ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Purification and characterization of Brine Lake salt of Afdera and Dobi

A Thesis submitted to the School of Chemical and Bio Engineering, Addis Ababa Institute of Technology in Partial Fulfillment of the Requirements for the Attainment of the Degree of Master of Science in Process Engineering.

By Nuru Ebrahim

Place and date of submission: School of Chemical and Bio Engineering, Jun 2019

Addis Ababa University

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

This is to certify that the thesis prepared by Nuru Ebrahim, entitled purification and characterization of Brine Lake salt of Afdera and Dobi, submitted in partial fulfillment of the requirement for the degree of Master of Science in Process Engineering complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the Examining comitee:

Dr.Ing.Birhanu Assefa _____ _____

Advisor: Signature Date

Dr.Shimels Kebede _____ _____

Internal examiner: Signature Date

Eng.Gizachew Shiferaw _____ _____

External examiner: Signature Date

DECLARATION

I declare that this thesis entitled purification and characterization of brine lake salt of Afdera and Dobi has not been submitted in any form for another degree, diploma, or an award at any university or other institution of the tertiary education. Information taken from published work of others has been acknowledged in the text and lists of references are given.The research work was done under the guidance of Dr. Ing Birhanu Assefa instructor in School of Chemical and Bio Engineering, Addis Ababa Institute of Technology, Addis Ababa University.

Name: Nuru Ebrahim

Signature _____

ACKNOWLEDGMENT

First, I would like to express my full gratitude to my advisor, Dr.Ing. Birhanu Assefa forhis positive attitude, guidance, valuable comments and suggestions up to the end of this research work.

I would like to extend my gratitude to Mr. Hintsa,Mrs. Demeku,Mr. Yosan,Mrs.Etsegenet and Mr.Aklilu for their tremendous help in the laboratory work.

I would also like to thank the Ministry of Education, the AAU and School of Chemical and Bio Engineering for providing the opportunity for this study.

Finally, my acknowledgement also goes to Mr. Yimam Abdu, Mr.Mohammed, and Mrs. Reisa who helped me for sample collection.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

FAAS	Flame Atomic Absorption Spectrophotometer
MDL	Method Detection Limit
WHO	World Health Organization
FMOH	Federal Ministry of Health
AOAC	Association of Official Analytical Chemists
ES	Ethiopian Standard of Specification
FMoH	Federal Ministry of Health
PVC	Polyvinyl Chloride
AOS	Automation Support Specialists
GFAAS	Graphite Furnace Atomization Spectrometer
AES	Atomic Emission Spectrometry
XRF	X-ray Fluorescence
IC	Ion Chromatography
UV	Ultra Violet
ICP-MS	Inductively Coupled Plasma Atomic Emission Spectrometry
ANOVA	Analysis of Variance

ABSTRACT

Improving the quality of salt using physic-chemical treatment process is an important issue for industrial and health benefit of the society. This study was performed to purify and characterize the brine lake salt of Afdera and Dobi. The salt samples were dried in an oven and the moisture content was determined. The levels of metal and heavy metal impurities were determined using FAAS after wet digestion using HNO_3. The concentration of Cd contents were not detected; however, the mean concentrations of other dissolved metals in the sample of Afdera in ppm were 296 for Ca, 818.9 for Mg, 0.1145 for Cu, 0.0144 for Pb, 0.0175 for Zn, and 2.0554 for Fe. For salt sample from Dobi the metals concentrations in ppm were 635.7 for Ca, 666.3 for Mg, 0.0472 for Cu, 0.0139 for Pb, 0.0139 for Zn, and 2.6342 for Fe. The percentage contents of sample from Afdera were 96.6 for NaCl, 1.09 for Loss of mass, 1.05 for matter insoluble, 1.08 for SO_4, 1.60 for alkalinity, 7.8 for pH. Similarly,the contents of sample from Dobi were 91.21 for NaCl, 1.25 for Loss of mass, 1.75 for matter insoluble, 8.12 for SO_4, 1.80 for alkalinity, and 7.9 for pH. The crude salt samples were treated by using NaOH, Na_2CO_3, and $BaCl_2$ to reduce Ca^{2+}, Mg^{2+}, and SO_4^{2-}. Using CCD with face centered statistical experimental design, interaction effects of process variable, optimum operating conditions and the optimum purity of salt that can be achieved at these condtions were determined. The selected operating conditions for salt sample of Afdera were 38.23 ^{0}C of reaction temperature, 2.65g of NaOH, and 2.69g of Na_2CO_3, 0.235g of $BaCl_2$ and 50.26min of reaction time, With an optimum salt purity of 99.63 %.Similarly, the selected operating conditions for salt sample of Dobi were 25^{0}C of temperature, 2.97g of NaOH, and 3g of Na_2CO_3, 5.29g of $BaCl_2$ and 27.58min of reaction time with an optimum salt purity of 99.68 %.The model adequacy was checked by analysis of variance.Based on the analysis for salt sample of Afdera, the correlation coefficients, R-Squared (R^2),adjusted R-Squared and predicted R-Squared havea value of 0.9997 , 0.9966, and 0.8105 respectively. For salt sample of Dobi,R-Squared (R^2), adjusted R-Squared and predicted R-Squared have a value of 0.9997,0.9970 and 0.8047 respectively.After purification the NaCl content of salt of Afdera and Dobi were enhanced to 99.65% and 99.60% respectively.

Key words: purification, crude salt, bio-toxicity, sample digestion,heavy metals,impurities Sodium Chloride, Loss of Mass, Matter Insoluble, Sulphate, Alkalinity

1. INTRODUCTION

1.1. Background

Although there are different types of salt, NaCl is the most known common evaporate salt which is made up fromchlorin, and e and sodiumions. It is inexpensive bulkily abundant mineral also known as halite, which is found in the form of rocks of coastal areas, underground deposit or in lagoons where trapped seawater was evaporated by the sun, salt, is deposited. Salt was produced only for human consumption purposes and later on, its multi-purpose applications were discovered. Due to the increase of industrial salt demand as raw material, it becomes one of the most important commodities of the centuries, comparable to the current use of oil (Lekkas and Korovessis, 2009).

After the industrial revolution, the use of the salt increase in the chemical industries and other applications. There are more than 14,000 reported applications of halite and along with other salts;it has played a very important role in human affairs (Kilic and Kilic, 2005). Production and trading of salt was the earliest form of commercial enterprise. From 2700-400 BC, Chinese and Indian civilizations, old mosaic, civilized Europe, Belgium cavemen, Babylonians, African such as Egyptian are the ancient players in salt origin .The growth of the industry has increased the demand for salt, both for direct human consumptions and as a raw material for producing other chemicals. There are three sources of salt: Brinelake water, seawater, and deposit of rock salt. Salt is produced from sea and brine lakes by evaporation. Rock salt may be mined directly as coal mining or extracted by drilling wells into the salt bed, forcing down pure water, and pumping up the saturated brine that forms (Fergusson, 1982).

Although sizeable salt is produced in dry tropical regions with solar power, many countries produce it all over the world irrespective of climatic conditions in modem industrial units. However, the traditional method of production requires certain geographical conditions. They are broadly topographical, geological, hydrological, and climatic. The most influential factors include high temperature, low humidity, low rainfall, dry wind, high evaporation, high saline brackish water, and flat loamy silt or clayey soil.

Salt production has a long history in northeast Ethiopian in general. According to the ministry of mine prior to the independent of Eritrea about 200,000tons of salt was obtained

from the red sea for human consumption. The Ethio – Eritrean war (1998 – 2000) interrupted Ethiopia's salt supply from Eritrea. As a result, Ethiopia started importing salt from neighboring countries, particularly Djibouti (Feyissa, 2011). Seeking to avoid dependence on the international market, the Ethiopian government explored domestic sources of salt. Although a small amount of salt is available in underground water in Tigray and from rocks in Somali and Oromiya regions, abundant salt is found in the Afar National Regional State, particularly from Lake Afdera and Dobi. Currently, Lake Afdera produces and distributes 95% of the total salt requirement of Ethiopia (Zewde, 2001). In fact, supply by far exceeds domestic demand. Ethiopia's annual domestic salt demand is estimated at 350,000 tons, whereas Afdera, alone has annual salt production capacity of 1.2 million tons (Feyissa, 2011).The current salt production in lake Afdera is below its capacity this is because of a production quota system.

Saline water is an inexhaustible source of common salt together with impurities such as; sodium sulphate, magnesium chloride, magnesium sulphate, calcium sulphate, calcium carbonate, etc (Aral et al.,2004).Supplying of unpurified salt for industries causes scale formation in the equipment, which leads to production loss due to periodic cleaning. Consumption of unpurified salt by the society may maximize the potential of exposure to diseases.In general, this maximizes medication expenses for the societies and loss of currency for importing of medicine.

Purification of salt involves dissolution of crude salt following filtration and chemical treatment using sodium hydroxide, sodium carbonate, and barium chloride. This process faces cost related issues of chemical reagents and electrical cost expenses for precipitation and recrystallization of salt.

A research by Ninawe, et al., (2004) developed purification process of salt by addition of calcium compound into the brine to crystallize Glauberite $(Na_2CaSO_4)_2$ and Glaserite $(K_3Na(SO_4)_2)$ which are isolated. In this process an important constituent of salt (Na^+) lost during the purification process. A study by Diyono et al, (2002) shows that the purification of crude salt from brine water can be achieved by free trial addition of reagents(NaOH,Na_2CO_3 and $BaCl_2$) ranging with 0.50g step changes.The optimum operating reagent concentrations and the optimum purity of salt that can be obtained in

these conditions were not investigated. Also they did not see the effect of temperature and reaction time on purity of salt.However, temperature significantly affects the precipitation of impurities after chemical treatment. Temperature has a significant influence on solubility and crystal growth of barium sul-phate(Amer et al., 2009). The solubility of $CaCO_3$ and $Mg(OH)_2$ increases with decreasing temperature.While the tempretarue icreases,the rate of precipitation also icreases (Rukuni et al., 2012). On the other hand, the interaction effect of reagent concentration,temperature, reaction time were not determined.

The aim of this thesis is purification and characterization of crude salt using physico-chemical treatment methods and the characterization includes determination of chemical and physical properties of the salt. The research was conducted to investigate the optimum reagent concentration,reaction temperature,reaction time and the optimum purity that can be achieved at these optimum conditions.

1.2. Statement of the problem

Ethiopia has a huge abundant of salt resources and suitable environment for production. However, these important salt deposits are not yet well developed commercially apart from traditional artisanal mining and some commercial producers. Also the quality of salt produced in Ethiopia have very poor values, the demand for refined salt is increasing in the market segment which indicates the process of modernization and mechanization in the salt industry. Many industries such as food, beverage, pharmaceutical, textile manufacturing, water purification, chloro-alkali, and bottling industries require high-quality salt in their manufacturing processes.

The method used in the traditional salt manufacturing process and hydro-extraction for removal of $CaSO_4$, and $MgSO_4$ is not efficient. Impurities, trapped inside the salt crystals do not removed by brine washing. Failure to purify the salt may have serious problem in industries and human health, even lethal consequences (Sedivy, 1996).

Earliest attempts to remove impurities from raw solar salt was based on the use of water washing to physically remove dirt and some of the surface impurities. This approach has practiced by some salt workers. Although marginal improvement achieved in the salt

quality, the washing operates at low efficiency and the quality improvement achieved at the expense of high salt losses of 10-20 %(Krebs, 1988).

According to my personal observation, salt produced from brine solution pumped out of the Lakes of Afdera and Dobi do not undergo chemical treatment. Due to this reason, salt produced from these lakes do not meet the quality of edible and industrial salt standards.

1.3. Objectives

1.3.1. General objective

The general objective of this research is to develop process for purifying brine lake salt of Afdera and Dobi, so that its quality meets the requirement of human and industrial use.

1.3.2. Specific objectives

- To characterize the brine lake salt and remove impurities such as, CA, Mg, and SO_4 from the salt produced from the two brine lakes through solar evaporation, so that they meet edible and industrial salt concentration requirements. This includes;
  - ✓ Analyzing sodium chloride, alkalinity, sulphate, moisture content, matter insoluble, and the pH of the salt.
  - ✓ Determining the concentration of some metal and heavy metal impurities such as Calcium, Magnesium, Cadmium, Lead, Zinc, Iron, and Copper.
- To investigate the effects of purification process variables (NaOH, Na_2CO_3, $BaCl_2$, temperature, and time) on purity of salt and determine the optimal operating condition.

1.4. Hypothesis

Salt purification is affected by reagent concentration (NaOH, Na_2CO_3, and $BaCl_2$), reaction temperature, and reaction time. The interaction effect of these purification process variables is significant.

1.5. Significance of the study

This study is an experimental study using physical and chemical treatment purification methods. The Purification and characterization of salt involves on the brine lake salt of Afdera and Dobi. Although the country has a huge deposit of salt resources and produces to satisfy the demand, yet quality of the salt is questionable.

The salt should be clean and free from extraneous matter and should satisfy the standard requirement of the ES,codex, and international salt producing country. There is a law, which forces all the players in salt business. However, the table salt and common salt quality and composition in Ethiopia is not well known (FMoH, 2005).

Although the country has a huge deposit of salt resources, yet most of Ethiopians are consuming unrefined salt. The country also not obtaining the expected benefits. As a result, production of purified salt has big significances which enables the country to export and in return to have foreign currency. In addition to this, it will supply pure salt for industrial inputs and healthy diet for the society in general.Supplying of purified salt for induastries reduces scale formation in the equipments which reduces production loss due to periodic cleaning. Using purifed salt the society minimizes the potential of exposure to diseases such as,cancer,heart diseases,mental disordernes and birth defects for women.In general this minimizes medication expenses for the societies and loss of currency for importing of medicine.

This study may fill certain gaps and initiates other researchers for further study regarding the purification and improving the quality of salt produced in the country.

2. LITERATURE REVIEW

2.1. Classification of salt

Salt could be produced in different methods and classified as unrefined salt (rock salt and sea salt), refined salt (table salt), and iodized salt. It is a crystalline white solid but the color might be, pale pink or light gray depending on the amount of impurities it contained, normally obtained from seawater, brine lake water or rock deposits. The color of salt mainly depends on the mineral content (Sedivy, 1996).

2.1.1. Unrefined salt

Unrefined salt does not undergo through the purification process, which is commonly used as ingredients' in bathing additives and cosmetics products. Bath salt uses sea salt as main ingredients and combining it with other ingredients for therapeutic and healing effects (Sedivy, 1996).

2.1.2. Refined salt

Refined Salt is inorganic solid compound, white in color, normally soluble in water and supplemented with sodium chloride and additives like aluminum silicate for a powdery and porous consistency. In the production process of refined salt, public salt is dissolved and filtered to remove insoluble impurities. Then the chemical treatment process was carried out by addition of chemical substances to the crude salt samples in order to enhance the NaCl content and to decrease the polluter compounds especially magnesium, calcium, and sulfate (Prof. Sudharto, 2013).

2.1.3. Iodized salt

Iodized salt is either edible table salt or iodized common salt, whichis mixed with a small quantity of potassium iodide or potassium iodate. Iodized salts are used to help reduce the incidence of iodine deficiency in humans (Zimmermann, 2007). Usually table salt or refined salt have purity of 97% to 99% NaCl. It usually contains substances that make it free-flowing (anti-caking agents) such as sodium silcoaluminate or magnesium carbonate. Sometimes people add uncooked rice grains in the salt as a desiccant, to absorb the moisture and breakdown clumps when anti-caking agents are not enough (Sedivy,1996).

2.2 Use and application of salt

2.2.1. Use of salt in Chemical Industries

Most of the chemical consumption of salt is by the chlor-alkali industry to produce caustic soda and chlorine, which are then used in the processing and manufacturing of other products. Using electrolysis, caustic soda, Chlorine, and hydrogen gasare produced from brine solution in an electrochemical cell (Curlin, 1991). The electrolysis can be expressed as;
$NaCl + H_2O \rightarrow Cl_2 + NaOH + H_2$

The chlorine is an activeantiseptic and is widely used for treatment of potable water, wastewater, and sewage, and as bleach in detergents and scouring powders and in papermaking to bleach the wood pulp. Chlorine is used to synthesize a number of chemicals including sodium hypochlorite (Curlin, 1991; Butts, 1993), sodium chlorate (Mendiratta and Duncan, 1993), vinyl chloride and polyvinyl chloride (PVC) and their derivatives and polymers for the manufacture of waxes, paraffin, synthetic fibersand synthetic rubber. Chlorine is usedwidely in metallurgical processes. For example, high-whiteness titanium dioxide pigment is produced from $TiCl_4$ prepared by the chlorination of titania substrates. Chlorine is a major ingredient for HCl production, and it is an important reagent in many industrial applications as discussed by Curlin, (1991).

Caustic soda (NaOH), is used in making sodium-based chemicals. It is used in the purifying of Kraft paper, detergents and in the production of soaps, in textiles and other synthetic fibers, in herbicide, insecticide and fungicide formulations and other uses. In the minerals industry, it is used in alumina production bya major process industry in Australia, metal processing and flotation(Curlin, 1991). Sodium chloride is used an input for production of sodium carbonate(Na_2CO_3). Soda ash also used in theproduction of sodium cyanide and sodium chromatewhich are used for production of glass,in the pulp and paper industries, production of rayon, soaps and detergents; in water treatment and iron and steel making (Habashi, 1997b). Sodium bicarbonate is used in textile industries, in leather processing , making glass and used as acid neutralizing agent besides its key use in baking industry.

2.2.2.Use of salt in leather industry

The raw hides and skin consist mainly of water and protein, which make them vulnerable to attack by microorganisms. Wet and dry salt treatments are used to prevent bacterial attack. Here salt at a level of 40%(based on green weight) is applied to the fresh skin for preservation. The salt absorbs the liquid contained in the skin, so that moisture and salinity become balanced. Salt makes the bacteria become dry and eventually die, so there is no breeding bacteria that cause the skin to be damaged (Kanagara and Babu, 2002).

2.2.3.Use of salt in textile industry

The textile substrate and dye molecule, not essentially ought to have of uniform characteristics to mix with one another. In such case, some catalysts are needed to facilitate coloring action on material. Salt plays this significant role of catalyst. It has an especial high affinity for water. Generally, Salt is critical in three ways, firstly, to drive dye into the textile throughout the colouring. Secondly, use of salt results in most exhaustion of dye molecules throughout coloring method in textiles (Acharya and Sanjit, 2014). Thirdly, it is used as associate in nursing solution for migration, sorption, and fixation of the coloring material to the polysaccharide material. Salt also increase the exhaustion and the attraction between the dye molecule and textile material. Typically, dye (direct & reactive) molecules have charges and therefore the material has negative charge on its surface. Salt decreases the repulsion of negative-negative charges and thence improves exhaustion (Iqbal and Naseem,2012).

2.2.4.Use of salt in water treatment

The use of disinfection to kill or inactivate pathogenic microorganisms is necessary if the raw water contains such organisms. Several disinfection methods are used in water treatment. Disinfection with chlorine is the most widely used method for large water supplies. Chlorination can be achieved by using liquefied chlorine gas, sodium hypochlorite solution, or calcium hypochlorite granules. Chlorine gas is very reactive and it is used for treatment of large public supplies. Chlorine is used not only as a primary disinfectant in water treatment, but is also added to provide adisinfectant residual to preserve the water in distribution.

2.2.5. Food Processing and Human Consumption

All animals and humans require both sodium (Na) and chloride(Cl) for life and health. Sodium is an essential nutrient, an element that the body cannot manufacture itself. People consumes about 3 to10 g of salt/day. If it is taken in moderation, it maintains relatively constant blood pressure by controlling the acid-base balance in the body, and aids potassium absorption(Aral,et al.,2004).

Ordinary salt is the world's oldest known food additive. Salt enhances the natural flavours of some foods by making them more palatable. It also used to preserve food by hindering the growth of bacteria and control the rate of fermentation process in the food processing (Bertram, 1997).

Salt is used largely in the dairy (cheese, margarine, butter), sauce, pickle, meat, bread, biscuit, flour and fish processing industries. Salt preserves foods by creating a hostile environment for certain bacteria. Salt brine dehydrates (kills) bacteria by altering the cell wall (osmotic) pressure. Salt enables gluten in bread dough to hold more water and carbon dioxide, allowing the dough to expand without tearing. In baked products, salt controls fermentation by retarding and controlling the rate of fermentation. Salt is also used to control fermentation in the making of pickled food, cheese, and sauerkraut. Salt improves the texture and tenderness in processed meats by promoting the binding of water by protein.

Salt is used as a colour enhancer in ham, bacon, hotdogs, and sauerkraut. Used with sugar and nitrate or nitrite, salt produces a “fresh meat” colour in processed meats, which some consumers find appealing. Salt enhances the crusty appearance of bread by reducing sugar destruction in the dough.Salt is also an essential nutrient for livestock, poultry, and other animals. Livestock also needs a nutritionally balanced diet to remain healthy, disease free, and to achieve optimum growth and reproduction rates. When animals do not get adequate amounts of salt from forages and other feeds, salt is added in their feed. Animal (or stock) salt is often added with trace minerals, molasses, and other nutrients. In the food, and food processing industry, salt is used in various products. It is used as a preservative, an emulsifier, an artificial colour , and a flavor enhancer(Aral,et al.,2004).

2.2.6. Other uses of salt

The other uses of salt include de-icing of roads, particularly in North America and Europe, since it lowers the freezing point of water. Salt is also an essential nutrient for livestock, poultry, and other animals. Livestock also needs a nutritionally balanced diet to remain healthy, disease free, and to achieve optimum growth and reproduction rates(Aral,et al., 2004).

2.3.Salt consumption world-wide

The chemical industry is the largest salt consumer.This industry converts the salt mainly into chlorine, caustic and soda ash without which petroleum refining, petrochemistry, organic synthesis, glass production, etc. would be unthinkable.The second largest user of salt is mankind itself. Humans need the salt to support their physiological functions and eating habits. Salt for food is the most "taken for granted" commodity, available from thousands of sources in hundreds of qualities as a table, cooking and industrial salt for food production.The third use of salt is for road deicing, water treatment, production of cooling brines and many other smaller applications(Sedivy, 1996).

Table 2.1:Salt consumption of worldwide

Salt user	Salt consumption
Chemical industry	60%
Food	30%
Other	10%

Source; Sedivy 2007.

2.4. Annual Salt production of the world

Recent statistics shows that the World production of salt was more than 200 million tons/annum. Salt production by evaporation of seawater and inland brines exceeds one-third of the total production of solar salt. The remaining third is obtained from rock salt mining, both on surface and underground deposit. The balance is obtained as brines, mainly

by solution mining. Salt solution may be used in thermally evaporated to produce vacuum salt or directly in diaphragm electrolysis(Sedivy.1996).

Table 2.2: World production of sodium chloride by region (in 10^3t)

Region	Year of production			
	2000	2002	2004	2006
Asia	58370	61459	60130	77963
Europe	59814	62252	68497	68048
North America	66614	60843	68696	68838
South America	13654	11943	14178	16367
Oceania	8977	10092	11182	12490
Africa	4024	4766	5487	5455
Middle East	3122	2994	3118	3131
Central America	2044	2173	2380	2396
World total	**216619**	**216522**	**233668**	**254688**

Source: The Economics of Salt, 12th ed., Roskill Information Services Ltd., London 2007.

2.5.Methods of salt production

Salt is produced from sedimentary deposits, which have been laid down over the millennia from the evaporation of seawater and brine lakes. These are produced by solar evaporation, mined directly from the underground deposit of rock salt, or using solution mining by dissolving the salt crystal and pumping out of the brine from the deposit. In this case, the salt is purified by manualprecipitation and evaporation of brine. Traditionally, the evaporation process was carried out in shallow open pans in which heat is supplied to facilitate rate of evaporation. Currently, the process is achieved in pans under vacuum (Kostick, 2011). The raw salt is refined to purify, improve its storage and handling characteristics. Usually, it involves recrystallization during which salt solution is treated with chemicals that precipitate most impurities such as; Mg, Ca, and SO_4. Many stages of evaporatorsare then used to collect pure salt crystals. Generally,there are three methods

used to produce salt: solar evaporation, vacuum evaporation, and rock salt mining(Morton salt, 2019).

2.5.1. Solar evaporation method

Solar evaporation is the oldest method of salt production. This production method is in use since salt crystal was noticed in the sea. It is practically used only when the climate is warm and the rate of evaporation is higher than the rate ofprecipitation. This practice is implemented either annually or for extended periods or monthly and ideally, where there are steady prevailing winds. Solar salt production is achieved by using artificial ponds and typically, the sun evaporates most of the water capturing of the salt in shallow ponds. The impurities that may be present in the brine will be precipitated and settled at the bottom. The concentrated brine precipitates the salt, whichis then gathered by mechanical harvesting machines or manpower.

In solar salt production, two types of ponds are used. The first is the concentrating pond, which is used to concentrate salty water from the ocean or brine lake. The second type is the crystallizing pond, in which the solar salt is produced. During the salt production season, the brine flows over these ponds. Whenwater is evaporated from the saturated brine, pure salt crystallized out of the solution. Chemical impurities that are settled at the bottom of the pond returned to the saltwater source (Morton Salt,2019).

2.5.2. Rock salt mining method

The second oldest method of producing salt is underground rock salt mining. This is the easiest method.Usually; large machines are used to collect the salt by cutting cave like structure performing different operation.

The first step of the operation is undercutting. The machines cut a slot of 10 or more feet in depth to penetrate across the bed of rock salt deposit. This leaves a smooth floor for picking up the salt after blasting. Then small vertical holes are drilled into a depth of 10 or more feet and electrical explosives are set off. After explosion large amount of salt lumps are blasted and fall on the mining floor. The salt is loaded or transported by different equipment or dragged to machines that crush and feed the salt onto a conveyor belt. The

salt crystals are conveyed to a series of stations for crushing and sizing of the lumps. The salt is then placed in a storage bin to wait to hoist to the surface.

