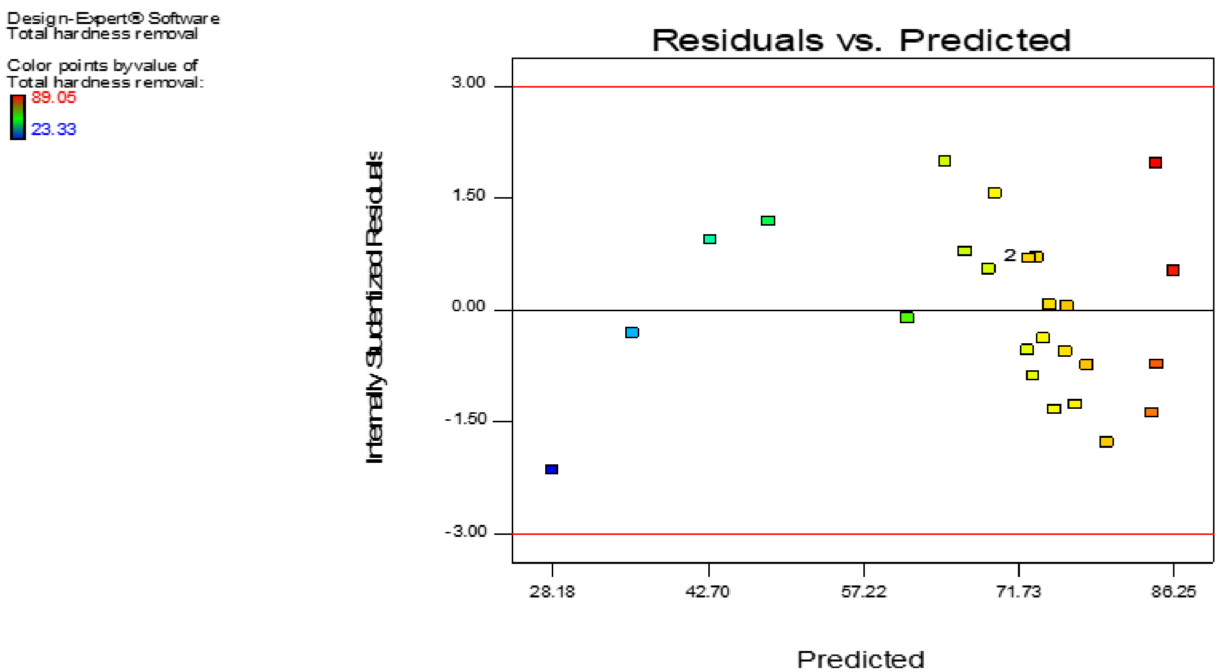
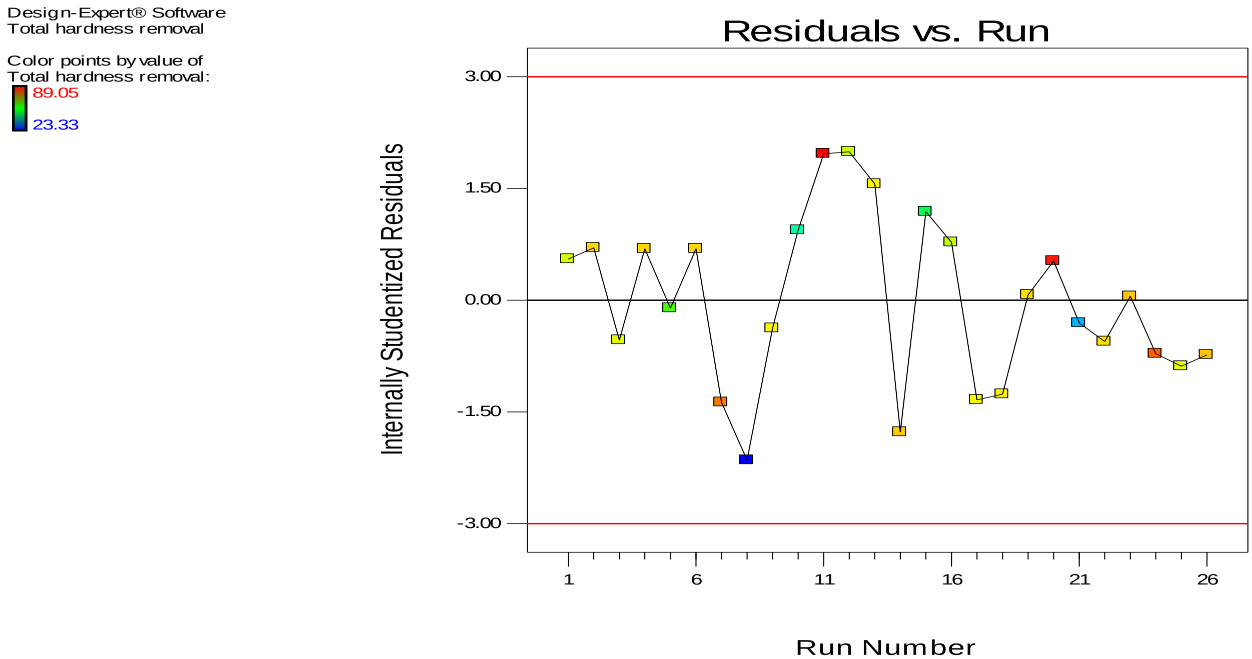
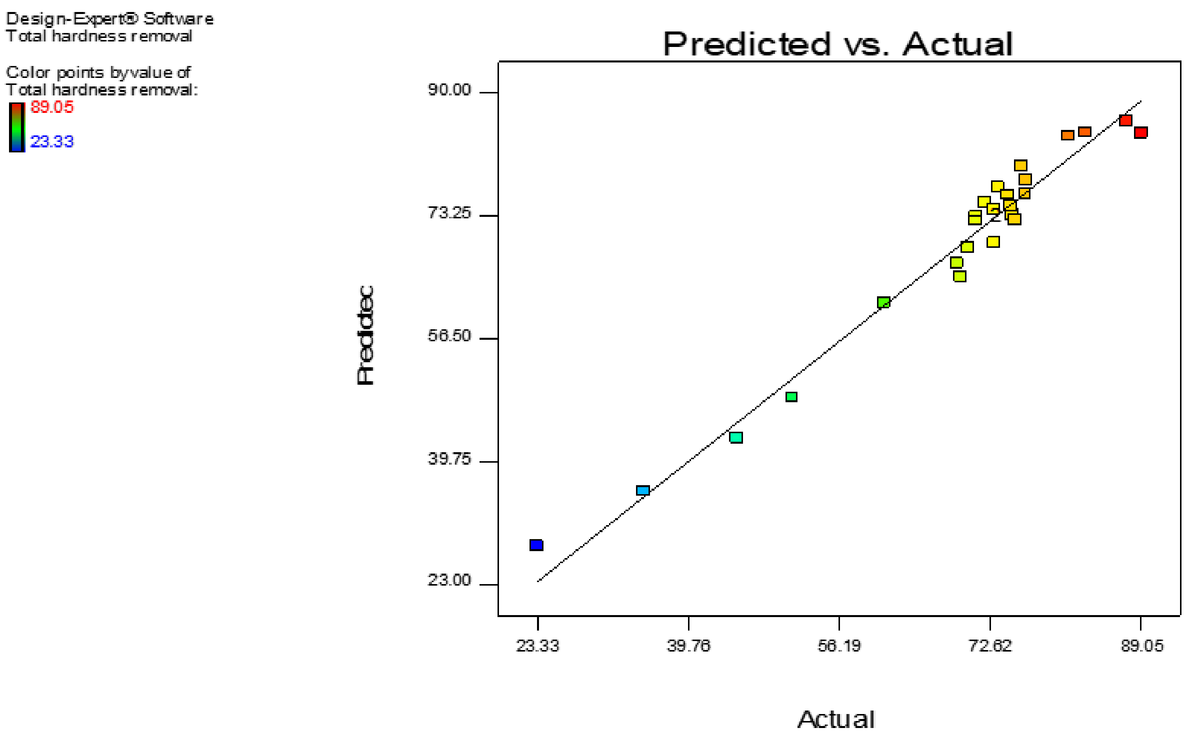


Figure C2: Residual Vs predicted experimental value for absorption hardness removal.



FigureC3: Residual Vs run experimental value for absorption hardness removal.



FigureC4: Predicted Vs actual experimental value for absorption hardness removal.

Appendix E: Laboratory Pictures

a) **Grinding to have uniform particle.**

b) **Weighting the absorbent dose.**

c) **Dry in oven**

d) **Jar test sampling**

e) **Filtering**

f) **Atomic Adsorption Spectroscopy**