The above ground extraction of rock salt involves direct screening of the mined salt into various marketable sizes by using mechanical operating screens. Then the salt is conveyed to its storage bin for packaging and shipping to the customers (Morton Salt, 2019).

2.5.3. Vacuum evaporation method

The other method of salt productioninvolves evaporation of brine water by using steam heating in large vacuum evaporators. The method yields highly purified salt, white, fine in texture, and principally used in process that requires high purityof salt.

The first process is solution mining in which wells are drilled from several hundred feet into the plain of salt bed. Lateral drilling connects the wells and the solution mining process starts: water is pumped into the first well, then salt is dissolved, and the resulting salt solution is forced to the surface through the next well. The pumped brine is piped into large storagetanks. Then the brine is pumped and recrystallized in the vacuum pans. Therecrystallization process takes place in huge closed vesselsthat operates under vacuum condition and arranged in a series of 3 to 5 pans, with in line under greater vacuum than the next one. This series of vacuum pans operates on a very simple principle: whenever pressure is lowered, the temperature at which water will boil is also lowered. In the vacuum pan process, steam is fed to the first pan. This heated the salt solution in the vacuum pan to boil. The steam from the first pan of the boiling brine is then used as a heat source for the second pan. The pressure of the second pan is lowered to enhance boilingof the brine in the pan. The pressure reduction continues further in each succeeding pan. This allows the steam made by the boiling brine in the preceding pan to boil the brine in the next pan. The heat from the first pan to the succeeding pan achieves the boiling and evaporation process with greater efficiency of energy (Morton Salt, 2019).

2.6. Quality of salt produced from different source and methods

Mexico and Australia are low cost producers of high quality solar salt for the South East Asian and Japanese chemical industries. The quality of Australian and Mexican solar salt continues to set the industry standard for internationally traded salt and the quality of the salt produced by the competitors, mainly India and China, has not yet achieved the standard set by Mexico and Australia. Saltis certified to the international standard for quality assurance standard ISO 9002.

Table2.3: Typical chemical analyses in dry basis of different types of salts

Salt type	NaCl (wt.%)	Mg (wt.%)	Ca (wt.%)	SO_4 (wt.%)	Mater insoluble in water (wt.%)
Pure vacuum evaporated salt	99.95	0.0001	0.002	0.04	Trace
Vacuum salt	99.7	0.01	0.01	0.2	Trace
Refined salt	99.0	0.05	0.06	0.2	0.02 - 0.03
Solar salt	96.0 - 99.0	0.01 - 0.17	NR	NR	0.5 - 0.06
Rock salt	90.0 - 99.0	0.01 - 0.17	0.04 - 1.1	0.2 - 1.3	0 - 5.0

NR = Not reported

Source: Mannar and Dunn (1995)

2.7. National Codex Committee

Codex is an international body developing food standards play a major role in ensuring food safety by protecting contamination in all food chain, from farm to fork. The mandate of the codex is to establish international food standards to protect the health of consumers and to ensure fair practices in the food trade while promoting coordination of food standards work undertaken by international governmental and non-governmental organizations (Alemanno, 2015). According to the Codex standard (2001), food grade salt can be obtained from the sea, brine lake or underground rock salt deposits. The content of NaCl shall not be less than 97% on a dry matter basis, exclusive of additives. Since ingredients or content of

safe food or food additives including edible salts are placed in the standard as requirements, products with limits beyond the requirements of the standard can be removed or sanctioned by the government before they reach the consumers. Standards are set not only at the final stage (end product) of the food but also from the beginning.This is because food and food products get contaminated during manufacturing, storage, transportation, etc. If all of these are not properly regulated, it is not possible to say the food is safe (Yalemtsehay, 2010).

2.8. Heavy metals

The term "heavy metals" used for any metallic elements with high density and toxicity even at low concentration (Lenntech, 2004). "Heavy metals" is a group term used formetalloids and metals with atomic density larger than 4 g/cm^3, or 5 times or more, greater than water (Hawkes, 1997). However, being a heavy metal has little relation with density and mainly concerns chemical properties. It includesPb, Cd, Zn, Hg, As, Ag,Cr,Cu, and Pt group elements. (Farlex, 2005).

2.9. Sources of heavy metals in saline water body

Heavy metals enter into the aquatic environment naturally through weathering of the earth crust. The main natural source of heavy metals in water is weathering of minerals. Moreover, their natural incidence, heavy metals may enter to the ecological system through human activities. The aquatic systems receive a large amount of heavy metals from natural occurring deposits and natural processes and anthropogenic activities (Wogu and Okaka, 2011).

2.10. Health effects of salt impurities

Few metals in minute amount are necessary for metabolic activity in human system while others cause acute and chronic diseases (Bodaghpour, et al.,2012). The most toxic heavy metals include Cr, Ni, Pb, Cd, and As. Ni and Cr (VI) are carcinogenic; Cd and As are teratogen, and Pb is neurological impairment and malfunctioning of the central nervous system (Markus, and McBratney, 2001).Even though some heavy metals (Fe, Co, Cu,Zn and Mn) are essential micronutrients, they are hazardous at high concentration (Ochieng, et al., 2007).

Table 2.4: Ethiopian standards of metal Contaminants in iodized common and table salt

Contaminants	Requirement	Test method
Lead	2 mg/kg	ES 309
Iron	10 mg/kg	ES 310
Copper	2 mg/kg	ES 312
Calcium	0.5 g/kg	ES 2482
Magnesium	0.5 g/kg	ES 2482

Food grade salt may not contain contaminants in amounts and in such form that may be harmful to the health of the consumer. The above maximum limits shall not be exceeded.

2.10.1. Selected heavy metals bio toxicity

The concentration of heavy metals in table salt should be rigorously controlled. Edible salt may contain contaminants in large amounts and in such form that may be harmful to the health of the consumer (Cheraghali, et al., 2010).

2.10.1.1 Lead

Pb is one of common heavy metal in general beyond desirable limit is metabolic poison and enzyme inhibitor (Gebrekidan and Samuel, 2011). It can also damage nervous connections and cause blood and brain disorders. Other than this the biochemical effects of lead is its interference with haemo synthesis, which leads to haematological damage (Mohod and Dhote, 2013).

According to Codex legislation, the maximum tolerated amount of Pb in salt is 2μg/g. The mean concentration of Pb found in table salt in Iran was 0.438μg/g (Abdol Majid, 2010). Recently, the heavy metal contents of refined and unrefined table salts from Turkey, Egypt and Greece have been studied (Soylak, et al., 2008). According to the reported data, the concentration of Pb in table salt was between 0.54-1.64 μg/g. Concentrations of Pb in table salts consumed in Brazil reported to be in the range of 0.03-0.1 μg/g (Amorim and Ferrerira, 2005).

2.10.1.2. Iron

Fe at low concentration is needed for enzyme activity (Salem,et al., 2000) but at high concentration, it accumulates in muscle, liver and affects brain and central nervous system (Luqueno,et al., 2013).

According to the Ethiopian standards of heavy metal Contaminants in iodized common and table salt, the concentration of iron should not exceed 10mg/kg. Analytical data for Dominion Salt's (New Zealand) unrefined Solar Sea Salt with no additives contains 99% NaCl and 22.4mg/kg of iron. A typical specification for raw salt and industrial salt recovered from the Dead Sea brines contains 2.5mg/kg of iron (Sabatin 2000).

2.10.1.3. Zinc

Zn as needed in lower concentration for acting as catalyst in enzyme activity of living system but it accumulates in muscle and liver (Luqueno,et al., 2013). The chronic health effects of Zn include cancer, birth defects, organ damage, disorders of the nervous system and damage to the immune system (USGAO, 2000).

A study conducted in Shiraz reported that the concentration of zinc was 0.34µg/g in recrystallized and 0.37 µg/g in washed samples. Another study in Tehran reported that Zinc content of edible salt was found to be 6.5µg/g (Pourgheysari,et al., 2012).The Concentration of zinc in edible and industrial salt of Khewra in Pakistan is 4.10mg/kg and 6.00mg/kg respectively.

2.10.1.4. Cadmium

Cd, classified as toxic trace element appears to accumulate with age, especially in the kidney and it is considered as an agent to cause cancer and cardiovascular diseases. Industrial contaminated drinking water causes bone and renal disease. With long-term exposure, it can replace calcium in bones and damage kidney (U.S.EPA, 1999). Cd may interfere with the metallothionein's (a protein that binds to excess essential metals to render them unavailable) ability to regulate Zn and Cu concentrations in the body which causes elevation in zinc in urine (U.S.EPA, 1990).

Based on Codex legislation, the maximum tolerated amount of Cd in salt is 0.5µg/g. The mean concentration of Cd found in table salt in Iran was 0.024µg/g (Abdol Majid, 2010).In a separate study Cd, levels of table salts used in Nigeria reported as high as 4.5 µg/g (Nnorom,et al., 2007). Concentrations of Cd in table salts consumed in Brazil reported to be in the range of 0.01-0.03 µg/g (Amorim and Ferrerira, 2005).

2.10.1.5. Copper

Cu is an essential element at lower concentration while, exposed for long term or high concentration can cause chronic diseases like nervous system disorder, liver and kidney failure. (Bent and Bohm, 1995).

The Ethiopian standards of heavy metal Contaminants in iodized common and table salt, the limit of concentration of copper should be 2mg/kg. From the Dominion Salt's Analytical data in New Zealand, unrefined Solar Sea Salt with no additives contains 99% NaCl and 0.32mg/kg of copper. A typical specification for raw salt and industrial salt recovered from the Dead Sea brines contains 2mg/kg of copper (Sabatin 2000).

2.11. Metal and nonmetal impurities

The Ethiopian standard specification for iodized common and table salt states, any food grade salt should fulfill the following minimum requirements.

Table 2.5: Ethiopian Standard Specification for both iodized Common and table Salts

Characteristics	Iodized common Salt	Iodized table Salt	Test method
Chloride content (NaCl), (%wt.)	96	98	ES ISO 2481
-Iodine as potassium iodate(mg/kg) -as iodine	60-80 36-48	60-80 36-80	ES ISO
Loss of mass at 110°C, (%wt.)	4	0.5	ES ISO 2483
Matter insoluble in water(%wt.)	1	0.2	ES ISO 2479
Calcium (g/kg)	-	0.5	ES ISO 2482
Magnesium(g/kg)	-	0.5	ES ISO 2482
Sulphate (as SO_4), (%wt.)	0.5	0.5	ES ISO 2480
Alkalinity (as Na_2CO_3), (%wt.)	0.2	0.2	ES ISO 308

2.12. Selected metal and nonmetals bio-toxicity

2.12. 1.Sodium chloride

Sodium chloride is an essential nutrient for the normal functioning of the body. It is important for nerve conduction, muscle contraction, correct osmotic balance of extracellular fluid, and absorption of other nutrients. Sodium chloride is not a hazardous material. However, excess sodium intake will cause elevated adverse effect by increasing blood pressure. Higher blood pressure is a known risk factor for chronic heart disease, stroke, and renal disease. For groups of individuals there is strong evidence of a dose- dependent rise in blood pressure with increased consumption of sodium as sodium chloride (Ducher,et al.,2003).

Food grade salt, which is used for food additive,accounts for 17.5% of salt production in the world (Sedivy, 1996). According to Codex standard (2001), food grade salt can be obtained from the sea, the lake underground rock salt deposits or from natural brine. The content of NaCl shall not be less than 97% on a dry matter basis, exclusive of additives. The quality of Australian and Mexican solar salt continues to set the industry standard for internationally traded salt and the quality of the salt varies from 99 to 99.95% NaCl (Mannar and Dunn, 1995).A study in Sir Lanka shows that a purity level can be achieved from 98.023 to 99.604 by physic-chemical treatment process(Rathnayaka ,2014).

2.12.2. Magnesium

Mg is associated with abnormal irritability of muscle, convulsions, and excess Mg with depression of the central nervous system (Budavari, 1997).

Magnesium also increases moisture content of the salt (Kelly, 1953).The Ethiopian Standard Specification for both iodized Common and Table Salts states that the concentration of Mg should not exceed 0.5g/kg. Salt produced from different source and different methods in Mexico and Australia contains 0.0001 to 0.17% Wt. Mg.

2.12.3. Calcium

In Mexico and Australia, chemical analyses in dry basis of different types of salt, the concentration of calcium varies from 0.002 to 1.1% wt. Similarly, the ES states that the amount of water-soluble impurities such as Calcium should not be greater than 0.5g/kg.

2.12.4. Sulphate

Based on the Ethiopian standards of table salt the amount of water-soluble impurities such as Sulphate (as SO_4), should not be greater than 0.5%wt.

Sulphate generally present in the salt as impurity and does not cause any health problem, but high concentration acts as a purgative (Kumar, 2001). The excess consumption of sulphate results in cathartic effects, due to purgation of the alimentary canal .However, with time human appear to be able to adapt to higher sulphate concentrations. Dehydration has also been reported as a common side effect following the ingestion of large amounts of sulphate (Müller-Lissner, 2005).

2.12.5. Alkalinity

The alkalinity of edible salt, which are processed in different methods in Uganda,vary from 0.13 to 1.3% (Kirabira,et al., 2013). (Binega, 2006) found high amount of alkalinity in the rock salt in Ethiopia 1.39 %which exceeds the standard set by the ES.

There have been a number of cases where excessive ingestion has caused moderate to severe toxic effects. The most prevalent symptoms are excessive carbon dioxide production, metabolic alkalosis, and cyanosis (Brown, 1981). Absorption of $NaHCO_3$ is known to cause alkalosis. The acid-base disturbance is usually transient in individuals with normal renal function, as the base excess will rapidly be excreted. However, the urinary pH can be elevated affecting tubular reabsorption and urinary elimination of weak acids and bases (AL-Saffar, 2012). The minimum dose causing adverse effects will vary strongly according to age and health condition (Jaeger, 1987).

2.12.6. Moisture content

Moisture is naturally present in the salt, or is abstracted from the air by hygroscopic impurities such as magnesium. Thus, the stability of iodine is affected by the level of impurities in the salt and the moisture content. Since the stability of the iodine in salt was clearly dependent on moisture, impurities, which provided moisture at the salt surface, had the most deleterious effect (Levente,et al., 1998).

According to the Ethiopian standard for iodized table salt and iodized common salt, loss of mass at 110 ^{o}C, should not be more than 0.2 and 4 %wt. respectively. In a study of different crude solar salt and refined solar salt analysis in Sir Lanka shows, that Moisture Content of the crude salts varies from 3.46 to 7.35% and 0.7294% for refined solar salt (Rathnayaka, 2014).

2.12.7. pH of salt

A study in iodized salt shows that pH values near 8 seemed to have the most adverse effects on iodine stability (Levente,et al.,1998). In other study of eight different samples of iodized common and table salts from Afdera and Dobi the pH of the salt varies from 7.85 to 8.75(Henok, 2016).The African standard specifies the pH of salt should be 7-8 (AOS, 2012).

2.12.8. Matter insoluble in water

Salts, which are obtained by solar evaporation in Uganda, contain 2.5 % insoluble matter (Kirabira,et al., 2013) .For salt with contaminants not exceeding 0.02 % insoluble matter (Diosady, 1997). (Kirabira,et al., 2013) reported 0.001% of insoluble matter in salt, which processed chemically. A comprehensive review of the literature by Kelly,(1953) reported that the stability of iodine in the salt is determined by the amount of insoluble matter found in the salt.

2.13. Effects of impurities of salt in the chemical industry

In the chemical industry, salt is mostly dissolved together with the impurities in water or brine. Prior to feeding the brine to the process, it is purified. Failure to purify the brine adequately may have serious, even lethal consequences (Sedivy, 1996).

2.13.1. Hydrogen evolution

In electrolytic cells, excessive magnesium will cause hydrogen evolution on the anode. Hydrogen and chlorine form an explosive mixture. Explosion in the cells or in the chlorine liquefaction may damage the equipment and release chlorine to the environment. Chlorine gas is highly poisonous and dangerous. Stringent safety measures are taken in the chloro-alkali industry to avoid this to happen but the elimination of magnesium is of prime concern (Sedivy, 2007).

2.13.2. Mercury butter

Impure brine in mercury cells will cause butter formation. Butter will disturb mercury flow, causing short circuits that burn the electrodes. Alternatively, a large electrode gap must be maintained which will increase the power consumption. Butter removal will expose workers to mercury vapours that are damaging the health. Disposal of mercury butter is costly and undesirable for the environment (Sedivy, 1996).

2.13.4. Contaminated sludge

Sludge from brine purification in chloro-alkali plants with mercury cells is contaminated with mercury. Sludge decontamination by distillation requires high temperatures, is costly and never complete. The disposal of mercury-contaminated sludge is environmentally objectionable and very costly. Avoiding the formation of sludge is better than having to dispose of it. This requires salt of high purity (Sedivy, 1996).

2.13.5. Membrane damage

Calcium and magnesium will damage the ion exchange membranes irreversibly. Erratic impurity content in salt may cause hardness breakthrough to the membrane cells. Membranes cost a fortune. The purer the salt, the more remote is the danger of membrane damage (Sedivy, 2007).

2.13.6. Encrustation

In soda ash production, excessive sulfate reduces the value of the product. Accumulating calcium in the process causes encrustation. Periodical scale removal is costly and leads to loss of production. Salt may be a cheap commodity. However, impurities in salt and their removal cost in many cases more than the salt itself (Sedivy, 1996).

2.14. Metal analysis

Direct determinations of trace metal ions in salt samples by flame atomic absorption spectrometry are difficult. Because sodium chloride is, a bulk matrix and some metals have a concentration in milligram per liter and microgram per liter range, which is near or below the limit of detection of method. Separation pre-concentration methods including solid phase extraction, solvent extraction, membrane filtration, cloud point extraction etc. can solve these problems (Dogan, 2001).

Most metals determination is for detecting trace quantities. These are determined by various spectroscopic or chromatographic methods, such as; atomic absorbance spectrometry using flame (FAAS) or graphite furnace (GFAAS) Atomization, Atomic emission spectrometry (AES),inductively coupled plasma atomic emission spectrometry (ICP-MS),X-ray fluorescence (XRF),and ion chromatography(IC) (De Souza, 2013).

FAAS is a suitable technique for determining metals at part per-million (ppm) concentration levels with good precision for many elements. FAAS offers air-acetylene and/or nitrous oxide flame atomizer. Samples are introduced into the atomizer as an aerosol by the nebulizer. FAAS technique provides fast analysis of 10-15 s per sample, with very good precision (repeatability), moderate interferences that can be easily corrected, and relatively low cost (Lajunen, 2004).

2.14.1. Sample digestion

Preparation of sample materials for determination of metal content uses Wet digestion method, which involves the use of both heat and acid. Acid that has been used in this digestion procedure includes H_2SO_4, HNO_3 and $HClO_4$ (Themir, 2003), either in combination or alone (Maria, 2002). Hydrogen peroxide (Tortor, 2003) is also used to enhance the reaction speed and complete digestion. Most laboratories have eliminated the use of $HClO_4$ due to risk of explosion. Wet digestion can be carried out in open vessels, in tubes, on a hot plate or in an aluminum-heating block or in closed vessels at elevated pressure (digestion bombs) with thermal or microwave heating.

The type of acid used in the preparation procedure can have important consequences in the measurement step. It is commonly known that in all atomic spectrometric techniques nitric

acid is the most desirable reagent. In spite of occasionally observed signal suppression in its presence (e.g.in ICP-OES), no severe analytical problems are encountered in practice with nitric acid at concentrations up to 10 %,sometimes higher, in all atomic spectrometric techniques as long as its concentration is similar in calibration and sample solutions. Hydrogen peroxide added in most mineralization procedures is also rarely responsible for analytical problems (Arruda, 2007).For the purpose of this study, wet digestion with nitric acid and Flame Atomic Absorption Spectroscopy (FAAS) were used to determine the concentration of heavy metals and metal impurities.

2.14.2. Contamination and Losses

The major problem in preparing samples for trace analysis is the risk of contamination. Contamination is associated with several probable causes, i.e. the grade of reagents used, sample storage container, steps of digestion or dilution of the sample and their previous history, and human intervention. Losses are a particularly significant problem in trace analysis. Container surfaces, for example, may present a significantly large area on which the analyte can be adsorbed. At higher levels, such a small absolute loss would have little effect on the concentration but at trace levels, a large proportion of the analyte may be stripped from the solution (Howard and Stathm, 1997).

During wet digestion, certain components of the sample can be lost, leading to the underestimation of particular elemental contents. Trace elements can be lost by adsorption to the vessel walls, volatilization, co-precipitation, and co-extraction. Although the exact nature of adsorption losses is unclear, it may be due to molecular and ionic interactions (Sawant, 1995).

2.15. Purification of salt

Independent farmers mostly carry out the salt production and only a small number of salt productions are conducted by commercially producing private companies. The salt production process in traditional method consists of solar evaporation, precipitation, and crystallization. The evaporation process may spend 7-10 days. After that, the evaporated seawater or brine lake water is transferred into the salt table for precipitation process. This process takes 10-15 days and the receipted saltwater flowed into the salt table for

crystallization process. The crystallization process will take 4-10 days relying on the weather (Korovessis and Lekkas, 2009).

The traditional method of salt production is relatively low in terms of productivity and quality. Usually the product contains sodium chloride (NaCl) and other impurities, i.e. magnesium, calcium, sulfate,etc. Hence, the development of salt production technology is needed to increase productivity and quality of salt product. Many researchers suggested that use of geomembrane and filtering-threaded technology could increase productivity and quality of salt product. Geomembrane technology is the method used to produce salt by coating the base of pond bed with geomembrane plastic. The main characteristics of geomembrane as a liner in salt ponds are economic value, durability, and resistance to any degradation such as biological, chemical and ultra violet (UV). The benefits of salt production through geomembrane technology are the productivity of salt increased, the evaporation process is shorter, the turnaround time is improved, the harvest and the quality of salt is improved and the long lifetime of geomembrane will reduce the preparation works (Suhendra, 2016). Filtering-threaded technology is the modified technology of salt production integrating geomembrane technology through the serial plots. The main principle of this technology is the evaporation process of seawater and brine lake water flowed through the serial plots in the salt tables. In addition, natural materials are added as filters to purify the brine water. The main advantages of implementing filtering-threaded technology are the color of salt product is white and pure, the purity of salt (NaCl) and price are higher than traditional process products (Susanto,et al., 2015).

2.15.1. Hydro extractor purification

In solar evaporating salt production from sea, Brine Lake or rock salt collected into a shallow pond to evaporate in the sun and this process is used in hot, sunny, dry places. The insoluble and some soluble impurities of the solution such as clay, sand, calcium and magnesium compounds settle at the bottom. Now the brine is allowed to flow into the next pond by gravity and calcium sulfate settles as evaporation continues. Then the brineis moved to the other pond and the salt starts to settle. The solution is allowed to move one more into pond before evaporation completed to prevent the settling of highly soluble

impurities such as magnesium sulfate and magnesium chloride. These substances may be collected for commercial purpose.

After evaporation completed, the salt is cooped by machine running to temporary railroad tracks laid on top of the layer of the salt. Now the salt will be washed by highly concentrated brine to wash out soluble impurities. Since the brine is highly concentrated, it cannot hold any more and the salt is washes not to contain impurities without dissolving the salt. The washed salt is removed from the brine and rinsed by small amount of fresh water and apply into huge stacks to drain for two or three months. In this stage the purity of salt reaches to 99.4% and can be used in different industries as input material. If high purity of salt is needed, it is rewashed and rinsed with fresh water, allowed to drain for one or two days. Finally the salt is dried in a hot air oven at 185^{o}C.The final product is about 99.8% pure salt and can be used for food processing (Adshed and Samuel , 1992).However in hydro extraction method Simple washing will remove some of the impurities by washing repeatedly but the more you wash, the more you lose.Conventional salt washing processes have typically an efficiency of 60% and salt losses of 10%. If such salt washing is employed in the saltworks, the "natural purification" continues, leading to an additional loss of some 5% of NaCl on the stockpile. Thus, the overall salt losses can be as high as 15% (Sedivy, 1996).

2.15.2. Chemical treatment purification

Crude salt can be produced from seawater, Brine Lake, and rock salt mining by the conventional solar evaporation process. During the solar salt production process, salt is crystallized from brine water. Most evaporation beds are made of soil and the brine is transferred from one bed to another bed by an open canal. The flow is achieved by gravity and maintaining differential levels at the two ends. Therefore, most of the time solar salt is contaminated with suspended solids throughout the process. $CaSO_4$and $MgSO_4$are identified as the main impurities of crude salt. With the excessive hydro attraction capacity, dried free flowing salt absorbs water because of these compounds (Feng, 2011).

Attractive chemical processes involve calcination which a thermal decomposition process and reactive precipitation. Chemical processes are conventionally applied in extraction of salts having similar chemical properties, which would make it difficult for high purity

extraction (Lee and Bauman, 1980). A research by Ninawe, et al., (2004) developed a process for the production of sodium chloride crystals from brine water contaminated by potassium chloride and sulphate ions. In their research, a calcium compound is added to brine to crystallize Glauberite ($Na_2CaSO_4)_2$, which is isolated. The resulting solution is then subjected to evaporation in order to crystallize sodium chloride which is then collected, and the mother liquor from the crystallization is subjected to cooling hence crystallization of Glaserite ($K_3Na(SO_4)_2$). Vohra, et al., (2004) developed a process for recovery of common salt, potassium chloride, concentrated magnesium chloride with enriched bromide, and high purity magnesia from brine in an integrated manner. Chirico, (1979) also presented a continuous process for the recovery of chemicals in saline water which involves converting the sulphates in the saline water feed to sodium sulphate. Separating and recovering in the oxide forms, essentially all of the magnesium and calcium from the saline water feed, preparation of sodium chloride fortified solution by mixing the feed with recycled sodium chloride, crystallizing and re- crystallizing, and then separating sodium chloride crystals in two evaporative crystallization processes.

Diyono et al, (2002) developed a process for the purification of crude salt from brine water. In their research, the improvement of public salt quality implemented by chemical treatment with addition of NaOH ranging from 0.50 to 3.00 grams, Na_2CO_3, and $BaCl_2$ranging from 0.50 to 3.5 grams with the step size of 0.50 gram. It could remove the concentration of impure ion such as Calcium (Ca^{2+}), Magnesium (Mg^{2+}) and sulphate (SO_4^{2-}) ions in brine solution through ionic reaction. Hence, the method could also increase the purity of Sodium Chloride (NaCl) content from 92.86% to 99.57% (dry base).

The refined salt was produced from crude solar salt by a Physico-chemical treatment method, which consists of precipitation and filtration. In this process, crude salt is dissolved by water and used as a raw material. In most brine process, multiple-effect evaporators with three or more closed metal conical bottoms are used. First, the solution is filtered to remove suspended and insoluble impurities. Then the filtrate is treated chemically to remove calcium and magnesium comkpounds. Then the impurities such as $MgSO_4$ and $CaSO_4$will be removed by precipitation reaction. After the reaction is completed $Mg(OH)_2$,$CaCO_3$ and $BaSO_4$ fill at the bottom of the cylinder and will be removed. The pure

brine in the first cylinder flows through the tube heated by steam. Now the brine is heated and some amount of water vaporizes which is used to heat the next cylinder. Then the steam from the second cylinder used to heat the third cylinder and so on. In each cylinder, condensation of the steam cases to drop the pressure and facilitates boiling of the brine at lower temperature. Salt is removed from the bottom of the cylinders as tick slurry. Then the slurry is filtered to remove excess brine, dried and passed through screen to separate the salt by particle size. The salt produced in this process is called vacuum pan salt and consists of small cubic crystals.

Brine may also process in a grainer. The brine is filtered and chemically purified. Then it pumped into a long open pan heated by a steam running through the pipe immersed in the brine. The brine is heated to a temperature slightly below the boiling point and flakes of salt are started to be form on the surface as it evaporates. Usually temperature around $90^{o}C$ is estimated to be sufficient for this process. When the operating temperature is low, large flakes are formed and high temperature produces small flakes. The flakes grow until they settle at the bottom of the pan where they are collected and dried. Grain salt consists of small flakes rather than cubes and is preferred for certain uses in food processing. Sometimes Alberger process is used, in which partially vaporized brine a vacuum evaporator is transferred to the grainer. This process produces a mixture of flakes and cubes, at this point multi-purpose salt is ready to be packed in bags or boxes and shipped to the consumer (Adshed and Samuel, 1992).The highest recommended standard of quality is vacuum salt. Usually, vacuum salt is produced from Brine Lake, underground mining of rock salt deposits and chemically purified. The quality of vacuum salt in this process will attain up to 99.95% purity.

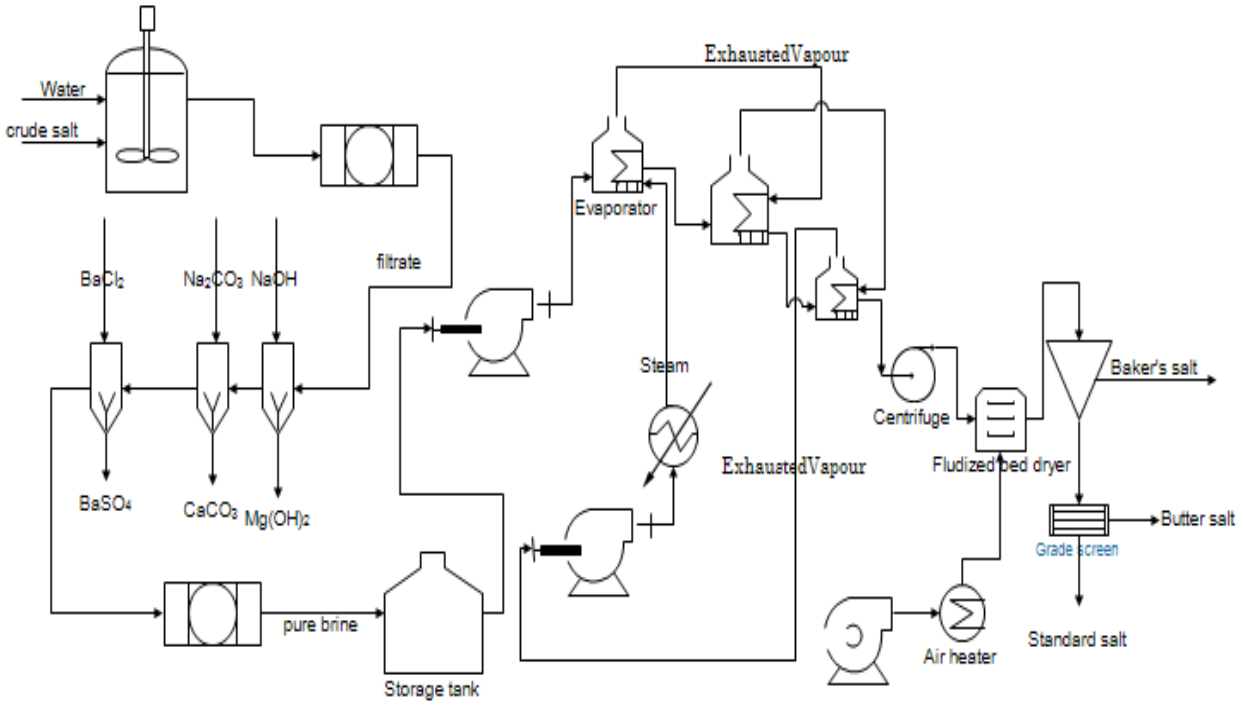

Figure 2.1:Chemical treatment and recrystallization of salt

2.15.3. Recrystallization

After purification, the resultant pure brine is evaporated in a triple-effect plant. The first effect operates at close to atmospheric pressure and the third at near vacuum, so the boiling point of the solution is lowered as it passes through the plant. The brine in each evaporator is drawn of through a loop and passed through a steam-heated heat exchanger which causes the vapour from the brine to evaporate and salt crystals to form in the supersaturated solution. By circulating the boiling brine, minute seed crystals are carried in suspension until they grow to a size and weight that makes them fall to the stationary section of the conical base. Vapour exhausted from the first effect is carried over to the second effect heat exchanger and in turn from the second to the third effect heat exchanger, thus giving the most economical heating.Vapour from the third effect passes to a direct contact condenser and is extracted in the cooling tower water circuit. Condensate from the heat exchangers is fresh water suitable for feeding boilers or for return to the stockpile to make more brine. Over time, soluble impurities build up in the evaporators, and eventually

would contaminate the salt crystals. To prevent this, once certain levels are reached the brine is purged and, in addition, the outgoing crystals are washed in clean incoming brine.

Salt crystals, which collect in the conical base of the evaporator,are removed as slurry and aredried by centrifuge and a fluid bed drier. As a protection against the effects of high humidity, the salt is given a thin coating of anti-caking agent before being passed through the fluid bed drier. The salt from this drier is pure dried vacuum salt (PDV salt) which appears as small, cubic, white crystals (Fergusson, 1982).

3.MATERIALS AND METHODS

3.1. Sampling

About 5 kg of each representative samples of salt were collected from commercial salt producer companies in Lake Afdera and Dobi, which are located in Afar regional state, Ethiopian.

3.2. Methods

3.2.1.Sample preparation

For further increasing the quality of salt, the crude salt samples were underwent various processing in the course of their preparation for purification. The collected salt were measured and dried in an oven to know the moisture content of the salt. Then theywere dissolved by distilled water and the solutions were filtered to determine the amount of solid suspended and insoluble impurities. Hence, the sample solutions were ready for the treatment process.

3.2.2.Analysis of moisture content

Moisture content was determined by oven drying method following the procedure (AOAC1999).For analysis of moisture content, 100 g of each salt sample were weighed and putted in a dish. Then the samples were dried in an oven at 110°C for 1 hour. The dishesweredetached from the oven, cooled, and measured for their weights. The process was repeateduntila constant weight was observed and the moisture was determined by equation 3.1.

$$\text{Moisture content of salt percent by mass} = \frac{W0-W1}{W0} * 100\% \quad (3.1)$$

Where; W_0=mass in g of crude salt before drying

W_1 = mass in g of crude salt after drying in an oven.

The moisture contents were expressed in g/100 g sample and the other values were reported on dry basis.

3.2.3. Analysis of water insoluble impurities

After determining the moisture content, each salt samples were dissolved by 2L of distilled water .Then the solutions were filtered by using vacuum pump (model- NEUBERGER N840), filter funnel, and filter paper with medium pore size of 15-20µm. The amounts of solid suspended and insoluble impurities were calculated.

$$\text{Insoluble Matter in water (\%wt.)} = \frac{W01 - W02}{W01} 100\% \quad (3.2)$$

Where; W_{01}=ass of crude salt before filtration in dry basis

W_{02}=mass of crude salt after filtration in dry basis

3.2.4. Determination pH of salt

For pH determination, about 50 g of crude salt samples were dissolved by 200ml of distilled water and the pH values were determined by using pH meter (model-JENWAY 3505).

3.2.5. Determination of Alkalinity

Alkalinity as Sodium carbonate was determined by (AOAC 1998). The flasks were washed by carbon dioxide free distilled water. About 20g of each samples of salt were weighed and dissolved in one liter of double de-ionized water and filtered the solution. Then, the residues were discarded and 50ml of the filtrates were titrated with 0.1N hydrochloric acid using methyl orange as an indicator.

3.6. Compositional analysis of salt of Afdera and Dobi

The two crude salts chemical composition were determined by Association of Official Analytical Chemists (AOAC, 2005) methods. The amount of soluble impurities such as $CaSO_4$, and $MgSO_4$, were analyzed by precipitating using sodium hydroxide, sodium carbonate, and barium chloride.

3.6.1. Determination of SO_4^{2-}

Gravimetric analysis is used to determine sulphate and chloride contents of samples. This process is based on the measurement of the mass or volume of a substance of well-known composition, which is chemically correlated to the analyte. Gravimetric analysis includes precipitation, volatilization, and electrode position methods. In precipitation, gravimetry of the analyte is carried out by the use of inorganic or organic precipitating agents. The two

common inorganic precipitating agents are silver nitrate, which is used to precipitate halide ions such as chloride, and barium chloride for precipitating sulphate ion.

To determine the amount of SO_4^{2-} gravimetric precipitation was used, about 25 g of sampleswere dissolved by 250ml of distilled water and transferred to a Pyrex beaker and the pH of the solutions were below three by adjusting using HCl solution. Then 10ml equal concentration of $BaCl_2$ solution was added to the salt solution, while the solutions boiled stirred by magnetic stirrer for about 2 hour at 90°C.Then the precipitates were dried in an oven at 110°C until constant weight of $BaSO_4$ was obtained.

3.6.2. Determination of chloride

About 0.25g of the salt samples were dissolved by 100ml of distilled water and filtered. After filtration, 25 ml of each salt solution were poured into volumetric flask and 1 ml of potassium chromate indicator was added. Then the samples titrated with 0.1M silver nitrate solution. The silver chloride that forms are white precipitates, the chromate indicator initially would give the cloudy solution a faint lemon-yellow color. The endpoint of the titration was identified as the first appearance of a red-brown color of silver chromate ions leads to formation of silver chloride precipitate.

3.6.3. Analysis of metals

Concentration of Zn, Pb, Cd, Fe,Cu,Mg and Ca were determined in salt samples. The analysis of metals in salt was conducted by using Atomic Absorption Spectrophotometer (model-ZEE nit 700P). The operating conditions for analysis by FAAS were seated and Calibration of the instrument was carried out with a range of standard solution.

However, in the use of FAAS for analysis trace metal, optimization of the operating condition is very crucial (Ebdon, 1998). To this effect, the wavelength, lamp current, burner alignment and split width were optimized for each element. Standardof Stock solution, 1000 mg/Liter in 2 % HNO_3 for each of the selected metals i.e., Fe, Zn, Pb, Cd,Cu,Mg,and Cawere used for making intermediate standard solutions each of 10 mg/L. Four standard solutions with different concentration were prepared by diluting the 10 mg/L using deionized water.

Four point calibrations were established by introducing the prepared working standard solutions in FAAS. Immediately after calibration of the instrument, the reagent blanks and samples were aspirated into the flame atomic absorption spectrophotometer(FAAS) consecutively and a minimum of three replicates were taken for each sample and each blank solution and the average value of the concentration signal was used for later calculations.

3.6.4. Method Validation (Recovery test)

The digestion method and FAAS analysis were validated by measuring the recovery of Zn, Pb, Cd, Fe and Cu spiked to salt samples. The known volume and concentration of standard solution were employed on the samples in order to determine recovery. The volume of 1.5 ml for Zn, Pb, Cu, Fe, Mg,Ca, and Cd were added to 1gm of salt. The spiked samples werethen digested in the same way as salt sample. The final volumes of the digestion were diluted to 50ml and run on FAAS and metal contents determined from the calibration curve.

The amount of spiked metals recovered after the digestion of spiked samples was used to calculate percentage recovery using (Burns, et al., 2002) formula given by equation 3.3.

$$\text{Recovery} = \frac{conc.spiked\ sample - unspiked\ sample}{conc.analyte\ added(spiked)} \times 100\% \quad (3.3)$$

The recovery percentages of spiked salt sample were obtained for metals under investigation varied between 94.6% and 100%.The results are in acceptable range which is mostly no less than 70% and no greater than 125% (Machado and Griffith, 2005) and which revealed that the digestion method and the FAAS analysis were reliable.

3.6.5. Method Detection Limit (MDL)

Based on EPA of America, MDL is the minimum measured substance concentration that can be recorded using 99% confidence level. Method detection limit (MDL) is the concentration that gives a signal 3*SD of the blank or background signal (Regassa, 2007). In this case, three standard blank solutions were digested and three replicates of readings were used for each sample.

$$\text{Method DetectionLimit} = \frac{Standard\ conc. * 3Std.Dev}{Mean\ \ Std\ conc.} \quad (3.4)$$

3.7. Experimental Design

The design of the experiments was carried out in this work because the percentage purity of salt is functionally related mainly to the interaction effect of factors: concentration of sodium hydroxide, sodium carbonate, barium chloride, reaction time, and reaction temperature. The experiments were conducted with the aid of statistical experimental design. By using the Central Composite, design (CCD) of Response Surface Methodology (RSM) with face centered central composite design (FCCCD) was employed to optimize purification of salt using physic-chemical treatment process.

For the two salt samples, the levels used for the experimental factors considered are shown in table 3.1 and 3.2. Using two levels of the five factors with two-center point, twenty -three (23) runs of experiments were carried out.

Table 3.1: Experimental factors and levels for salt sample of Afdera

Factors	Unit	Levels	
		-1	1
Sodium hydroxide	g	1	3
Sodium carbonate	g	1	3
Barium chloride	g	0.2	0.27
Reaction temperature	ºC	25	45
Reaction time	Min	20	60

Table 3.2: Experimental factors and levels for salt sample of Dobi

Factors	Unit	Levels	
		-1	1
Sodium hydroxide	g	1	3
Sodium carbonate	g	1	3
Barium chloride	g	4.2	5.5
Reaction temperature	ºC	25	45
Reaction time	Min	20	60

3.7.1. Optimization of Process Variables using Response Surface Methodology

Response surface methodology (RSM) is a very effective mathematical and statistical technique to identify the optimal conditions as well as to determine the effect of process parameters and the interaction of input variables (Wang, 2012). It is considered as the faster and less laborious technique as it requires minimum experimental runs for optimizing multiple independent variables (Sharif, 2013). In Response Surface Methodology, several factors are simultaneously varied. The multivariate approach reduces the number of experiments, improves statistical interpretation possibilities, and evaluates the relative significance of several affecting factors even in the presence of complex interactions. It is employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariable equations simultaneously.

3.7.2. Statistical analysis

The experimental plan was designed and the results obtained were analyzed using statistical experimental design. An analysis of variance (ANOVA) and R^2 (coefficient of determination) statistic was used to check the adequacy of the developed model. F-test was used to test the variation of the data around the fitted model (lack of fit). The significance level was stated at 95%, with p-value 0.05. The optimal process variables for purification of salt were obtained using the numerical optimization function.

3.8. Chemical treatment purification of salt

3.8.1. Purification process

Experimental work was conducted by using chemical treatment process. The chemicals that used in this process were sodium hydroxide, sodium carbonate, and barium chloride. The result from the purification process depends on the rate of reaction between the chemical used to treat salt impurities and its precipitation.

About 200g of crude salt was dissolved in 400ml distilled water, stirred to achieve saturation condition, and separated from the suspended insoluble solid polluter. Then 100 ml of the solutions were added into a measuring cylinder as a sample of brine solution. Afterwards, sodium hydroxide was added to the brine solutions at different weights and

stirred gently. From the reaction, insoluble precipitates were settled at the bottom of the cylinder. The precipitates were filtrated, dried in a hot oven, and weighed, while the filtrates were used to the next process (Monod, 1991). The second step was addition of sodium carbonate at various weights was implemented to the filtrate and then carefully stirred. Similarly, from the reaction insoluble precipitates were settled at the bottom of the cylinder. The precipitated impurities were filtrated, dried in an oven and measured.Then the filtrate continued to the succeeding process. The last settling was conducted by adding barium chloride at various weights, followed by stirring. The precipitated sediments were then filtrated and measured, while the filtrates were analyzed as a product. Schematically, the purification of crude saltis presented in the following figure.

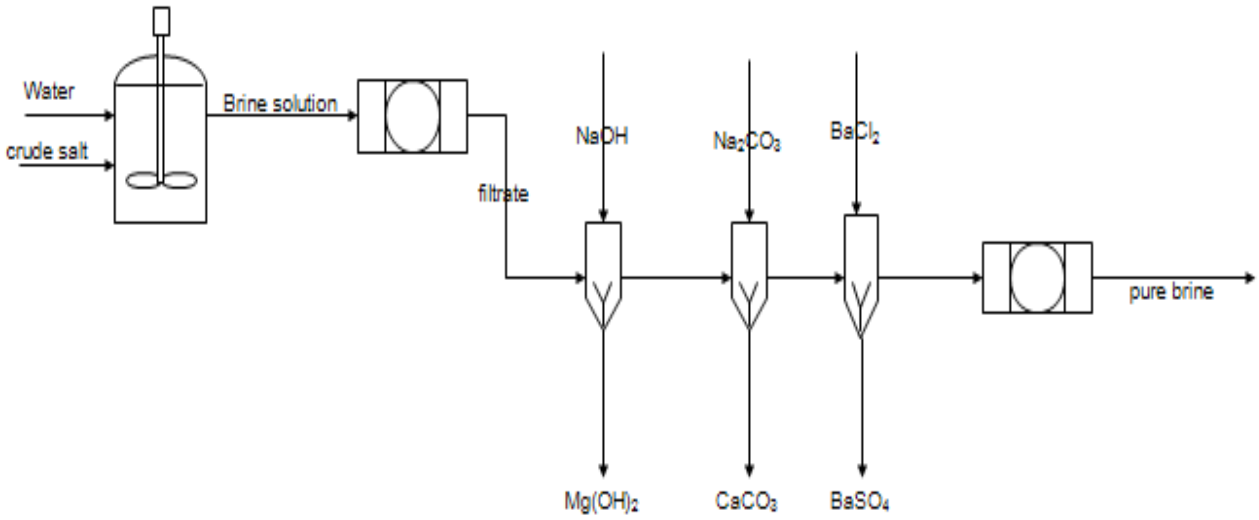

Figure 3.1: Schematic Diagram of Crude Salt Purification

The chemical treatment purification process was takes place with the addition of NaOH, Na_2CO_3, and $BaCl_2$in the above three series mixer.Sudharto(2002) stated the possible chemical treatment reaction as follow:

The chemical reaction for addition of NaOH;

$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$

$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$

$CaCl_2 + NaOH \rightarrow Ca(OH)_2 + 2NaCl$

The chemical reaction for addition of Na_2CO_3;

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$

$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + NaOH$

The chemical reaction for addition of $BaCl_2$;

$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

4. RESULT AND DISCUSSION

The two salt samples wereanalyzed in the laboratory to characterize, so as to the degree of impurities and their contents. According to the results summarized in table 4.1, the contents for salt sample from Afdera were 96.6 ± 0.21 for NaCl, 1.09± 0.501 for Loss of mass, 1.05±0.08 for matter insoluble, 1.08 ± 0.00 for SO_4, 1.60 ± 0.38 for alkalinity, 7.8± 0.10 for pH. Similarly, the contents for sample from Dobi were 91.21± 0.37 for NaCl, 1.25 ± 0.074 for Loss of mass, 1.75 ± 0.01 for matter insoluble, 8.12 ± 0.05 for SO_4, 1.80 ± 0.02 for alkalinity, and 7.9±0.04 for pH. .

Table 4.1: Essential composition of salt samples collected from Afdera and Dobi

Analysis	Sample name		ES/Codex
	Afdera	Dobi	
Moisture content (%wt.)	1.09± 0.501	1.25±0.074	0.5-4
Water Insoluble mater (%wt.)	1.05±0.08	1.75±0.01	0.2-1
Ph	7.8± 0.10	7.9±0.04	8
Alkalinity (%wt.)	1.60± 0.38	1.80±0.02	0.2
Sodium Chloride content (%wt.)	96.60± 0.21	91.21±0.37	96-98
Sulphate content (%wt.)	1.08± 0.00	8.12±0.05	0.5

4.1. Sodium chloride

The results summarized in Table 4.1 shows that salt sample from Afdera had the purity level of 96.6 % and sample from Dobi had 91.21% NaCl. The Ethiopian standards of specification (ES) stated that the purity level of iodized table salt should not be less than 98%.According to CODEX standard (2001); food grade salt can be obtained from the sea, the lake underground rock salt deposits or from natural brine. The content of NaCl shall not be less than 97% on a dry matter basis, exclusikve of additives.The salt samples produced from Lake Afdera and Dobi through solar evaporation were failed to agree the ES and Codex legislations.

The quality of Australian and Mexican solar salt continues to set the industry standard for internationally traded salt and the quality of the salt varies from 99 to 99.95% NaCl (Mannar and Dunn, 1995).A study in Sir Lanka shows that a purity level can be achieved from 98.023 to 99.604 by physic-chemical treatment process(Rathnayaka,2014). When the purity of both salt samples was compared with salt produced in Australia, Mexico, and Sir Lanka, it was very low.Therefore, the quality of both samples should be improved using physic-chemical treatment process. .

4.2. Moisture Content

Table 4.1 shows that the moisture content of salt sample from Afdera and Dobi were 1.09 and 1.25% respectively. The Ethiopian standard of specification states that the maximum allowable limit of loss of mass percentage (%wt.) at 110^{o}C for table salt and common salt should be 0.2 and 4 respectively. This indicates that both salt samples were agreed with the specification of common salt but two of them failed to agree the table salt standard of specification stated by ES and Codex.

A study in Sir Lanka shows that Moisture Content of the crude salts varies from 3.46 to 7.35% and 0.7294% for refined solar salt (Rathnayaka, 2014). The crude salt produced in Ethiopia have better quality relatively to crude salt produced in Sir Lanka and less than refined salt. The moisture contained in the salt can be due to the hygroscopic nature of the salt, which absorbs moisture from the surrounding in addition, the producers might not remove all of the moisture of the salt.

4.3. Matter insoluble in water

Matter in soluble in water in the two salt sample was analyzed by dissolving the salt, filtering, drying and measuring of the weight of the precipitate. Table 4.1 shows salt sample from Afdera contains 1.02% and salt sample from Dobi contains 1.75%.The ES specifies mater insoluble in iodized table salt and iodized common salt should not exceed from 0.2 and 1% respectively. Both salt samples do not meet the ES specification.

Kirabira (2013) reported that 0.001% of insoluble matter in salt, which processed chemically. Salts, which are obtained by solar evaporation in Uganda, contain 2.5 %

insoluble matter. The purity of the salt produced from the two brine lakes is lower than chemically processed salt. When comparing to the solar salt produced in Uganda, they have relatively better quality. This is due to the reason that subsequent blowing of wind towards the lakes and artificial evaporating ponds, which contains solid suspended matter, volcanic ashes and dust particles.

4.4. pH of salt

Table 4.1 shows the pH of the salt samples was not significantly different. The salt sample from Afdera was 7.8, while the salt sample from Dobi is 7.9. The ES the maximum allowable limit for pH of salt is eight. The African standard also specifies the pH limit of salt should be 7-8, (AOS, 2012). Thus, salt samples from Afdera and Dobi agreed with the African and the ES standard of salt pH specification.

In a study of eight different refined samples of iodized common salt and table salt from Afdera and Dobi, the pH of the salt varies from 7.85 to 8.75,(Henok,2016).Hence, the pH of both samples was agreed with the literature.

4.5. Sulphate

Table 4.1 shows the concentration of SO_4^{2-} in the two salt samples of Afdera and Dobi were 1.08 and 8.12%wt respectively. This indicates that the sulphate content of both samples were higher than maximum allowable concentration of Ethiopian standards (0.5%wt.).

The sulphate contents of salt produced from different source and methods in Mexico and Australia indicates that, Rock salt has 0.2to 1.3 %wt., refined salt 0.2%wt., vacuum salt 0.2%wt and pure vacuum evaporated salt 0.04%wt.The amount of sulphate in salt sample from Afdera wasagreed with only rock salt quality produced in Mexico and Australia but salt sample from Dobi totally failed to agree.

Sulphate generally present in the salt as impurity and does not cause any health problem, but high concentration acts as a purgative (Kumar, 2001). The excess consumption of sulphate results in cathartic effects, due to purgation of the alimentary canal. However, with time human appear to be able to adapt to higher sulphate concentrations. Dehydration has also been reported as a common side effect following the ingestion of large amounts of

sulphate (Müller-Lissner, 2005).Therefore, the salt samples should be purified to meet both the industrial and human consumption requirements.

4.6. Alkalinity

Table 4.1 shows the alkalinity of salt sample from Afdera was 1.6%wt And from Dobi was 1.8%wt. The Ethiopian standard specifies that, alkalinity of iodized common salt and iodized table salt to be 0.2(wt.%). The results indicate that, the alkalinity of both salt samples were significantly higher than the ES standard of specification.

The alkalinity of edible salt which are processed in different methods in Uganda showed 1.3%, 1% and 0.1298 % respectively (Kirabira,et al., 2013).The alkalinity of both samples were higher that the edible salt processed in Uganda using different methods.

Absorption of $NaHCO_3$ is known to cause alkalosis (AL-Saffar, 2012). The acid-base disturbance is usually transient in individuals with normal renal function, as the base excess will be rapidly excreted. However, the urinary pH can be elevated affecting tubular reabsorption and urinary elimination of weak acids and bases (AL-Saffar, 2012). The minimum dose causing adverse effects will vary strongly according to age and health condition (Jaeger, 1987).

4.7. Metals and heavy metals

Heavy metals are natural constituents of lake waters, and some of the essential ones are present at low concentrations (Wu, 2007). Researchers reported the presence of trace elements in the salt (Haddy, 2006; Steinhauser et al.,2006). Determinations of trace metal ions in refined and non refined salts have been performed by various researchers around the world (El Ghawi and Al-Sadeq, 2006; Makhoni and Alemasova, 1992; Chimilenko and Baklanov, 2000; Boppel, 1976; Ali, 1999; Amorim and Ferreira 2005; sovylak, et al., 2003).Table 4.2 shows the Heavy metals concentration of Afdera and Dobi salt samples. In each experiment, the result was recorded by three replicate and reported as mean ± standard deviation.

Table 4.2: values of metal and heavy metal impurities in the two salt samples

Metal impurities	Afdera	Dobi	ES/Codex
Cadmium(mg/kg)	N.D	N.D	0.5 mg/kg
Calcium(g/kg)	0.2960±0.05^{f}	0.6357±0.07^{g}	0.5g/kg
Copper(mg/kg)	0.1145±0.00^{a}	0.0472±0.00^{b}	2 mg/kg
Iron(mg/kg)	2.0554 ±0.12^{c}	2.6342 ±0.12^{c}	10mg/kg
Lead(mg/kg)	0.0144±0.00^{d}	0.0139±0.01^{d}	2 mg/kg
Magnesium(g/kg)	0.8189±0.026^{h}	0.6663±0.03^{i}	0.5g/kg
Zinc(mg/kg)	0.0175±0.12^{e}	0.0139±0.25^{e}	14mg/kg

N.D =Not detected. Detection limit of Cd is 0.012 ppm

$^{A-i}$, Means within the same raw of different letterers are significantly different at ($p<0.05$).

Mean± SD=mean± standard deviation.

4.7.1. Cadmium

Table 4.2 shows the metal and heavy metals content of analyzed crude salt samples. The Content of cadmium was below instrumental detection limits, perhaps due to low loading of the contaminant into the lakes.

A according to the Codex legislation, the maximum tolerated amounts of Cd in salt is 0.5 µg/g. The mean concentration of Cd found in table salt in Iran was 0.024µg/g (Abdol Majid, 2010).

4.7.2. Calcium

The concentration of Ca in the salt samples of Afdera was 0.3g/kg., and sample from Dobi was 0.6g/kg. This indicates that sample from Afdera agreed but sample from Dobi was failed to agree with the maximum allowable concentration limit stated by the Ethiopian standards (0.5g/kg).

Chemical analyses in dry basis of different types of salt in Mexico and Australia, the concentration of calcium vary from 0.002 to 1.1% wt. Even though, the concentrations of calcium in both samples was found in the range of different types of salt in Mexico and

Australia, the salt sample from Dobi was failed to agree with the ES. Therefore,they should be further purified to increase the purity level of the salt.

4.7.3. Copper

The two salt samples were analyzed for determination of copper content. Table 4.2 shows that, the concentration of copper in the samples from Afdera and Dobi was 0.1145mg/Kg and 0.0472 mg/Kg respectively.

The Ethiopian standards of heavy metal Contaminants in iodized common and table salt, limits concentration of copper should be 2mg/kg. Therefore, the concentration of copper in both salt samples was agreed with the ES specification.

From the Dominion Salt's Analytical data in New Zealand, unrefined Solar Sea Salt with no additives contains 99% NaCl and 0.32mg/kg of copper. A typical specification for raw salt and industrial salt recovered from the Dead Sea brines contains 2mg/kg of copper (Sabatin, 2000). Hence, the quality of salt sample from Afdera and Dobi were better than the New Zealand, unrefined Solar Sea Salt. In addition,Cu is an essential element at lower concentration while, exposed for long term or high concentration can cause chronic diseases like nervous system disorder, liver, and kidney failure. (Bent and Bohm, 1995).

4.7.4. Iron

Table 4.2 shows the amount of iron present in both salt samples, sample from Afdera was 2.0554 mg/kg, and from Dobi was 2.6342 mg/kg. The result shows that the difference was not significant. Both salt samples also meet salt quality requirement of the country which is10 mg/kg.

Analytical data for Dominion Salt's (New Zealand) unrefined Solar Sea Salt with no additives contains 99% NaCl and 22.4mg/kg of iron. A typical specification for raw salt and industrial salt recovered from the Dead Sea brines contains 2.5mg/kg of iron (Sabatin, 2000). The iron content of the two salt samples was almost similar to raw salt and industrial salt recovered from Dead Sea brine.

Iron at low concentration is needed for enzyme activity (Salem, 2000) but at high concentration, it accumulates in muscle, liver and affects brain and central nervous system (Luqueno,et al., 2013).

4.7.5. Lead

Table 4.2 shows in analyzed samples, the concentration of Pb of both samples were almost similar. The concentration of Pb in sample from Afdera was 0.0144mg/kg and in salt sample from Dobi was 0.0139mg/kg. According to Codex legislation, the maximum tolerated amounts of Pb in salt is 2 µg/g. Similarly Ethiopian standards of heavy metal Contaminants in iodized common and table salt the maximum limit of lead is 2mg/kg. The lead content of both samples were agreed the ES as well as codex legislation limit.

Recently, the heavy metal contents of refined and unrefined table salts from Turkey, Egypt and Greece have been studied (Soylak,et al., 2008). According to the reported data, the concentration of Pb in table salt was between 0.54-1.64 µg/ g. Concentrations of Pb in table salts consumed in Brazil reported to be in the range of 0.03-0.1 µg/g (Amorim and Ferrerira , 2005). The mean concentration of Pb found in table salt in Iran was 0.438µg/g (Abdol Majid, 2010). This indicates that the concentration of lead in salt sample from Afdera and Dobi were lower than the concentration of lead in refined and unrefined table salts from Turkey, Egypt and Greece, table salts consumed in Brazil and Iran.

Lead is one of common heavy metal in general beyond desirable limit is metabolic poison and enzyme inhibitor (Gebrekidan and Samuel, 2011).

4.7.6. Magnesium

Table 4.2 shows in the analyzed samples, from Afdera the concentration of Mg was 0.8189g/kg while in salt sample from Dobi it was 0.6663g/kg. The Ethiopian Standard Specification for both iodized Common and table salts states that the concentration of Mg should not exceed 0.5mg/kg. The samples did not meet the ES specification.

Salt produced from different source and different methods in Mexico and Australia contains 0.0001 to 0.17% Wt. Mg. This indicates that the concentrations of Mg in both salt samples were found within the range of salt produced from different sources and methods in Mexico and Australia. However,the concentration of magnesium in both samples were higher than the ES, the samples should be chemically treated.

Mg is associated with abnormal irritability of muscle, convulsions, and excess Mg with depression of the central nervous system (Budavari, 1997). Magnesium also increases moisture content of the salt (Kelly, 1953).Therefore; both salt samples should undergo chemical treatment purification.

4.7.7. Zinc

Table 4.2 shows the concentration of zinc in the analyzed sample of Afdera was 0.0175mg/kg and in sample from Dobi was 0.0139mg/kg. As the result shows zinc content of both salt sample were agreed with the maximum limit of ES and codex (14mg/kg).

A study conducted in Shiraz reported that the concentration of zinc in recrystallized and washed samples were 0.34µg/g and 0.37 µg/g respectively. Another study in Tehran reported that Zinc content of edible salt was found to be 6.5µg/g (Pourgheysari,et al., 2012).The Concentration of zinc in edible and industrial salt of Khewra in Pakistan is 4.10mg/kg and 6.00mg/kg respectively.

When comparing to recrystallized and washed samples in Shiraz, edible salt zinc content reported in Tehran, and edible and industrial salt of Khewra in Pakistan, the two solar salt samples were more appreciable.

Zinc is needed in lower concentration for acting as catalyst in enzyme activity of living system but it accumulates in muscle and liver (Luqueno,et al., 2013). The chronic health effects of Zn include cancer, birth defects, organ damage, disorders of the nervous system and damage to the immune system (USGAO, 2000). K2

4.8. Analysis of salt purification

The purification process of salt was carried out using 500ml flask. The purity of salt from the purification processes was determined from titration is calculated by assuming complete conversion of the limiting reactant barium chloride, multiplied by 100.

$$\text{Purity of salt (\%wt.)} = \frac{V*N*58.44}{mass\ of\ sample} * 100 \qquad (4.1)$$

Where: V = volume of standard silver nitrate

N = normality of standard silver nitrate

The statistical analysis and experimental results for salt sample of Afdera and Dobi are shown in table 4.3 and 4.4 respectively.

Table 4.3: Experimental result for salt sample of Afdera

Run	Factors					Mass of precipitates			Titrant	purity of salt
	NaOH	Na_2CO_3	$BaCl_2$	Temperature	Time	$Mg(OH)_2$	$CaCO_3$	$BaSO_4$	$AgNO_3$	
	g	g	g	°C	Min	g	g	g	ml	%wt.
1	2.00	2.00	0.24	35.00	76.42	0.161	0.085	0.205	16.74	99.16
2	2.00	2.00	0.24	35.00	40.00	0.153	0.11	0.254	16.79	99.47
3	2.00	2.00	0.24	35.00	40.00	0.153	0.102	0.254	16.78	99.42
4	2.00	3.82	0.24	35.00	40.00	0.187	0.25	0.24	16.86	99.89
5	2.00	0.18	0.24	35.00	40.00	0.124	0.005	0.161	16.49	97.7
6	3.00	3.00	0.20	45.00	20.00	0.187	0.164	0.194	16.62	98.45
7	0.18	2.00	0.24	35.00	40.00	0.005	0.13	0.309	16.72	99.05
8	2.00	2.00	0.24	35.00	3.58	0.119	0.083	0.224	16.53	97.9
9	2.00	2.00	0.30	35.00	40.00	0.165	0.0718	0.292	16.86	99.85
10	3.82	2.00	0.24	35.00	40.00	0.246	0.097	0.324	16.87	99.89
11	2.00	2.00	0.24	53.21	40.00	0.119	0.091	0.227	16.70	98.91
12	1.00	3.00	0.20	45.00	60.00	0.026	0.131	0.3	16.74	99.14
13	1.00	3.00	0.27	25.00	60.00	0.063	0.172	0.239	16.75	99.2
14	3.00	1.00	0.27	45.00	20.00	0.184	0.038	0.255	16.76	99.26
15	3.00	1.00	0.27	25.00	60.00	0.196	0.033	0.214	16.57	98.15
16	1.00	1.00	0.20	25.00	20.00	0.111	0.054	0.177	16.50	97.73
17	1.00	3.00	0.27	45.00	20.00	0.086	0.1801	0.235	16.77	99.35
18	3.00	3.00	0.20	25.00	60.00	0.199	0.19	0.188	16.46	97.48
19	2.00	2.00	0.17	35.00	40.00	0.165	0.137	0.292	16.82	99.59
20	1.00	1.00	0.27	45.00	60.00	0.06	0.041	0.381	16.77	99.34
21	3.00	1.00	0.20	45.00	60.00	0.16	0.027	0.339	16.80	99.5
22	2.00	2.00	0.24	16.79	40.00	0.084	0.089	0.194	16.51	97.79
23	3.00	3.00	0.27	25.00	20.00	0.189	0.18	0.243	16.83	99.69

Table 4.4: Experimental result for salt sample of Dobi

Run	Factors					Mass of Precipitates			titrant	Purity of salt
	NaOH	Na_2CO_3	$BaCl_2$	Temperature	Time	$Mg(OH)_2$	$CaCO_3$	$BaSO_4$	$AgNO_3$	
	G	g	g	^0C	Min	g	g	g	ml	(%wt.)
1	2.00	2.00	4.85	16.79	40.00	0.044	0.03	4.669	16.68	98.83
2	1.00	3.00	4.20	45.00	60.00	0.043	0.086	4.645	16.79	99.45
3	3.00	3.00	4.20	45.00	20.00	0.089	0.062	4.384	16.49	97.65
4	2.00	2.00	4.85	35.00	3.58	0.052	0.028	4.749	16.70	98.94
5	3.00	1.00	4.20	45.00	60.00	0.099	0.121	4.41	16.52	97.88
6	2.00	2.00	3.67	35.00	40.00	0.074	0.092	4.355	16.32	96.67
7	3.00	3.00	4.20	25.00	60.00	0.097	0.057	4.601	16.80	99.5
8	3.00	1.00	5.50	45.00	20.00	0.121	0.028	5.707	16.86	99.86
9	2.00	2.00	4.85	35.00	76.42	0.065	0.057	4.347	16.87	99.9
10	3.82	2.00	4.85	35.00	40.00	0.131	0.03	4.79	16.88	99.99
11	0.18	2.00	4.85	35.00	40.00	0.027	0.074	5.166	16.77	99.34
12	2.00	2.00	4.85	53.21	40.00	0.079	0.045	4.989	16.85	99.8
13	2.00	2.00	4.85	35.00	40.00	0.064	0.041	4.608	16.58	98.23
14	2.00	0.18	4.85	35.00	40.00	0.079	0.073	4.598	16.26	96.29
15	3.00	3.00	5.50	25.00	20.00	0.092	0.179	5.275	16.84	99.75
16	2.00	2.00	6.03	35.00	40.00	0.072	0.029	5.742	16.86	99.86
17	1.00	1.00	4.20	25.00	20.00	0.043	0.113	4.594	16.78	99.37
18	3.00	1.00	5.50	25.00	60.00	0.093	0.07	5.489	16.77	99.35
19	1.00	3.00	5.50	45.00	20.00	0.03	0.07	5.36	16.84	99.74
20	1.00	1.00	5.50	45.00	60.00	0.047	0.017	5.285	16.84	99.72
21	1.00	3.00	5.50	25.00	60.00	0.038	0.043	5.012	16.86	99.87
22	2.00	3.82	4.85	35.00	40.00	0.062	0.192	4.811	16.78	99.41
23	2.00	2.00	4.85	35.00	40.00	0.065	0.038	4.596	16.58	98.18

4.9. Statistical analysis on factors affecting purification of salt of Afdera

The central composite design conditions and response, and the statistical analysis of the ANOVA for salt sample from Afdera are given in Tables 4.5 and 4.6 respectively. The multiple regression coefficients were obtained by employing a least square technique to predict a quadratic polynomial model for percentage purity of salt (Table 4.6).

Table 4.5: Experimental and predicted values for purification of salt

Run Order	Actual Value	Predicted Value	Residual	Leverage
1	99.16	99.17	-0.0121	0.950
2	99.47	99.42	0.0454	0.358
3	99.42	99.42	-0.0046	0.358
4	99.89	99.90	-0.0121	0.950
5	97.70	97.71	-0.0121	0.950
6	98.45	98.44	0.0067	0.985
7	98.97	98.98	-0.0121	0.950
8	97.90	97.91	-0.0121	0.950
9	99.95	99.96	-0.0121	0.950
10	99.89	99.90	-0.0121	0.950
11	98.91	98.92	-0.0121	0.950
12	99.14	99.13	0.0067	0.985
13	99.23	99.22	0.0067	0.985
14	99.25	99.24	0.0067	0.985
15	98.15	98.14	0.0067	0.985
16	97.73	97.72	0.0134	0.939
17	99.35	99.34	0.0067	0.985
18	97.48	97.47	0.0067	0.985
19	99.46	99.47	-0.0121	0.950
20	99.34	99.33	0.0067	0.985
21	99.50	99.49	0.0067	0.985
22	97.79	97.80	-0.0121	0.950
23	99.69	99.68	0.0067	0.985

4.9.1. Model adequacy check

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared (R^2), adjusted R-Squared and predicted R-Squared having a value of 0.9997,0.9966,and 0.8105 respectively. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in table 4.6 based on 95% confidence level. F-value is a test for comparing model variance withresidual (error) variance. If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P-value less than 0.05. It is calculated by model mean square divided by residual mean square. Here themodel F-value of 321.93 implies that, the model is significant. There is only a 0.31% chance that a"Model F-Value" this large could occur due to personal error or disturbance.

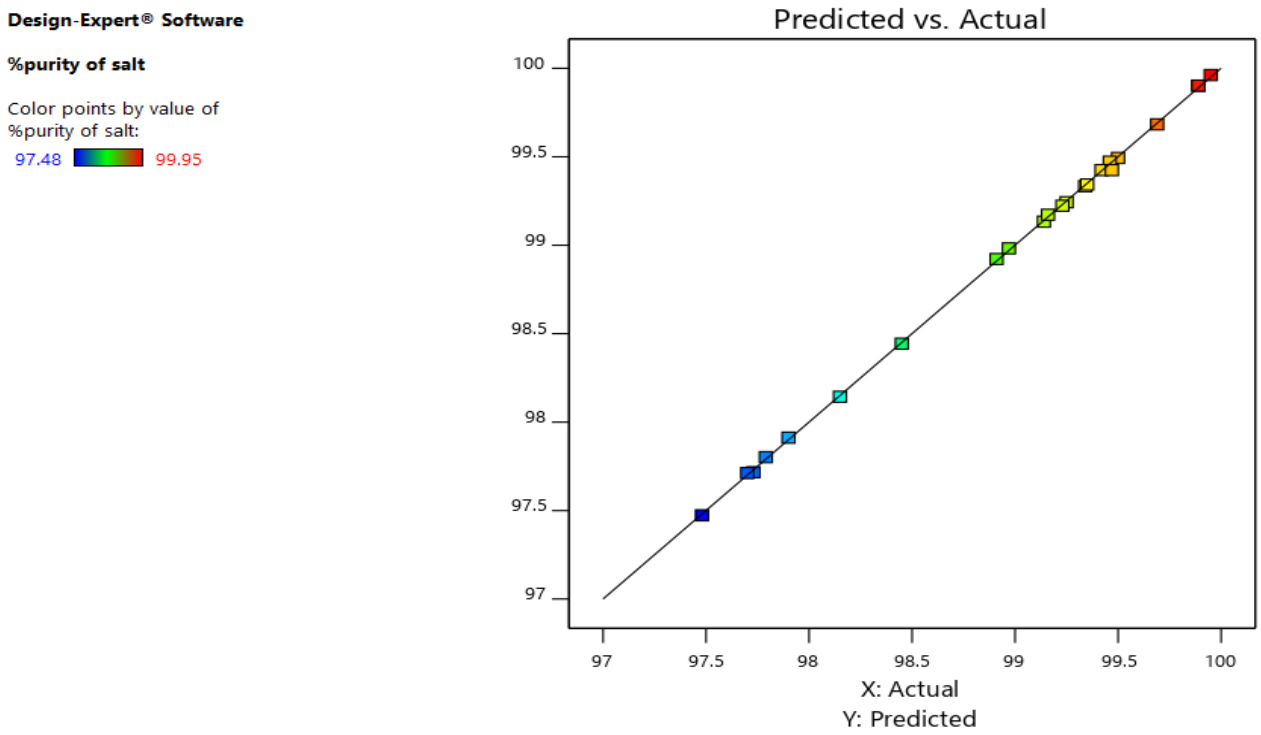

Figure 4.1: Predicted versus measured purity of salt

Table 4.6: Analysis of variance (ANOVA) for the regression model equation and coefficients

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	13.480	20	0.6739	321.93	0.0031	Significant
A-NaOH	0.4232	1	0.4232	202.18	0.0049	
B-Na_2CO_3	2.4000	1	2.4000	1145.67	0.0009	
C-$BaCl_2$	0.1201	1	0.1201	57.350	0.0170	
D-Temperature	0.6272	1	0.6272	299.64	0.0033	
E-Time	0.7938	1	0.7938	379.24	0.0026	
AB	0.6170	1	0.6170	294.78	0.0034	
AC	0.4527	1	0.4527	216.29	0.0046	
AD	0.1752	1	0.1752	83.700	0.0117	
AE	0.3061	1	0.3061	146.26	0.0068	
BC	0.3353	1	0.3353	160.17	0.0062	
BD	0.0928	1	0.0928	44.330	0.0218	
BE	0.7194	1	0.7194	343.69	0.0029	
CD	0.8994	1	0.8994	429.67	0.0023	
CE	0.1211	1	0.1211	57.850	0.0169	
DE	0.3555	1	0.3555	169.85	0.0058	
A^2	0.0005	1	0.0005	0.2305	0.6785	
B^2	0.5966	1	0.5966	285.04	0.0035	
C^2	0.1339	1	0.1339	63.990	0.0153	
D^2	1.7700	1	1.7700	843.95	0.0012	
E^2	1.2200	1	1.2200	582.21	0.0017	
Residual	0.0042	2	0.0021			
Lack of Fit	0.0029	1	0.0029	2.3500	0.3680	not significant
Pure Error	0.0012	1	0.0012			
Cor Total	13.480	22				

The Model F-value of 321.93 implies the model is significant. There is only a 0.31% chance that an F-value this large could occur due to personal error or disturbance.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AB, AC, AD, AE, BC, BD, BE, CD, CE, DE, B^2, C^2, D^2, E^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. This shows that the concentration of NaOH,Na_2CO_3.and $BaCl_2$, reaction temperature and reaction time, interaction between NaOH and Na_2CO_3, NaOH and $BaCl_2$, NaOH and reaction temperature, Na_2CO_3 and reaction time, $BaCl_2$ and temperature, temperature and reaction time, the square of; NaOH, Na_2CO_3, $BaCl_2$, reaction temperature and reaction time affects the percentage purity of salt significantly.

The Lack of Fit F-value of 2.35 implies the Lack of Fit is not significant relative to the pure error. There is a 36.80% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good we want the model to fit.

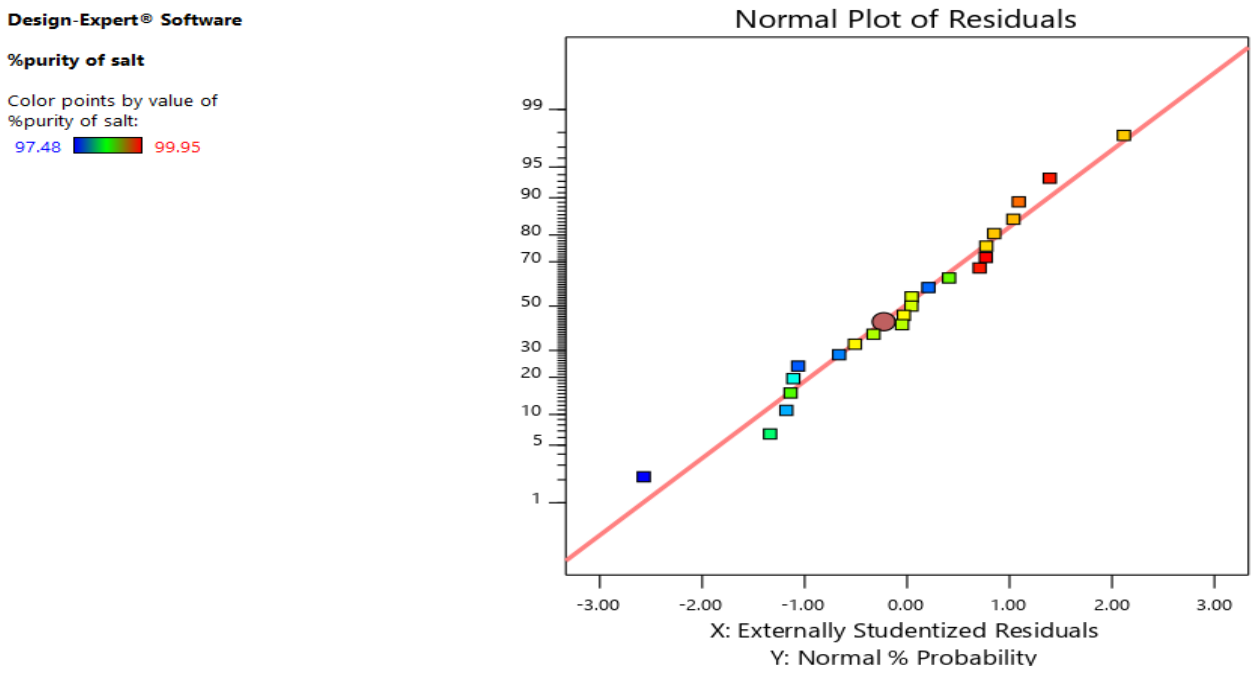

Figure 4.2: Normal plot of standardized residuals

The normal probability plot indicates the residuals following a normal distribution, in which case the points follow a straight line. This shows that the quadratic polynomial model satisfies the assumption of ANOVA. The error distribution is approximately normal.

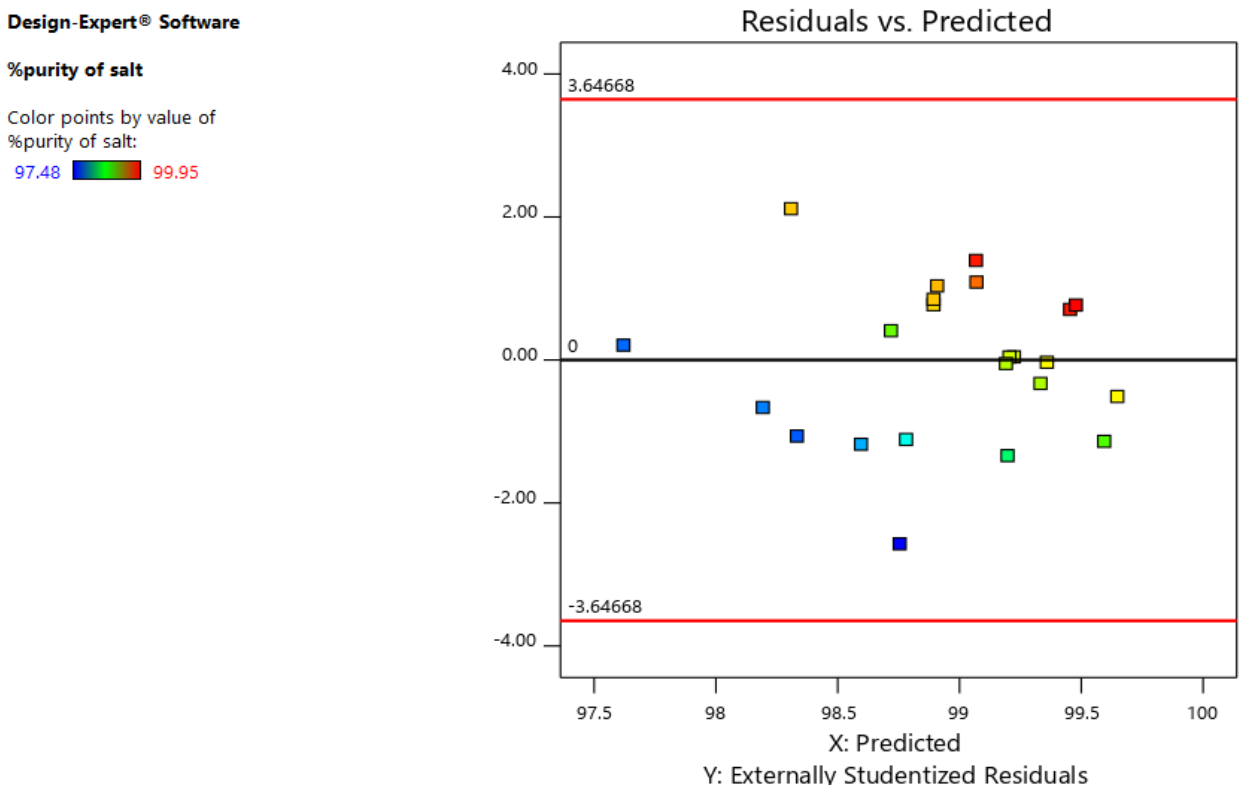

Figure 4.3: Plot of residuals versus model predicted values

If the model is correct and the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

Table 4.7: Comparison of model fitting for purification of salt of Afdera

Sources	R^2	Adjusted R^2	Predicted R^2	
Linear	0.9230	0.9004	0.7566	
Quadratic	0.9997	0.9966	0.8105	Suggested
Cubic	0.9996	0.9917	-	Aliased

The effect of various salt purification process operating parameters were determined for the purification of salt samples of Afdera. A linear multiple regression programs were used to derive the interaction effect of reagent concentration, temperature, and time on the purity of salt in the response variables.

The feasibility of fitting experimental data to a statistical model was checked on a linear model such as a two-factor interaction model, a quadratic model, and a cubic model as shown in table 4.6 and 4.7. Based on this for salt sample of Afdera the model and lack of fit p-value (probability value) which were reported to be 0.0031 and 0.3680, respectively. The value of R^2, adjusted R^2 and predicted R^2 were 0.9997, 0.9966 and 0.8105 , respectively. It was decided to utilize a quadratic model for the present experimental data.

4.9.2. Development of regression model equation

The model equation that correlates the response (% NaCl) to the purification process variables in terms of coded value after excluding the insignificant terms was given below. Eq. 4.2 gives the predicted model for percentage of salt in terms of the coded factors.

$$\begin{aligned}\text{purity of salt(\%wt.)} =& +99.42+0.2526*A+0.6013*B+0.1345*C+0.3075*D+0.3459*E \\ & -0.4493*AB+0.3849*AC+0.2394*AD-0.3165*AE+0.3312*BC \\ & -0.1742*BD-0.4852*BE+0.5425*CD+0.1991*CE+0.3411*DE \\ & +0.0053*A^2-0.1862*B^2+0.0882*C^2-0.3203*D^2-0.2661*E^2 \qquad (4.2)\end{aligned}$$

Where A =sodium hydroxide

B = sodium carbonate

C = barium chloride

D= reaction temperature

E= reaction time

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

4.9.3. Effect of salt purification process variables

Based on the analysis of variance, the purification of salt sample from Afdera and Dobi was significantly affected by various process variables and their interactions. The process variables are; reagent concentration (NaOH(A),Na_2CO_3(B) and $BaCl_2$(C)), reaction temperature(D), and reaction time(E). This result demonstrated the advantage of using design of experiments in capturing the interaction between variables that affects the salt purification process. The individual process variables were involved in interaction effect. As a result, the effects of process variable on purification of salt were plotted in Appendix B and C.

4.9.5. Effect of Interaction between Process Variables

The process variables were found to have significant interaction effects. The following Figures from 4.4 to 4.15 show the interaction between reagent concentration (sodium hydroxide, sodium carbonate, and barium chloride), reaction time, and temperature with respect to each other on percentage purity of salt.

Generally, an increase in reagent concentration, reaction temperature, and reaction time are found to increase the purity of salt. This is due to similar explanation given in the previous section.

4.9.5.1. Effects of Temperature and NaOH

As it observed from Figure 4.4, temperature and sodium hydroxide have an interaction effect on the purity of salt and it has minimum effect on the purity of salt. When the concentration of sodium hydroxide increased from 1g to 3g and at a temperature 25ºC, the purity of salt was almost constant. On the other hand, as concentration of sodium hydroxide increased from 1g to 3g and at temperature of 45 ºC, the purity of salt has slightly increased. Therefore, better quality of salt can be achieved at 45 ºC Perhaps this is due to the reason that at higher temperature solubility of Mg and Ca decrease and can be easily filtered from salt solution.

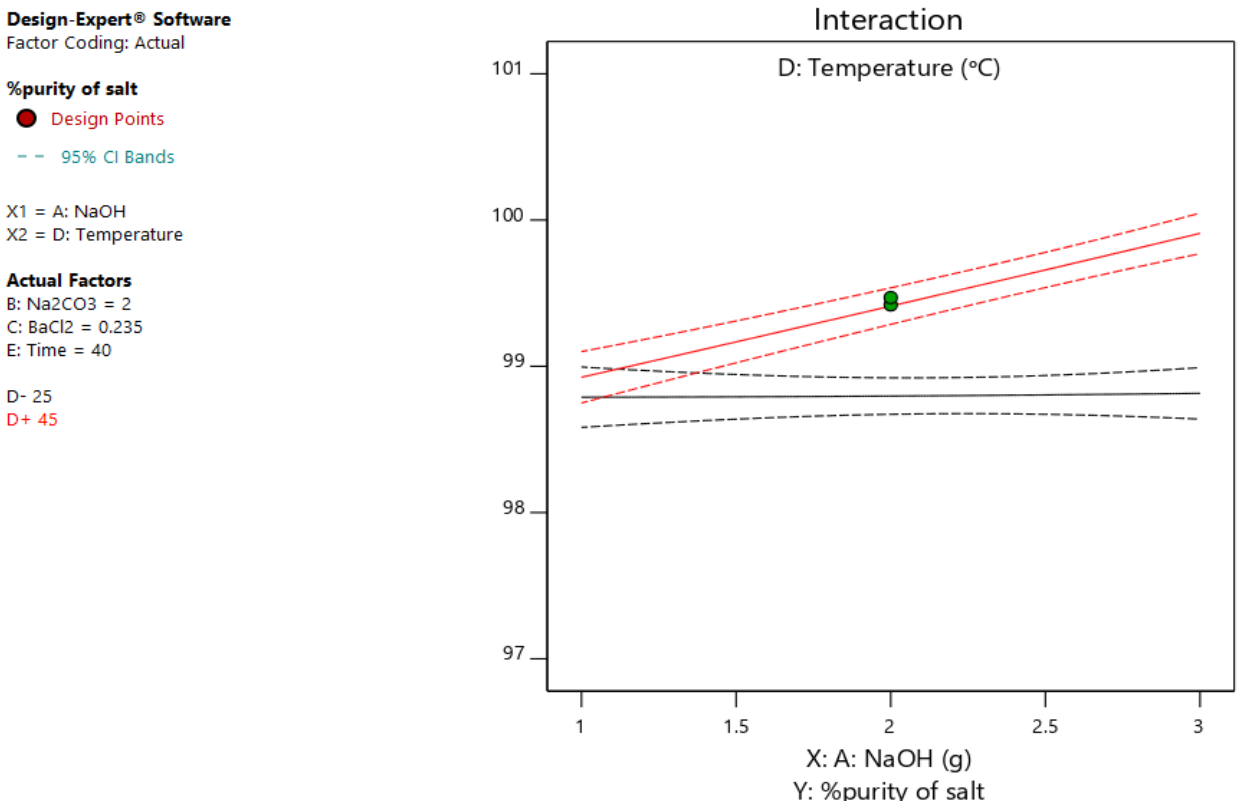

Figure 4.4: Effect of temperature and NaOH on purity of salt

4.9.5.2. Effects of NaOH andNa_2CO_3

The resulting plot of concentration of NaOH versus Na_2CO_3 shows that, they have an interaction effect on purity of salt. As shown in the Figures 4.5 , when the concentration of NaOH increased from 1g to 3g and the concentration of Na_2CO_3 was 1g the change in the purity of salt was significant. While the concentration of NaOH increased from 1g to 3g and the concentration of Na_2CO_3kept 3g, the purity of saltwas slightly decreased. This might be the presence of unreacted Na_2CO_3 in the salt solution. Therefore, the optimum concentrations of both reagents were 2g and at this reagent concentration, the purity of salt was 99.98%.

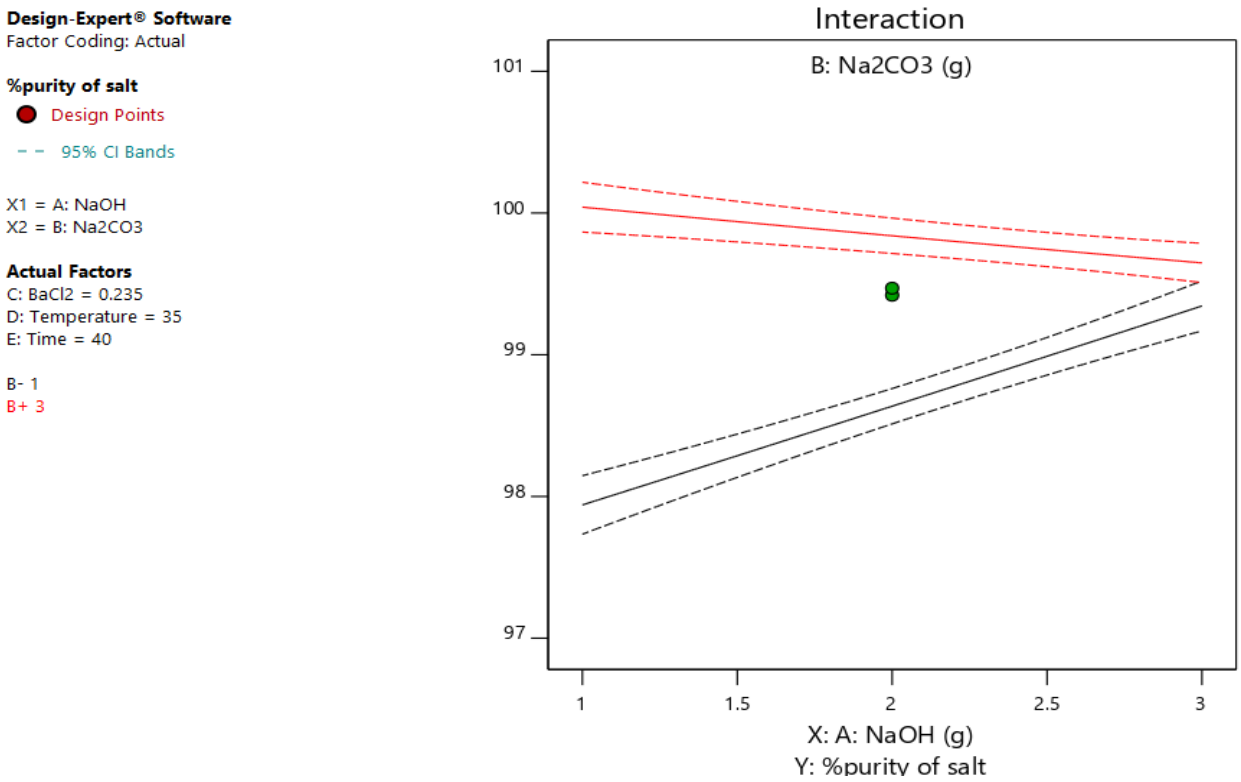

Figure 4.5: Interaction Effects of NaOH and Na_2CO_3 on purity of salt

4.9.5.3. Effects of NaOH and $BaCl_2$

Figure 4.6 shows the interaction effect of NaOH and $BaCl_2$. When the concentration of barium chloride was kept 0.27 and the concentration of sodium hydroxide increased from 1g to 3g, the purity of salt also increased significantly. While the concentration of Sodium hydroxide increased and the concentration of barium chloride kept constant 0.2g, the purity of salt slightly decreased. This might be due to the conversion of sodium hydroxide to sodium carbonate and sodium sulphate.These impurities produced by the conversion of sodium hydroxide will completely dissolved in water and cannot be removed unless excess barium chloride addition.so that the optimum concentration of NaOH and$BaCl_2$ Were 3g and 0.27g respectively,at these concentration levels the purity of salt was 99.98%.

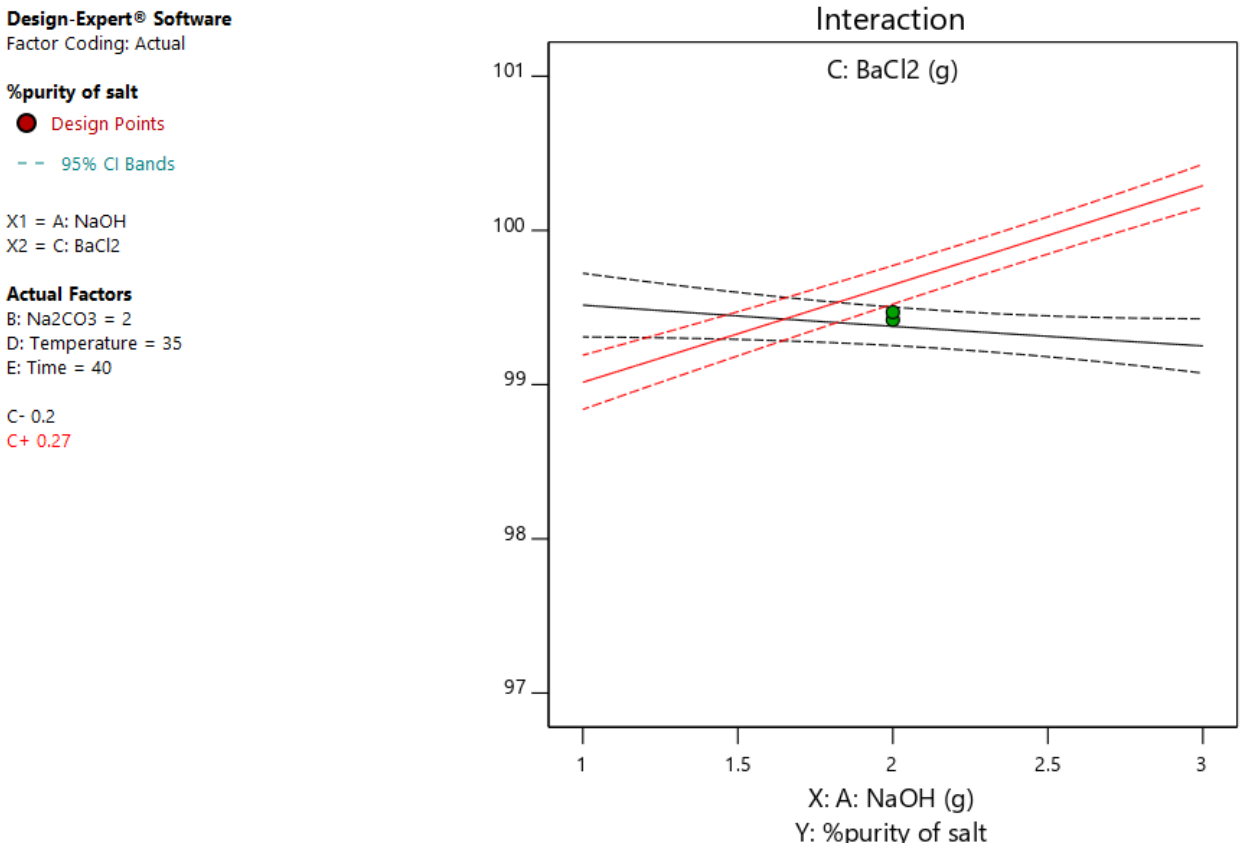

Figure 4.6: Interaction Effects of NaOH and $BaCl_2$ on purity of salt

4.9.5.5. Effects of NaOH and reaction time

figure 4.7 shows that, when the concentration of sodium hydroxide increased and the reaction time was 20 min the purity of salt was increased from 98.5 to 99.15%. whereas at higher reaction time of 60 min, when the concentration of sodium hydroxide increased from 1g to 3g the change on purity of salt was not significant. This is due to the reason that the concentration of reagent was decreased when the reaction continued. As the plot shows below, the optimum purity of salt that can be achieved at lower concentration of sodium hydroxide and higher reaction time was 99.5%.

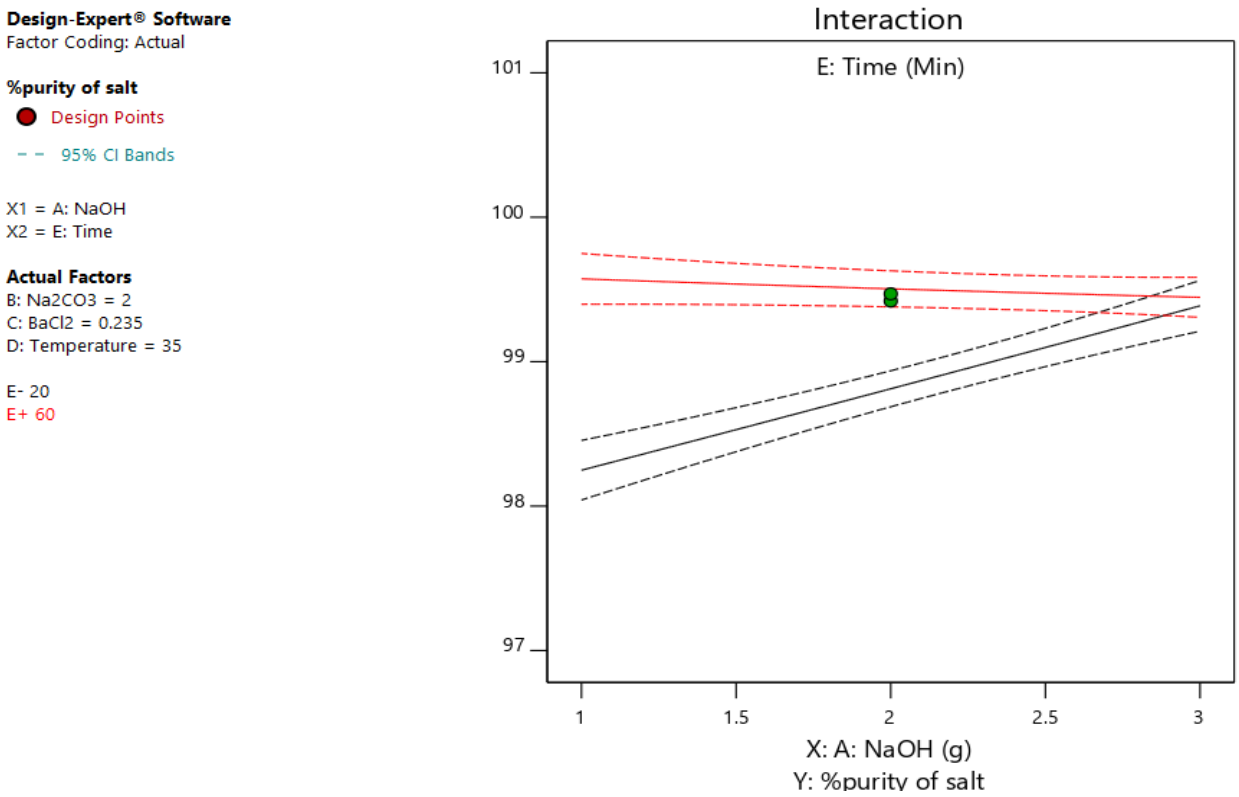

Figure 4.7: Interaction Effects of NaOH and time on purity of salt

4.9.5.6. Effects of Na_2CO_3 and reaction time

Figures 4.8 shows the interaction effect ofNa_2CO_3 and reaction time on the purity of salt. When the concentration of Na_2CO_3 increased at higher reaction time the purity of salt slightly increased. However, at lower reaction time, when the concentration of Na_2CO_3increased, then the purity of salt increased rapidly. This indicates that the reaction is mainly depends on the concentration of reagents. Therefore, the optimum purity of salt can be achieved at lower reaction time of 20min and concentration of Na_2CO_3 3g, at this point the purity of salt was 99.92%. This indicates that the reaction is mainly depends on the concentration of the reagent.

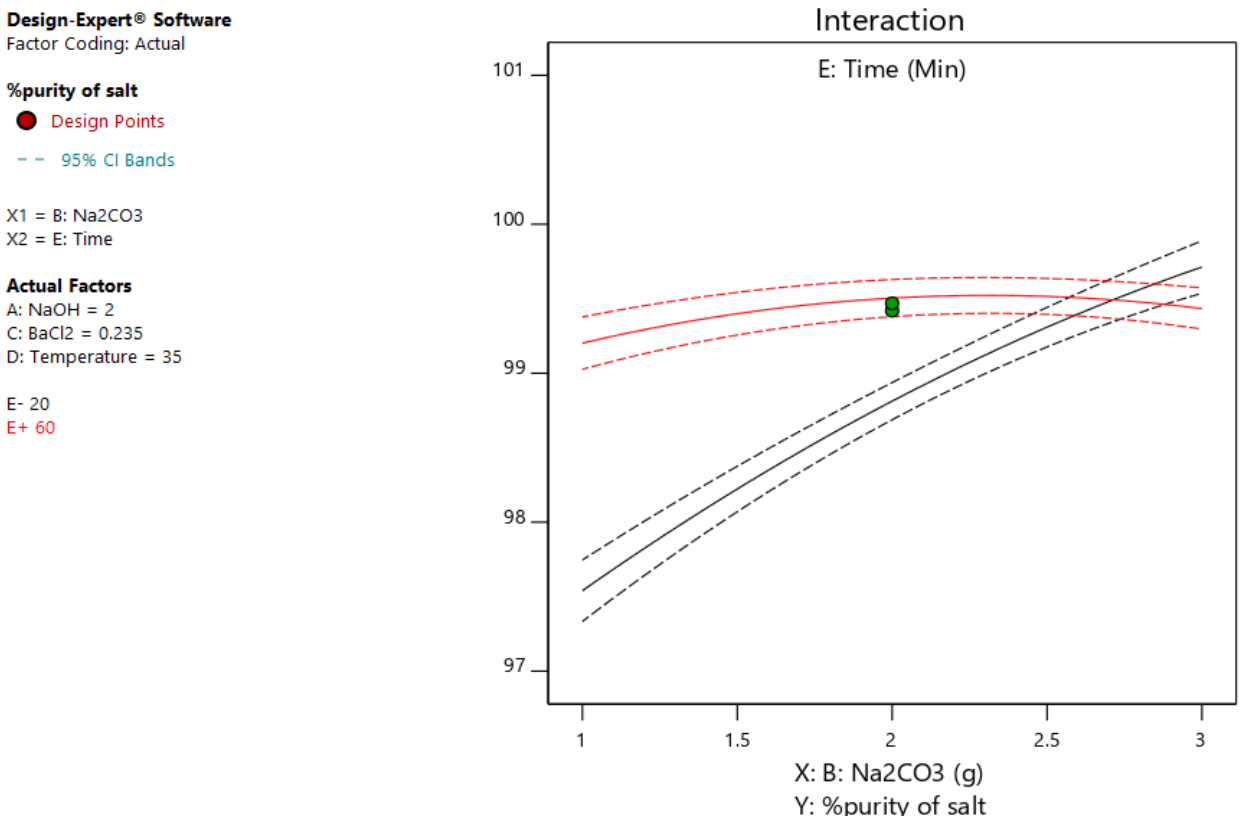

Figure 4.8: Interaction Effects of Na_2CO_3 and time on purity of salt

4.9.5.7 Effects of $BaCl_2$ and temperature

Barium chloride and reaction temperature has an interaction effect. Asthe concentration of $BaCl_2$increased at lower temperature, the purity of salt was slightly declined. However, at higher temperature, when the concentration of $BaCl_2$ increased, then the purity of salt increased.Thus the purification process was depend significantly on the concentration of $BaCl_2$ and temperature. Then the optimum purity of salt can be achieved at higher temperature of 45°C and concentration of $BaCl_2$ was 0.27g, at this point, the purity of salt was 99.98%. Theinteractions effects areplotted in Figure 4.9.

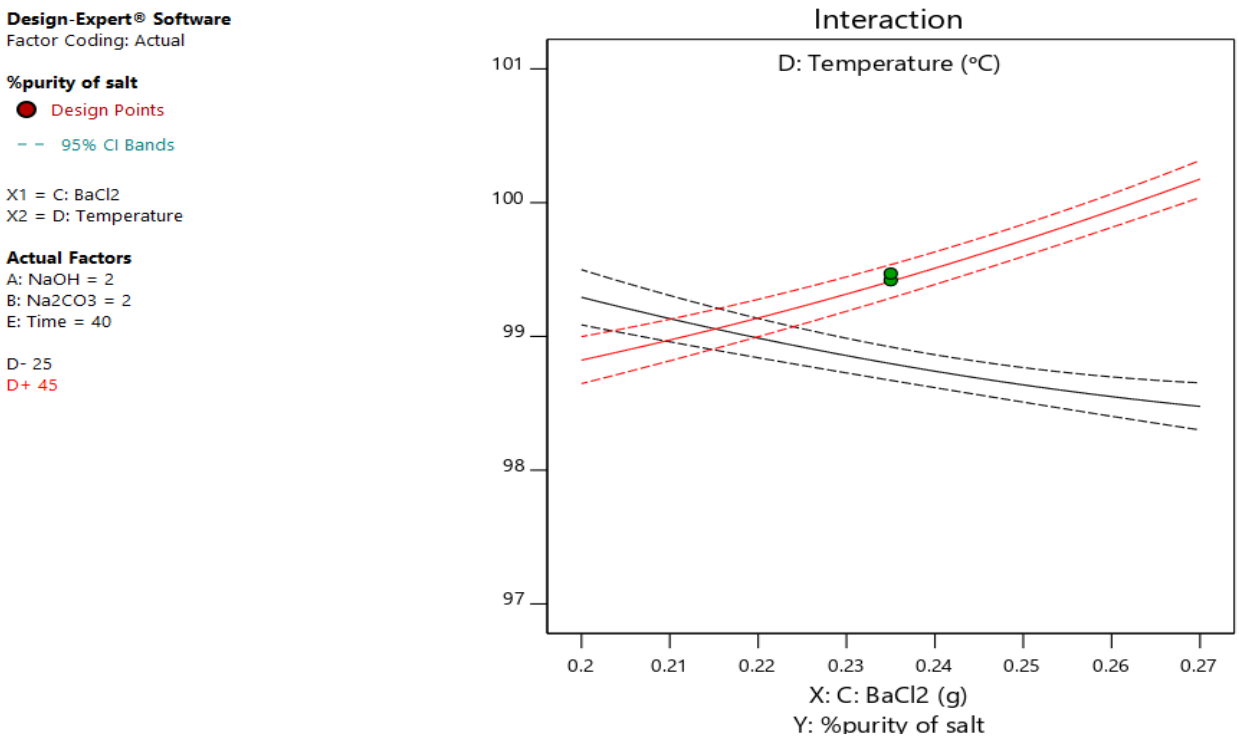

Figure 4.9: Interaction Effects of $BaCl_2$ and temperature on purity of salt

4.9.5.8. Effect of $BaCl_2$and reaction time

Barium chloride and reaction temperature has an interaction effect. As the concentration of $BaCl_2$increased at lower reaction time, the purity of salt was decreased. However, at higher reaction time, when the concentration of $BaCl_2$ increased, then the purity of salt slightly increased. Then the optimum purity of salt can be achieved at higher reaction time of 60min and concentration of $BaCl_2$ was 0.27g, at this point, the purity of salt was 99.98%. This indicates that at lower reaction time, minimum conversion of impurity can be achieved. On the other hand, at higher reaction time and maximum reagent concentration maximum conversion of impurity can be achieved. This is due to as duration of reaction time increases the precipitation reaction goes to completion.

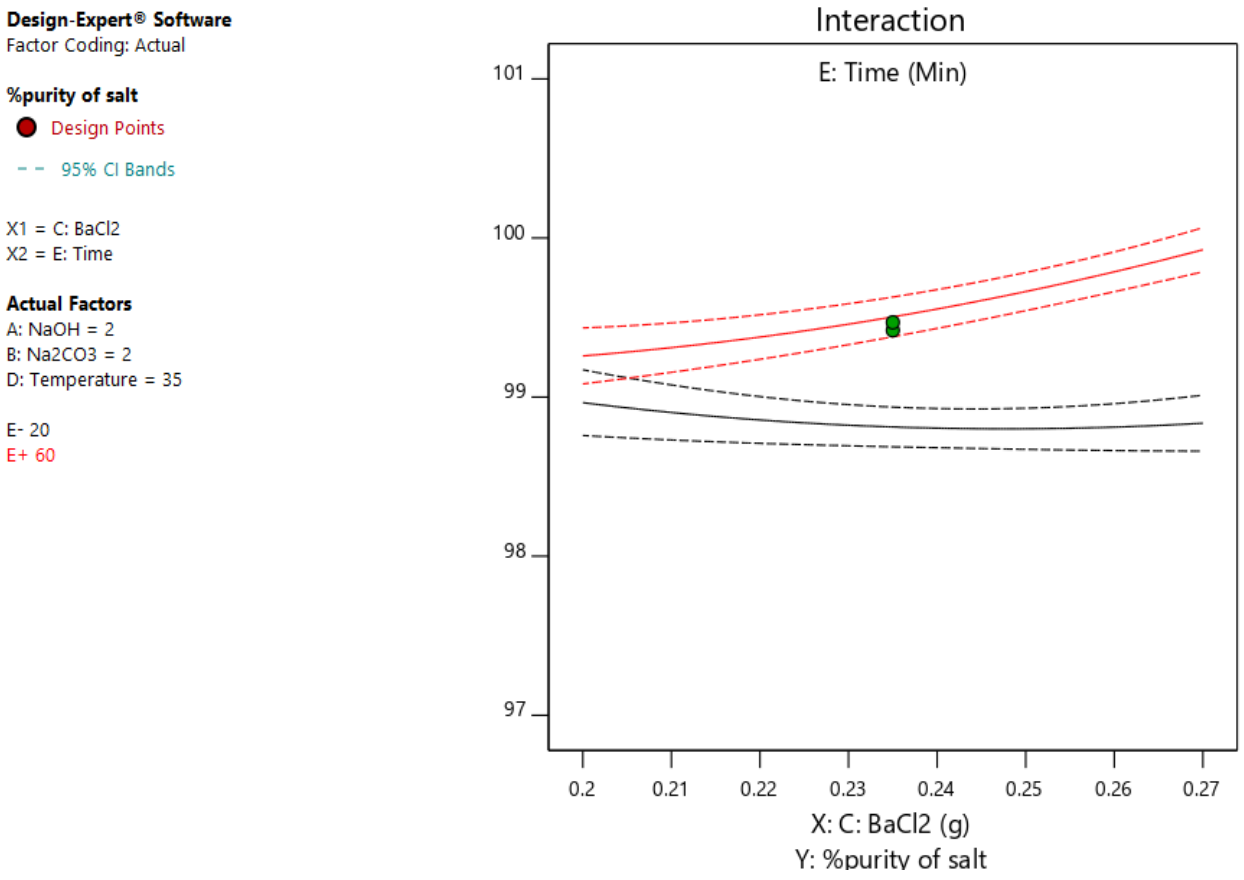

Figure 4.10: Interaction effect of $BaCl_2$ and time on purity of salt

4.9.5.9. Effect of reaction temperatureand reaction time

Both reaction temperature and reaction time have an interaction effect. As shown in figure 4.11,when the reaction temperatureincreased from 25 to 35 °C at lower reaction time, the purity of salt wasslightly increased and finally starts to decline. However, at higher reaction time, when reaction temperatureincreased, then the purity of salt significantly increased. Then the optimum purity of salt can be achieved at higher reaction time of 60min and reaction temperature of 45 °C, at this point the purity of salt was 99.96%. Therefor the interaction effect of reaction temperature and time significantly affects the precipitation reaction and the rate of settling of impurities. Then as the temperature increased, the impurities settled at the bottom and easily filtered. On the other hand, as duration of reaction time increased, the precipitation reaction goes to completion.

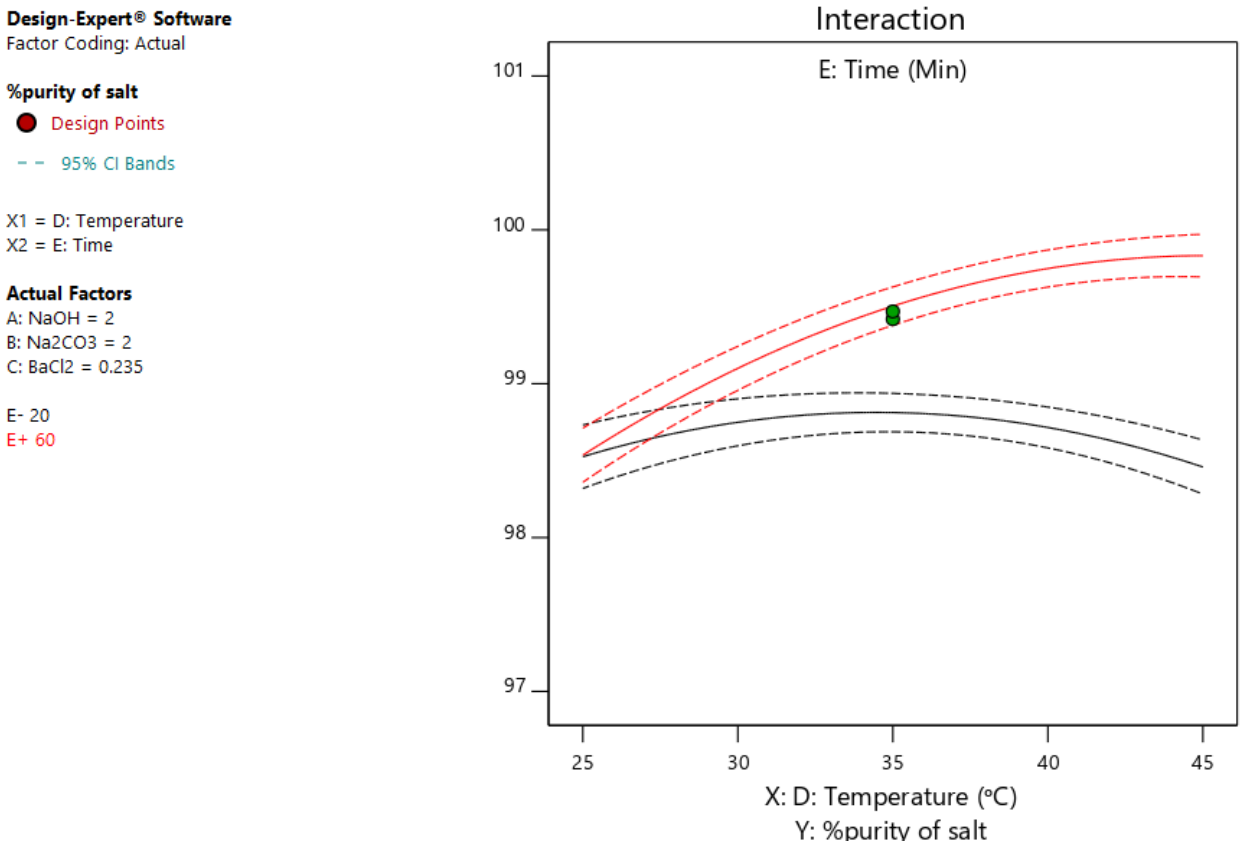

Figure 4.11: Interaction effect of temperature and time on purity of salt

4.10. Statistical analysis on factors affecting purification of salt of Dobi

The analysis of variance (ANOVA) for salt sample from Dobi is given in Tables 4.8 and 4.9 respectively. The multiple regression coefficients were obtained by employing a least square technique to predict a quadratic polynomial model for percentage purity of salt. As shown in table 4.8, the predicted and measured value(purity of the salt) obtained after purification was somewhat equal. This indicates that the residual between the statistical experimental design prediction and the measured purity was very small and the experimental data has a good precision.

Table 4.8: Experimental and predicted values for purification of salt

Run Order	Actual Value	Predicted Value	Residual	Leverage
1	98.83	98.85	-0.0166	0.950
2	99.45	99.44	0.0092	0.985
3	97.65	97.64	0.0092	0.985
4	98.94	98.96	-0.0166	0.950
5	97.88	97.87	0.0092	0.985
6	96.67	96.69	-0.0166	0.950
7	98.41	98.40	0.0092	0.985
8	99.86	99.85	0.0092	0.985
9	99.90	99.92	-0.0166	0.950
10	99.99	100.00	-0.0166	0.950
11	98.64	98.66	-0.0166	0.950
12	99.80	99.82	-0.0166	0.950
13	98.23	98.18	0.0529	0.358
14	96.29	96.31	-0.0166	0.950
15	99.75	99.74	0.0092	0.985
16	99.86	99.88	-0.0166	0.950
17	99.37	99.35	0.0184	0.939
18	99.35	99.34	0.0092	0.985
19	99.74	99.73	0.0092	0.985
20	99.72	99.71	0.0092	0.985
21	99.87	99.86	0.0092	0.985
22	99.41	99.43	-0.0166	0.950
23	98.18	98.18	0.0029	0.358

4.10.1. Model adequacy check

The analysis of variance test shows that, the regression model was highly significant with the correlation coefficients of determination of R-Squared (R^2), adjusted R-Squared and predicted R-Squared having a value of 0.9997,0.9970and 0.8047 respectively. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4.8, with 95% confidence level. F-value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P-

value less than 0.05. It is calculated by model mean square divided by residual mean square. Here the model F-value of 362.79 implies that, the model is significant. There is only a 0.28% chance that a "Model F-Value" this large could occur due to personal error or disturbance.

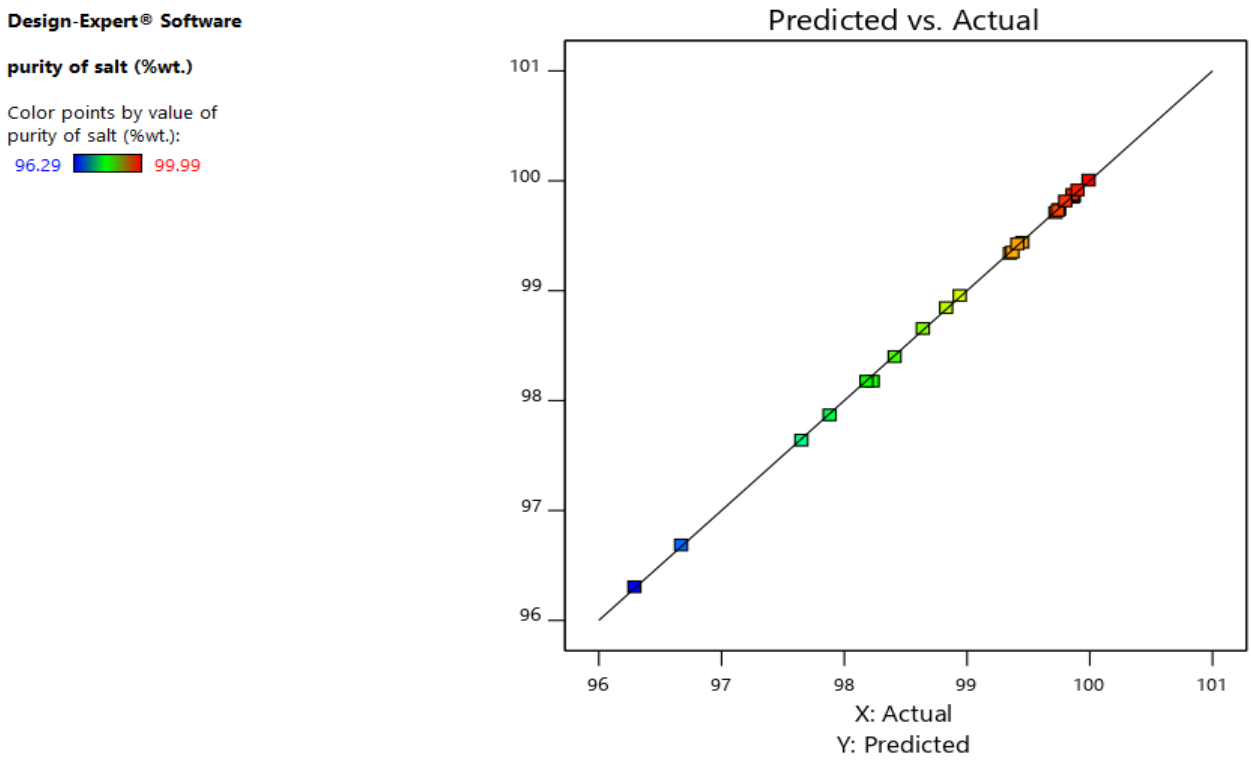

Figure4.12: Predicted versus measured purity of salt

Table 4.9: Analysis of variance (ANOVA) for the regression model equation and coefficients

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	24.480	20	1.2200	362.790	0.0028	Significant
A-NaOH	0.9112	1	0.9112	270.090	0.0037	
B-Na2CO3	4.8700	1	4.8700	1442.63	0.0007	
C-BaCl2	5.0900	1	5.0900	1508.09	0.0007	
D-Temperature	0.4704	1	0.4704	139.440	0.0071	
E-Time	0.4608	1	0.4608	136.580	0.0072	
AB	0.3094	1	0.3094	91.7100	0.0107	
AC	0.6191	1	0.6191	183.490	0.0054	
AD	0.0853	1	0.0853	25.2900	0.0373	
AE	0.1649	1	0.1649	48.8900	0.0198	
BC	0.0126	1	0.0126	3.72000	0.1934	
BD	0.0058	1	0.0058	1.72000	0.3196	
BE	0.2209	1	0.2209	65.4800	0.0149	
CD	1.2700	1	1.2700	376.140	0.0026	
CE	0.9317	1	0.9317	276.150	0.0036	
DE	1.4500	1	1.4500	430.190	0.0023	
A^2	2.0900	1	2.0900	618.310	0.0016	
B^2	0.1508	1	0.1508	44.7100	0.0216	
C^2	0.0171	1	0.0171	5.07000	0.1532	
D^2	2.0900	1	2.0900	618.310	0.0016	
E^2	2.4800	1	2.4800	735.890	0.0014	
Residual	0.0067	2	0.0034			
Lack of Fit	0.0055	1	0.0055	4.40000	0.2833	not significant
Pure Error	0.0012	1	0.0012			
Cor Total	24.490	22				

The Model F-value of 362.79 implies the model is significant. There is only a 0.28% chance that an F-value this large could occur due to personal error or disturbance.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AB, AC, AD, AE, BE, CD, CE, DE, A^2, B^2, D^2, E^2 are significant model terms. Values greater

than 0.1000 indicate the model terms are not significant. This shows that the concentration of NaOH, Na_2CO_3, and $BaCl_2$, reaction temperature and reaction time have significant interaction effects on the percentage purity of salt.

The Lack of Fit F-value of 4.40 implies the Lack of Fit is not significant relative to the pure error. There is a 28.33% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good we want the model to fit.

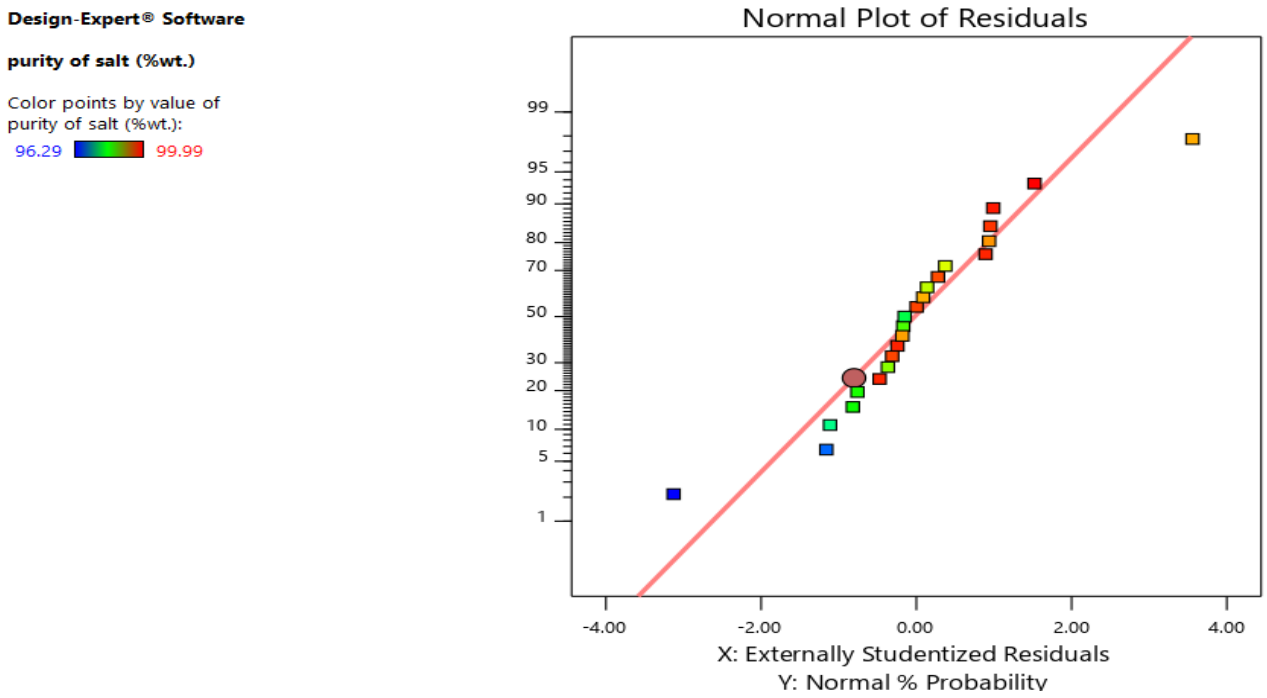

Figure 4.13: Normal plots of residuals

The normal probability plot indicates the residuals following a normal distribution; in this case, the points follow a straight line. This shows that the quadratic polynomial model satisfies the assumption of ANOVA. The error distribution is approximately normal.

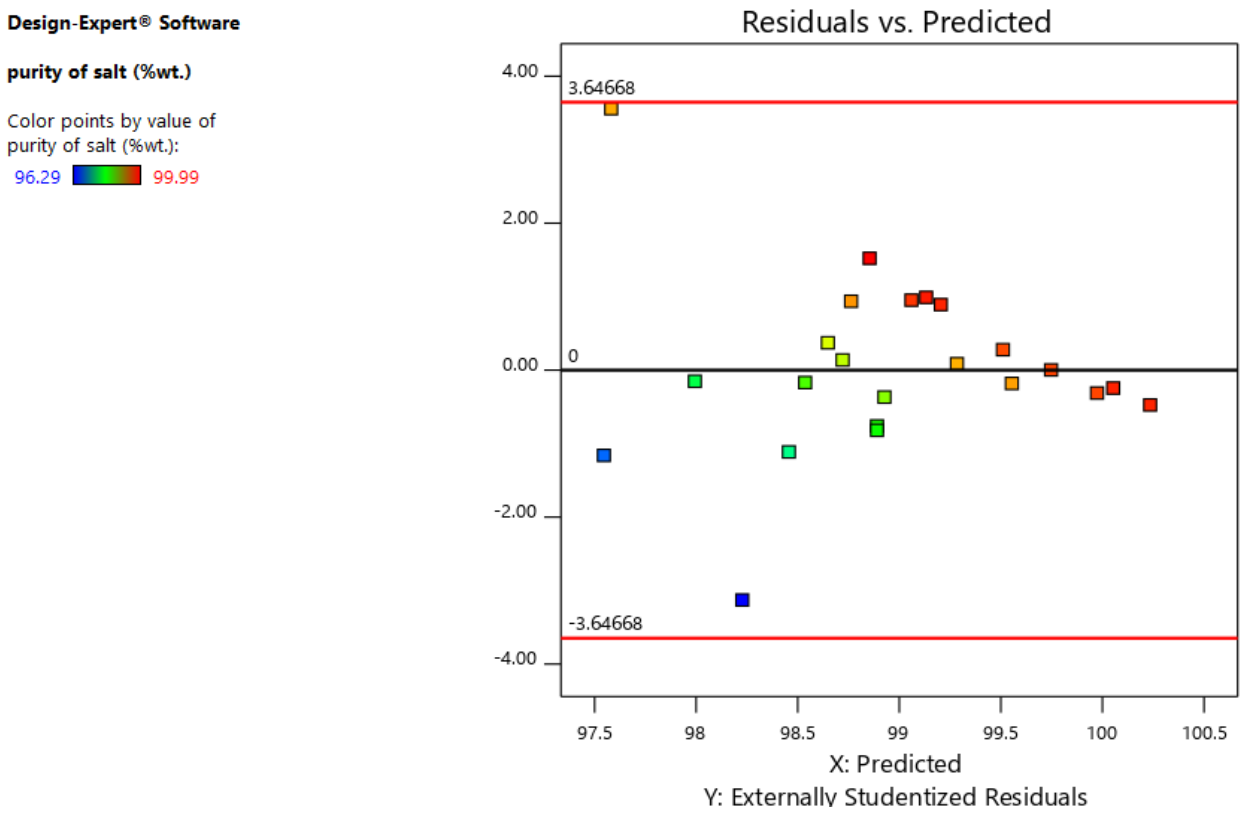

Figure 4.14: Plot of residuals versus model predicted values

If the model is correct and the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

Table 4.10:Comparison of model fitting for purification of salt of Dobi

Source	R^2	Adjusted R^2	Predicted R^2	
Linear	0.4632	0.3054	-0.1349	
Quadratic	0.9997	0.9970	0.8047	Suggested
Cubic	0.9999	0.9989	-	Aliased

From table 4.9 and 4.10,for salt sample of Dobi the model and lack of fit p-value (probability value) which were reported to be 0.0028 and 0.2833, respectively. the value of R^2, adjusted R^2 and predicted R^2 were 0.9997, 0.9970 and 0.8047 , respectively. it was decided to utilize a quadratic model for the present experimental data.

4.10.2. Development of regression model equation

The predicted model for percentage purity of salt in terms of the coded factors is given by Eq. 4.3.

$$\begin{aligned}\text{Purity of salt (\%wt.)} =& +98.18+0.3706*A+0.8566*B+0.8758*C+0.2663*D+0.2636*E \\ & -0.3182*AB+0.4501*AC+0.1671*AD+0.2323*AE+0.0641*BC \\ & +0.0436*BD+0.2689*BE+0.6444*CD+0.5522*CE+0.6892*DE \\ & +0.3481*A^2-0.0936*B^2+0.0315*C^2+0.3481*D^2+0.3798*E^2 \end{aligned} \quad (4.3)$$

4.11. Effect of Interaction between Process Variables

An increase in reagent concentration, reaction temperature, and reaction time are found to increase the purity of salt. This is due to similar explanation given in the previous section.

4.11.1. Effects of Temperature and NaOH

As it observed from figure,4.15 temperature and sodium hydroxide have an interaction effect on the purity of salt. Addition of excess sodium hydroxide at lower temperature of 25ºC, the purity of salt has a slight decrement. On the other hand, as concentration of sodium hydroxide increased from 1g to 3g and at temperature of 45ºC, the purity increases slightly from 98.8 to 99.8%. Therefore, better quality of salt can be achieved at 45 ºC. Perhaps this is due to the reason that, at higher temperature solubility of Mg and Ca decrease and can be easily filtered.

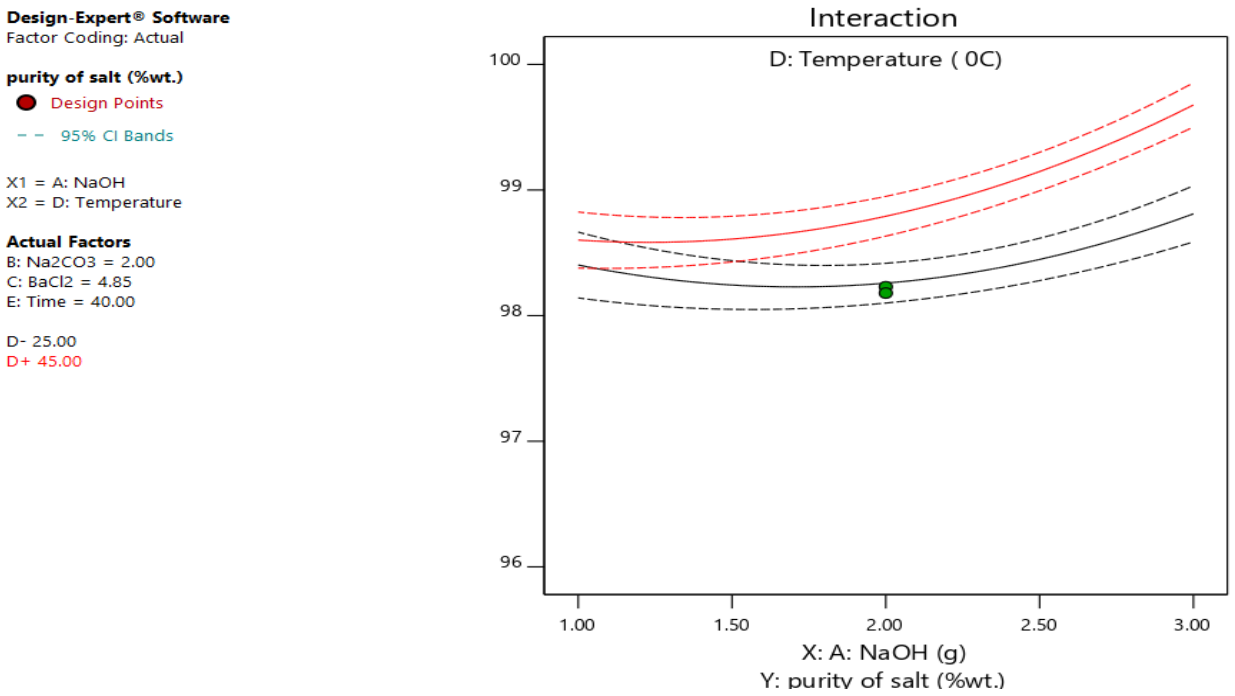

Figure 4.15: Interaction effect of NaOH and temperature on purity of salt

4.11.2. Effects of NaOH and Na_2CO_3

As shown in the figure 4.16 when the concentration of NaOH increased from 1g to 3g and the concentration of Na_2CO_3 was kept 1g, the purity of salt was increased from 96.9 to 98.2%. While the concentration of NaOH increased from 1g to 3g and the concentration of Na_2CO_3 kept 3g, the purity of salt slightly decreased. The optimum concentrations of sodium hydroxide and sodium carbonatewere found to be 1g and 3g respectively, at these reagents concentration the purity of salt was 99.3%.

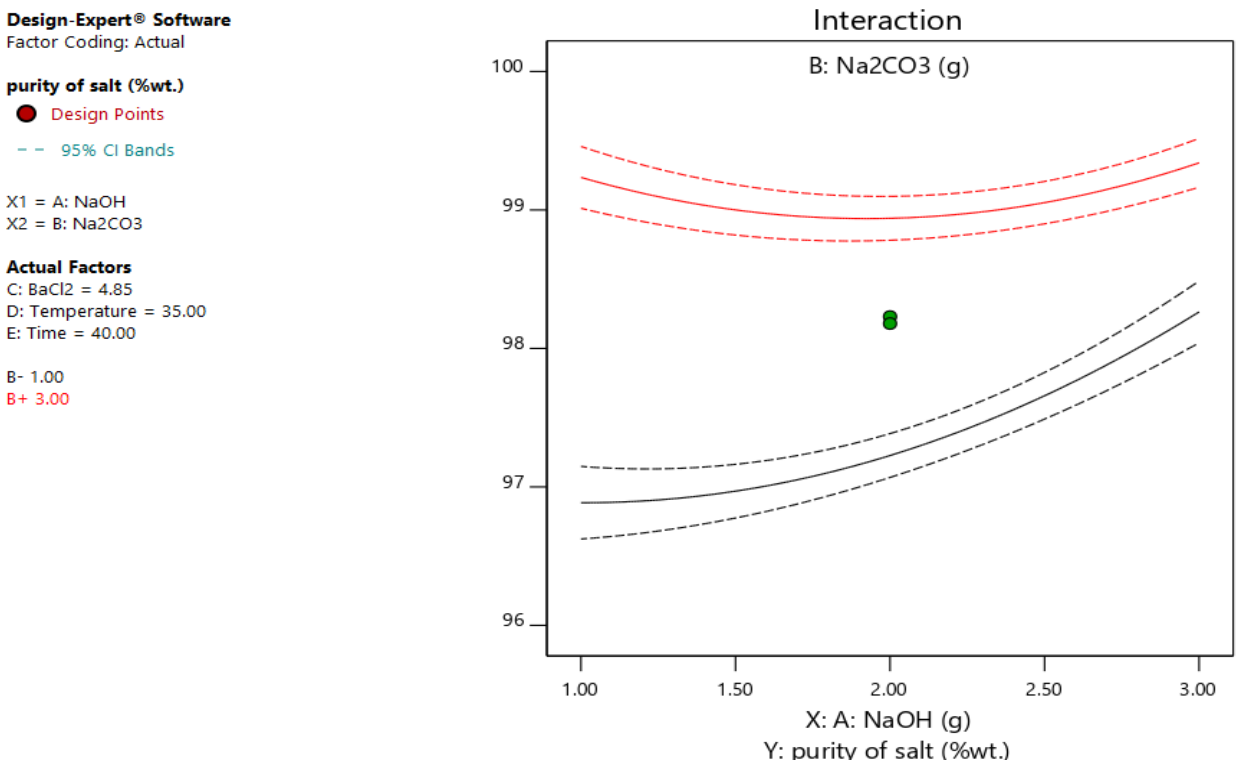

Figure 4.16: Interaction effect of NaOH and Na_2CO_3 on purity of salt

4.11.3. Effects of NaOH and $BaCl_2$

Sodium hydroxide and barium chloride has an interaction effect. As the concentration of sodium hydroxide increased from 1g to 3g while the concentration of $BaCl_2$was kept 4.2g, the purity of salt was slightly declined. When the concentration of sodium hydroxide increased while the concentration of barium chloride was kept 5.5g, then the purity of salt increased significantly. Then the optimum purity of salt can be achieved at higher concentration of 3g NaOH and 5.5g of $BaCl_2$, at this point the purity of salt was 99.98%. The interactions effects are plotted in appendix C. Similarly, the interaction effect of NaOH and reaction time, Na_2CO_3 and reaction temperature, Na_2CO_3 and $BaCl_2$, Na_2CO_3 and reaction time, $BaCl_2$ to reaction temperature, $BaCl_2$ and reaction time, reaction time to reaction temperature are shown in Appendix C.

4.12. Optimization of Process Variables on purification of salt

The process variables were optimized to obtain the highest percentage purity of salt using the model regression developed. Statistical experimental design was used to predict the optimum condition of process variables for 25 g of salt sample. The above results show that the five process variables and their interaction affected the purity of salt. The next step was to optimize the process variables in order to obtain the maximum purity by using the model regression developed. Based on the result, the minimum concentration of reagents was selected to minimize material purchasing expense and the lowest reaction temperature was selected to minimize electrical or energy consumption. Even though, the purification process was significantly affected by the reaction time, it affects the rate of purification. Then the lowest reaction time was selected to increase the rate of purification and the maximum purity of salt was selected to minimize the level of impurity which leads to improve the quality of salt. The optimum operating conditions for salt sample of Afdera and Dobi were selected based on the statistical data as shown in table 4.11 and 4.12 respectively.

Table 4.11:Optimization of Process Variables for purification of salt of Afdera

Number	Factors					%purity of salt	Desirability	Remark
	NaOH	Na_2CO_3	$BaCl_2$	Temperature	Time			
1	3.00	3.00	0.27	25.00	20.00	99.69	1	
2	2.65	2.69	0.235	38.23	50.26	99.63	1	Selected
3	2.79	1.86	0.213	35.39	29.21	99.30	1	
4	1.67	1.47	0.26	32.30	50.00	98.90	1	
5	1.31	2.41	0.23	30.12	57.09	99.56	1	
6	2.97	2.66	0.22	43.55	25.07	99.14	1	
7	1.00	1.00	0.20	25.00	20.00	97.72	1	
8	1.00	3.00	0.27	25.00	60.00	99.20	1	
9	2.00	2.00	0.235	35.00	40.00	99.44	1	
10	1.00	3.00	0.27	45.00	20.00	99.35	1	

Table 4.11 shows that for salt sample of Afdera the following were the selected process conditions; 38.23^{0}C of reaction temperature, 2.65g of NaOH,2.69g of Na_2CO_3,0.235g of $BaCl_2$ and 50.26min of reaction time, an optimum salt purity of 99.63 % can be obtained. In order to verify this prediction, an experiment was conducted in the selected optimum process variables and the result was compared with the statistical experimental design prediction. After the experiment was conducted, the percentage purity of the salt found to be 99.65% .This result shows that the experimental result was agreed with the predicted value.

Table 4.12: Optimization of Process Variables for purification of salt of Dobi

Number	Factors					%purity of salt	Desirability	Remark
	NaOH	Na_2CO_3	$BaCl_2$	Temperature	Time			
1	2.74	3.00	5.50	25.00	28.44	99.68	1	
2	3.00	2.97	5.50	30.13	20.00	99.60	1	
3	3.00	2.75	5.50	25.00	23.47	99.70	1	
4	3.00	3.00	5.32	25.13	21.88	99.63	1	
5	2.71	2.93	5.47	25.00	21.72	99.52	1	
6	2.63	2.99	5.49	26.93	20.00	99.41	1	
7	2.97	3.00	5.29	25.00	27.58	99.68	1	Selected
8	3.00	3.00	5.22	25.00	25.18	99.60	1	
9	3.00	2.59	5.49	31.10	28.86	99.74	1	
10	2.49	3.00	5.50	25.48	33.85	99.60	1	

Table 4.12 shows that for salt sample from Dobi the following were the selected process conditions; 25 ^{0}C of reaction temperature, 2.97g of NaOH,3g of Na_2CO_3,5.29g of $BaCl_2$ and 27.58min of reaction time, an optimum salt purity of 99.68 % can be obtained. This prediction was verified by conducting experiment in the selected optimum process variables and the result was comparable with the statistical experimental prediction. After the experiment was conducted, the percentage purity of the salt found to be 99.60% .This result shows that the experimental result was agreed with the predicted value. Based on

this, the physico-chemical treatment of salt to improve the quality of salt for industrial and human consumptions are significantly affected by the individual process variables as well as their interactions.

4.13. Characterization of purified salt

Table 4.13: Essential composition of the purified salt

Analysis	Sample name		ES/Codex
	Afdera	Dobi	
PH	7.86± 0.10	8±0.03	8
Alkalinity (%wt.)	0.12± 0.03	0.18±0.02	0.2
Sodium Chloride content (%wt.)	99.65± 0.20	99.60±0.27	96-98
Sulphate content (%wt.)	0.18± 0.02	0.3±0.03	0.5
Calcium (g/kg)	0.06±0.04	0.13±0.01	0.5
Magnesium (g/kg)	0.08±0.02	0.06±0.03	0.5

Table 4.13 shows that the purity of salt sample from Afdera had been enhanced to 99.65 % and sample from Dobi to 99.60% NaCl. After purification the two salt samples were agreed the ES and Codex legislations.

The quality of Australian and Mexican solar salt varies from 99-99.95% NaCl (Mannar and Dunn, 1995).A study in Sir Lanka shows that a purity level can be achieved from 98.023 to 99.604 by physic-chemical treatment process(Rathnayaka,2014). The purity of both salts samples were in the rangeof salt produced in Australia, Mexico and Sir Lanka. Therefore, the qualities of both samples were improvedto acceptable level through physic-chemical treatment process.

Table 4.13 shows the pH of the salt samples was slightly affected by the treatment process. The pH value of salt sample from Afdera was increased from 7.8-7.86, while the salt sample from Dobi was increased 7.9-8. The ES the maximum allowable limit for pH of salt is eight. The African standard also specifies the pH limit of salt should be 7-8, (AOS, 2012). Thus,

salt samples from Afdera and Dobi agreed with the African and the ES standard of salt pH specification.

Table 4.13 shows that, after purification the SO_4^{2-} content of salt sample of Afdera were reduced from 1.08 to 0.18%, while salt sample from Dobi was reduced from 8.12% to 0.3%.The sulphate content of both samples were agreed with the Ethiopian standards of specification (0.5%wt.).

The sulphate contents of salt produced from different source and methods in Mexico and Australia indicates that, Rock salt has 0.2to 1.3 %wt., refined salt 0.2%wt., vacuum salt 0.2%wt and pure vacuum evaporated salt 0.04%wt.The amount of sulphate in salt sample from Afdera was within the range of rock salt, refinedsalt, and vacuum salt quality produced in Mexico and Australia.However, salt sample from Dobi was in the range of rock salt quality of Mexico and Australia but lower than the quality of refined salt and vacuum salt. Generally, the purity of both salt samples was improved to acceptable level by the physic-chemical treatment process.

The result in table 4.13 shows the alkalinity of salt sample from Afdera was reduced from 1.6 to 0.12%wt and from Dobi was reduced from 1.8 to 0.18%wt. The results indicate that, the alkalinity of both salt samples were within the ES standard of specification (0.5%wt.).

The alkalinity of edible salt which are processed in different methods in Uganda showed 1.3%, 1% and 0.1298 % respectively (Kirabira, 2013).after purification the alkalinity of salt sample from Afdera and Dobi were agreed with edible salt in Uganda which are processed in different methods.

From table 4.13 the concentration of Ca in the salt samples of Afdera was reduced from 0.3 to 0.06% wt., and sample from Dobi was reduced from 0.6 to 0.13% wt. This indicates that after purification of both salt samples, their purity levels were agreed with the ES limit (0.5%wt.). Chemical analyses in dry basis of different types of salt in Mexico and Australia, the concentration of calcium vary from 0.002 to 1.1% wt. The concentrations of calcium in purified salt samples were found to be in the range of both Mexican and Australian salt quality.

The experimental result in table 4.13 shows in the purified samples, from Afdera the concentration of Mg was 0.08%wt.while in salt sample from Dobi was 0.06%wt.The EthiopianStandard Specification for both iodized Common and table salts states that the concentration of Mg should not exceed 0.5%wt. The samples were met the requirements of the ES specification.

Salt produced from different source and different methods in Mexico and Australia contains 0.0001 to 0.17% Wt. Mg. This indicates that the concentrations of Mg in both salt samples were found to be within the range of salt produced from different sources and methods in Mexico and Australia.

4.14. Comparison of brine lake salt of Afdera and Dobi

The compositions of salt samples from Afdera and Dobi were differing very widely but the heavy metal impurities were nearly the same for both samples. The main impurities of the two salt samples were calcium, magnesium, and sulphate.

The results summarized in table 4.1 shows that salt sample from Afdera had the purity level of 96.6 % and sample from Dobi had 91.21% NaCl. The purity levels of the two crude salt samples were significantly different. Table 4.10 shows that the purity of salt sample from Afdera had been enhanced to 99.65 % and sample from Dobi to 99.60% NaCl. After purification, the purity level of the two salt samples became almost similar and agreed with the ES and Codex legislations.

Table 4.1 shows the concentration of SO_4^{2-} in the two salt samples of Afdera and Dobi were 1.08 and 8.12%wt respectively. This result indicates that the sulphate content of salt sample from Dobi was significantly higher than salt sample from Afdera. After purification the SO_4^{2-} content of salt sample of Afdera was reduced to 0.18%, while salt sample from Dobi was reduced to 0.3%.The sulphate content of both chemically treated samples were became almost equal and also agreed the Ethiopian standards of specifications.

The concentration of Ca in the crude salt samples of Afdera was 0.3g/kg., and sample from Dobi was 0.6g/kg. From table 4.13 the concentration of Ca in the salt samples of Afdera was reduced to 0.06g/kg., and sample from Dobi was reduced to 0.13g/kg. This indicates that

after purification of both salt samples, their purity levels had little difference but they were within the range of the ES limit (0.5g/kg).

Table 4.3 shows in the analyzed samples, from Afdera the concentration of Mg was 0.8189g/kg while in salt sample from Dobi it was 0.6663g/kg. The experimental result in table 4.13 shows in the purified samples, from Afdera the concentration of Mg was 0.08g/kg. While in salt sample from Dobi was 0.06g/kg. The Ethiopian Standard Specification for both iodized Common and table salts states that the concentration of Mg should not exceed 0.5g/kg. The samples were met the requirements of the ES specification.

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

In this study, purification and characterization of brine lake salt from Afdera and Dobi were carried out. The influence of different factors such as, reagent concentration (NaOH, Na_2CO_3, and $BaCl_2$), temperature, and reaction time on the chemical treatment purification of salt was determined. Varying of these operating conditions is the pre-dominant factors for the quality of both edible and industrial salt. The concentrations of metal and heavy metal impurities of salt (Fe, Zn, Pb, Cd, Mg, Cu, and Ca) have been analyzed by FAAS using wet digestion of the samples. The result shows that Cd was not detected and the concentration of other metal and heavy metals impurities in both salt samples were below or within the range of the recommended limit of ES and codex legislation except Ca and Mg. However, the concentrations of Mg and SO_4 in salt sample from Afdera exceed the recommended limits.Similarly Ca, Mg and SO_4 in salt sample of Dobi were significant and exceed the recommended limits. After the purification, process was carried out the NaCl content of salt of Afdera and Dobi enhanced from 96.6 to 99.65% and 91.21 to 99.60% respectively. This purity is suitable to meet community and industrial demands. After chemical treatment, the concentration of impurities level of the salt samples were lower than the permitted maximum level for industrial and human consumption as prescribed by ES specification and codex legislation.

5.2. Recommendations

For purification of salt, the following should be considered:

- ✓ Further research work should be done to compare chemical treatment purification with other methods to improve the quality of salt.
- ✓ Detailed chemical analysis should be conducted to identify the mount of impurities with higher precision.
- ✓ The country should have more emphases for the quality of salt.
- ✓ Producers would have explored the possible methods how to meet the expected edible and industrial salt standards.

REFERENCES

Abdol MajidCheraghali a, Farzad Kobarfard b and Noroldin Faeizy,(2010). Heavy Metals Contamination of Table Salt Consumed in Iran. Iranian Journal of Pharmaceutical Research, 9 (2): 129-132

Acharya and e.a. Sanjit, Chemical cationization of cotton fabric for improved dye uptake. Cellulose, 2014. 21(6): p. 4693-4706.

Adshed,Samuel A.M. (1992). "salt and civilization.MackMillan".

A D Sawant, pp.,(1995).Sample dissolution for elemental analysis. 4503 4510.

AL-Saffar, S. (2012). Pathological effect of Daily Consumption of Indomy on Lung, Kidney and Spleen in Albino Rat. Proceeding of the Eleventh Veterinary Scientific Conference.

Amorim FAC and Ferrerira SL,((2005). Determination of cadmium and lead I table salt by sequential multi- element flame atomic absorption spectrometry. Talanta,65: 960-964.

ANE.(2010).NaCl manufacturing from potash mining tailings.

Aral, H., Hill, B.D., and Sparrow, G.J.,(2004).Salts from Saline Waters and Value Added Products from the Salts.Value Adding to Salts Recoveredfrom Saline Waters in Disposal Basins in the Murray-Darling Basin,CSIRO Minerals ,Report DMR-2378C

Arruda. M.A.Z., (2007).Trends in sample preparation: Nova Science Publishers: New York.

Bent, S. and Bohm, K.,(1995) “Copper induced liver cirrhosis in a 13- month-old boy”, Gesundheitswesen, 57, 10,, pp. 66-79.

Bertram, B.M., (1997). Sodium Chloride. In Encyclopedia of Chemical Technology, Kirk-Othmer, ed.Fourth Edition, John Wiley & Sons, New York, Vol. 22,pp. 354-377.

Binega, Y. (2006). "Chemical analysis of the Assale (Ethiopia) rock salt deposit." Bulletin of the Chemical Society of Ethiopia 20(2): 319-324.

Bodaghpour, S., Joo, N.B. and Ahmadi, S.,(2012) “A review on the existence of chrome in pp.cementand environmental remedies to control its effects”, International Journal of Geology, 2, 6, 62-67.

Brow.(1981). "Acute bicarbonate intoxication from a folk remedy”. American J. Dis. 135: 965- 965.

Budavari, S., (1997).The Merck Index . New Jersey, USA: Merck & Co, Inc.

Butts, D.,(1993).Chemicals fom Brine. In Encyclopedia of Chemical Technology, Kirk-Othmer, ed.Fourth Edition, John Wiley&Sons, New York, Vol. 5, pp. 817-837.

Cheraghali AM, Kobarfard F, Faeizy N.,(2010). Heavy metals contamination of table salt consumed in Iran.Iranian journal of pharmaceutical research.9(2):129-32

Codex,(2006). Codex standard for food grade salt. CX STAN 150- 1985, Amend. 3- 2006, 1-7.

Curlin, L.C., Bommaraju, T.V. and Hansson, C.B.(1991). Alkali and chlorine products, Chlorine and sodium hydroxide. In Encyclopedia of Chemical Technology, Kirk-Othmer,ed.Fourth Edition, John Wiley&Sons, New York, Vol. 1, pp. 938-1025.

De Souza, A.L. (2013)."An overview of spectrometric techniques and sample preparation for the determination of impurities in uranium nuclear fuel grade." J. Micro Chem. 106: 194-201.

Dogan,M. , (2001). "Atomic absorption spectrometric determination of copper, cobalt, cadmium, lead, nickel and chromium in table salt samples after preconcentration on activated carbon." Kuwait J. Sci Eng. 28: 2-6.

Ducher, M., Fauvel, J.-P., Maurin, M., Laville, M., Maire, P., Paultre, Ch. Z., Cerutti, C.,(2003). “Sodium Intake and Blood Pressure in Healthy Individuals”, J. Hyper-tension 21 no. 2, 289-294.

Duruibe, J.O., Ogwuegbu, M. O. C. and Egwurugwu, J. N., (2007) “Heavy metal pollution and human bio-toxic effects”, International Journal of Physical Sciences, 2, 5, pp.112-118.

Ebdon, (1998). An Introduction to Analytical atomic Absorption Spectrometry, John wily and Sons: NY; PP: 8-50.

Engelhardt H.-J, Gaertner, R and Hellberg Chr., (2000). The production of halite of high purity. In Proceedings, 8th World Salt Symposium (Salt 2000), R. Geertman, ed. Elsevier Science B.V., Amsterdam, Vol. 1, pp. 107-112.

Euro Chlor,(2012).Answer to a request for additional information concerning various topics.

Farlex Incorporated,(2005).Definition:Environment, TheFreeDictionary, FarlexInc., U.S.A. (www.thefreedictiona-ry.com/)

Feng,, (20 11)."Wen Jun Method for removing $CaCl_2$ and MgCl2 from finished salt". China patent CN 102120591A.

FMoH.,(2004). National guide line for control and prevention of micro nutrient Deficiencies. Federal Ministry of Health, Family Health Department. Addis Ababa, Ethiopia.

FMoH., (2007).Mapping and Assessment of Salt producers in Ethiopia. Addis Ababa: Ministry of Health

Gebrekidan M., Samuel, Z., (2011). "Concentration of Heavy Metals in Drinking Water from Urban Areas of the Tigray Region, Northern Ethiopia", MEJS, 3, 1, pp.105-112.

Habashi, F., ed., (1997b).Sodium. In Handbook of Extractive Metallurgy. Wiley- VCH, Weinheim, Vol. IV, chapter 51, pp. 2053-2139.

Howard, G.and Stathm,P. J. ,(1997). Inorganic trace analysis, philosophy and practice. John Wiley and sons Ltd.

Iqbal and e.a. Naseem, Asymmetric bioreduction of activated carbon–carbon double bonds using Shewanella yellow enzyme (SYE-4) as novel enoate reductase. Tetrahedron, 2012.68(37): p. 7619-7623.

Jaeger, A., (1987)."Clinical features and management of poisoning due to antimalarial drugs." Medical toxicology and adverse drug experience 2(4): 242-273.

Fergusson,J.E.,(1982). "Inorganic Chemistry and the Earth"; Pergamon Press;Department of Chemistry , Univer sity of Auckland; Stage One InorganicChemistry Laboratory Manual; Department of Chemistry, University of Auckland.

Kanagara and Babu, (2002). Alternatives to salt curing technique. Iscundres Vol.61

Kelly, F. (1953). "Studies on the stability of iodine compounds in iodized salt."Bulletin of the World Health Organization 9(2): 217.

Kirabira, J. B., Kasedde, H., & Semukuuttu, D. (2013).Towards the improvement of salt extraction at Lake Katwe. Int J. Sci Tec Res. 2: 76-81.

Kirk-Othmer, (2002).'Chlorine', Kirk – Othmer Encyclopedia of Chemical Technology.

Kostick, D.,(2011) Salt Minerals Yearbook. p. 63.1 – 63.24

Krebs & co ltd, 1988).The Indian institute of chemical engineering, international seminar on membrane cell technology for the chloroalkali industry.at Vadodara.

Kumar, S.(2001). "Determination of iodate and sulphate in iodized common saltby ion Chromatography with conductivity detection." Talanta53(4): 701-705.

Lajunen, LH, Perämäki. P.,(2004). Spectrochemical analysisby atomic absorption and emission. Cambridge UK. Royal Society of Chemistry; pp 6-8.

Levente, L., Diosady and Joseph O., Albert,(1998). Stability ofIodine in IodizedSalt Used for correction of iodine deficiency disorder.

Luqueno, F.F., Valdez,F.L., Melo, P.G., Suarez,S.L., Gonzalez,E.N.A., Martinez, A.I., Guillermo, M.S.G., Martinez, G.H.M., Mendoza, R.H., Garza, M.A.A. and Velazquez, R.P.,(2013).“Heavy metal pollution in drinking water - a global risk for human health: A review”. African Journal of Environmental Science and Technology, 7, 7, pp. 567-584.

Maria B., (2002). Sample digestion methods for determination of traces of precious metals By Spectrometric techniques, Analytical Science, 18,737-750.

Markus, J. &McBratney, A. B., (2001). A review of the contamination of soil with lead II. Spatial distribution and risk assessment of soil lead. Environ. Int, 27, 399-411.

Mendiratta, S.K. and Duncan, B.L., (1993). Chlorine oxygen acids and salts. Chloric acid and chlorates.InEncyclopedia of Chemical Technology, Kirk- Othmer, ed.Fourth Edition, John Wiley&Sons, New York, Vol.5, pp. 998- 1016.

Mohod, C.V. and Dhote, J., (2013). "Review of heavy metals in drinking water and their effect on human health", International Journal of Innovative Research in Science, Engineering and Technology, 2, 7, pp. 2992- 2996.

Morton salt, (2019). Salt Productionand Processing. https://www.mortonsalt.com/salt-production-and-processing/may 16/2019.

Nnorom IC, Osibanja O andOgugua K. ,(2007) .Trace heavy metal levels of some bouillon cubes, and foodcondiments readily consumed in Nigeria. Pak. J. Nutr. 6:122-127.

Ochieng, E. Z, Lalah, J. O.& Wandiga, S. O. (2007). Analysis of heavy metals in water and Surface sediment in five Rift Valley Lakes in Kenya for assessment of recent increase in anthropogenic activities.Bull.Environ.Contam. Toxicol, 79, 570-576.

Pourgheysari. H , Moazeni M, Ebrahimi.(2012). "Heavy metal content in edible salts in Isfahan and estimation of their daily intake via salt consumption".

Regassa, G.(2007). Investigation of metals in Ethiopia Tobacco leaves and processed. Tombacco.AAU, Dep. Of Chem., Faculty of Science.pp.37.

Sabatin, O., (2000). Salt production and processing in Jordan. In Proceedings, 8th World Salt Symposium ,R.Geertman, ed. Elsevier Science B.V., Amsterdam, Vol. 1, pp. 555-557.

Salem, H.M., Eweida, A.E., Farag,A.,(2000). "Heavy metals in drinking water and their environmental impact on human health", proceedings in ICEHM,CairoUniversity, Egypt, pp.542- 556.

Sedivy. V.M.,(1996). Purification of salt for chemical and human consumption. Industrial

Minerals.

Sedivy, V.M.,(2009). Processing of salt for chemical and human consumption. Volume 2, 1385-1402 of 9 th International Symposium on Salt (ISBN 978-7-80251-2139).4th-6th. Beijing International Convention Centre, Beijing, China.

Soylak M, Peker DSK and Turkoglu O.,(2008). Heavy metal contents of refined and table salts from Turkey, Egypt and Greece. EnvironmentalMonitoring and Monitoring and Assessment 143: 267-72.

Suhendra A., (2016). Increasing The Productivity of Salt Trought HDPE Geomembrane Indonesia Case History in Salt Evaporation Pond. EJGE 11:4272-4280.

Susanto H, Rokhati N, Gunawan W , Santoso.(2015). Development of Traditional Salt Production Proses for Improving Product Quality dan Quality in JeparaDistrict, Central Java.

Thomas Brinkmann,Germán Giner Santonja, Frauke Schorcht, Serge Roudier,Luis Sancho, (2014). Best Available Techniques (BAT) Reference Document for the Production of Chlor – alkali Industrial Emissions Directive 75/EU(Integrated Pollution Prevention and Control)

U.S.EPA.,(1999).“Drinking Water and Health” in reports of EPA 816- k-99-001.

U.S.EPA.,(1990). “Drinking Water Health Advisory for Molybdenum”, Prepared by the Office of Water.

USGAO., (2000). “Health Effect of lead in drinking water” in reports of U.S. General Accounting.

Wogu, M.D. and C.E. Okaka, (2011)."Pollution studies on Nigerian rivers: heavy metals insurface water of warri river, Delta State." J. Bio and Env Sci. 1: 7-12.

Wu,Y.,Hou,X., Cheng,X., Yao,S., Xia,W.&Wang,S.(2007).Combining geochemicaland Statistical methods to distinguish anthropogenic source of sediment: a case study in Dongjiu Lake, Taihu Lake catchment, China. Environ.Geol, 52,1467-1474.

APPENDICES

Appendix A:FAAS Analysis result

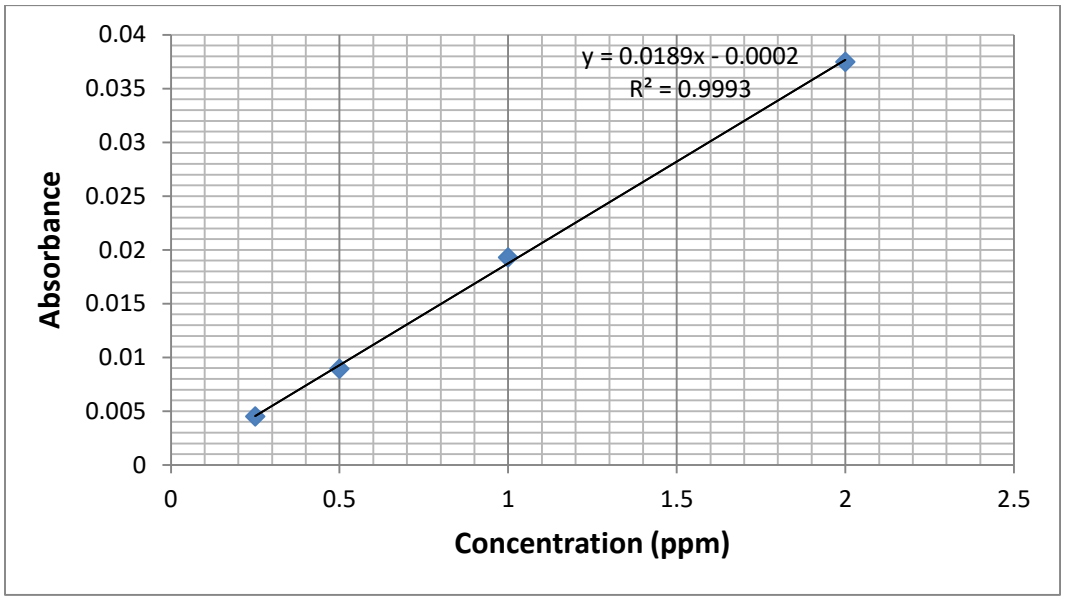

Figure A1: Calibration curve of Ca

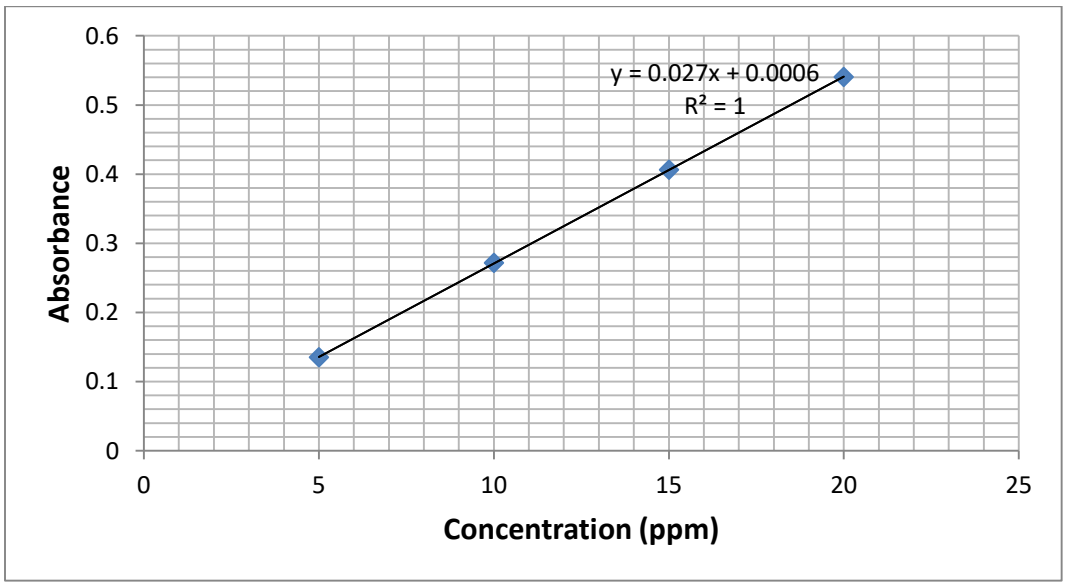

Figure A2: Calibration curve of Fe

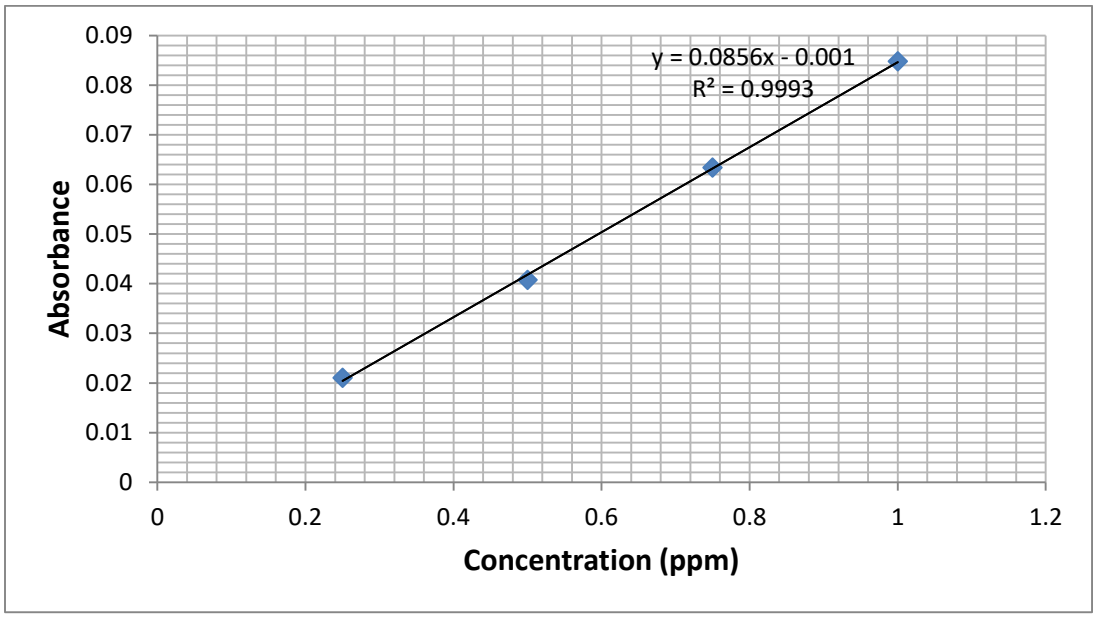

Figure A3: Calibration curve of Mg

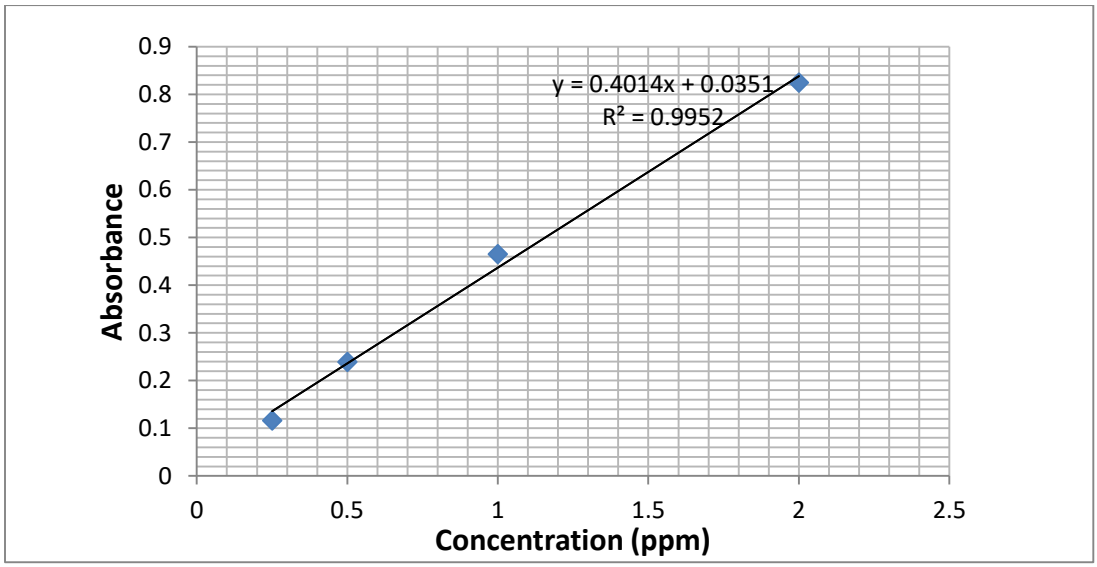

Figure A4: Calibration curve of Zn

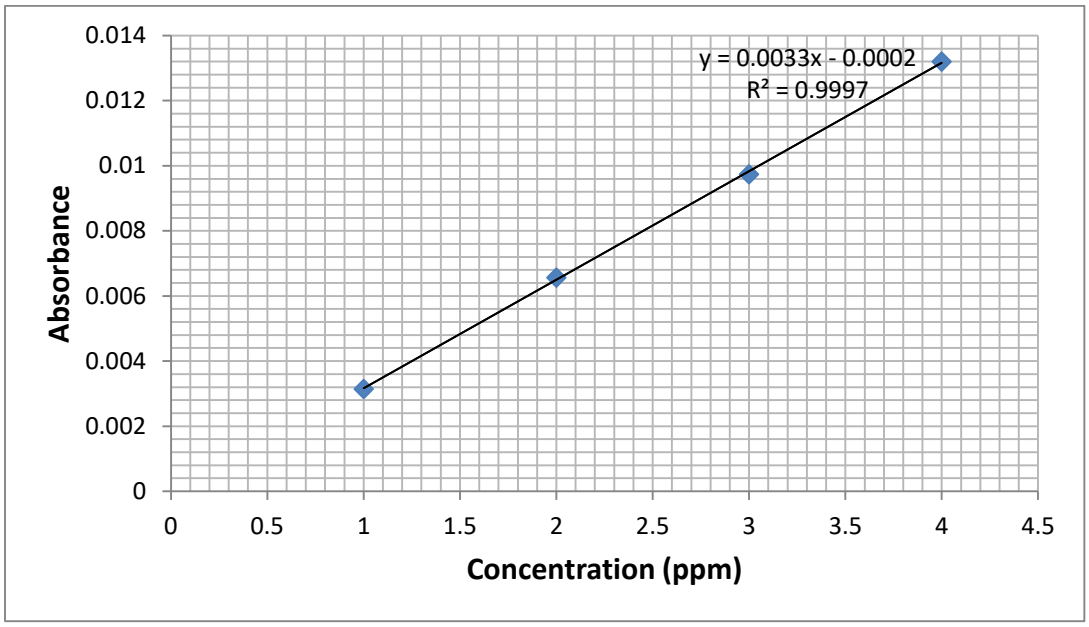

Figure A5: Calibration curve of Pb

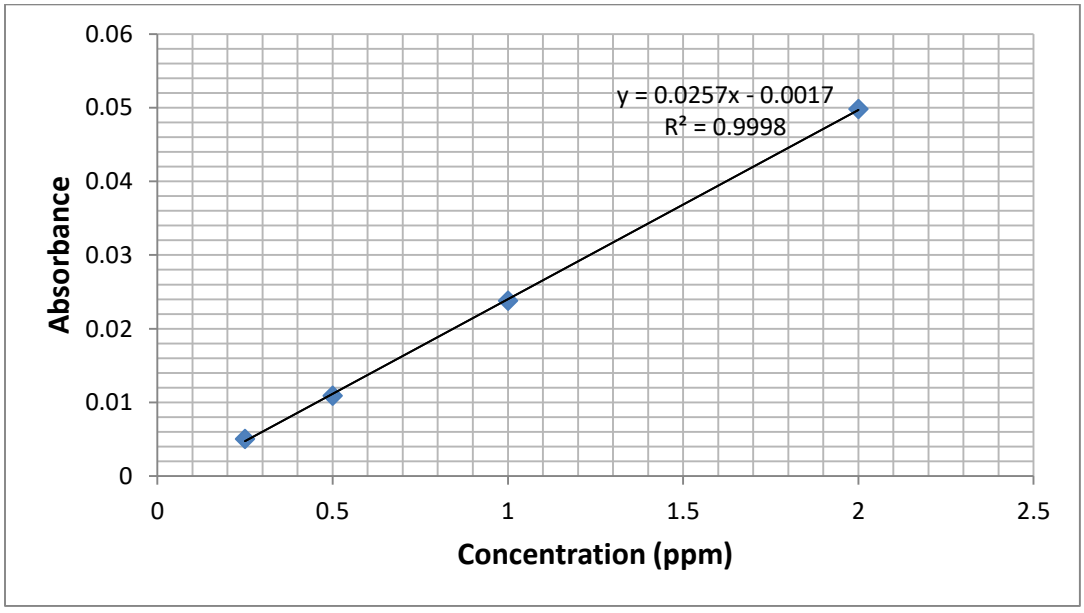

Figure A6: Calibration curve of Cu

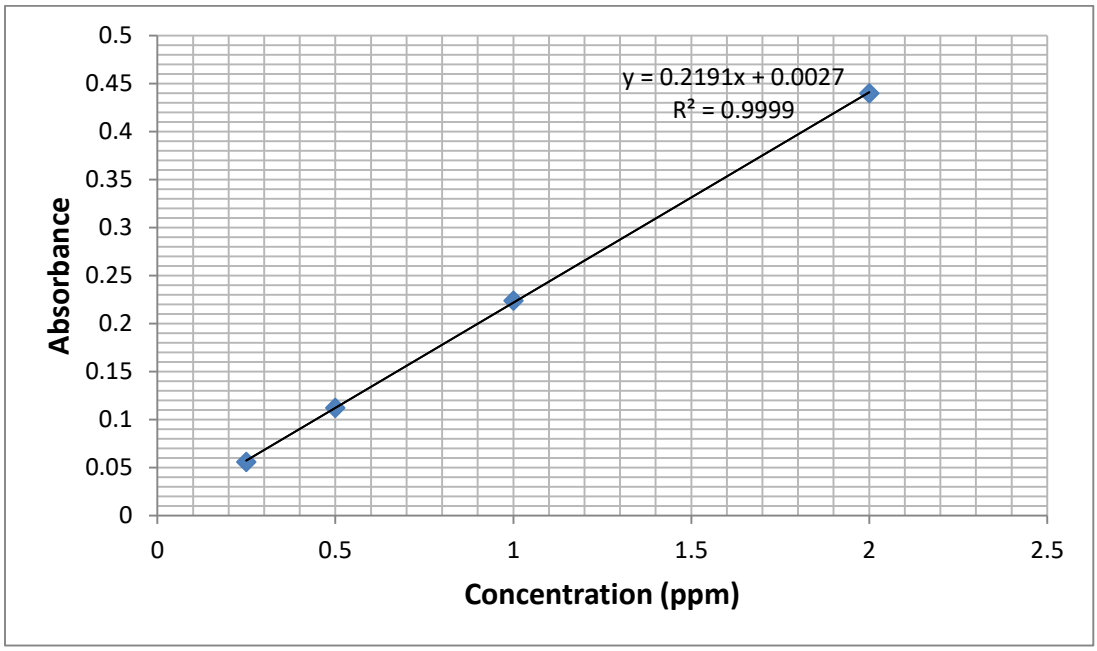

Figure A7: Calibration curve of Cd

Appendix B: Plots of individual Effect of process variables on salt of Afdera

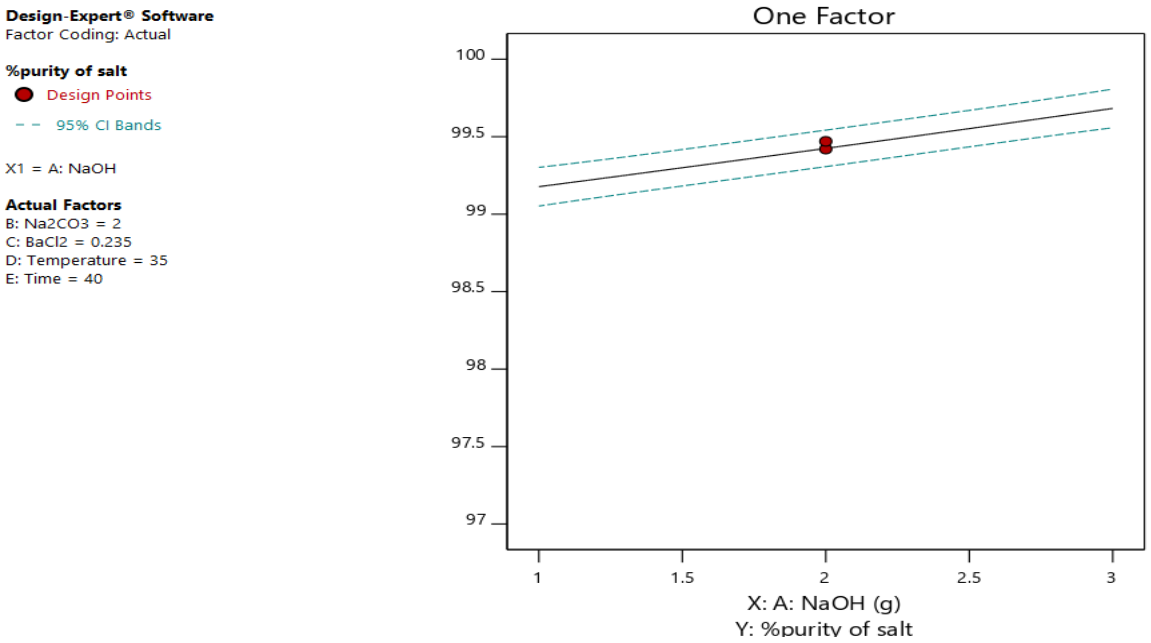

Figure B1: Effect of NaOH on purity of salt

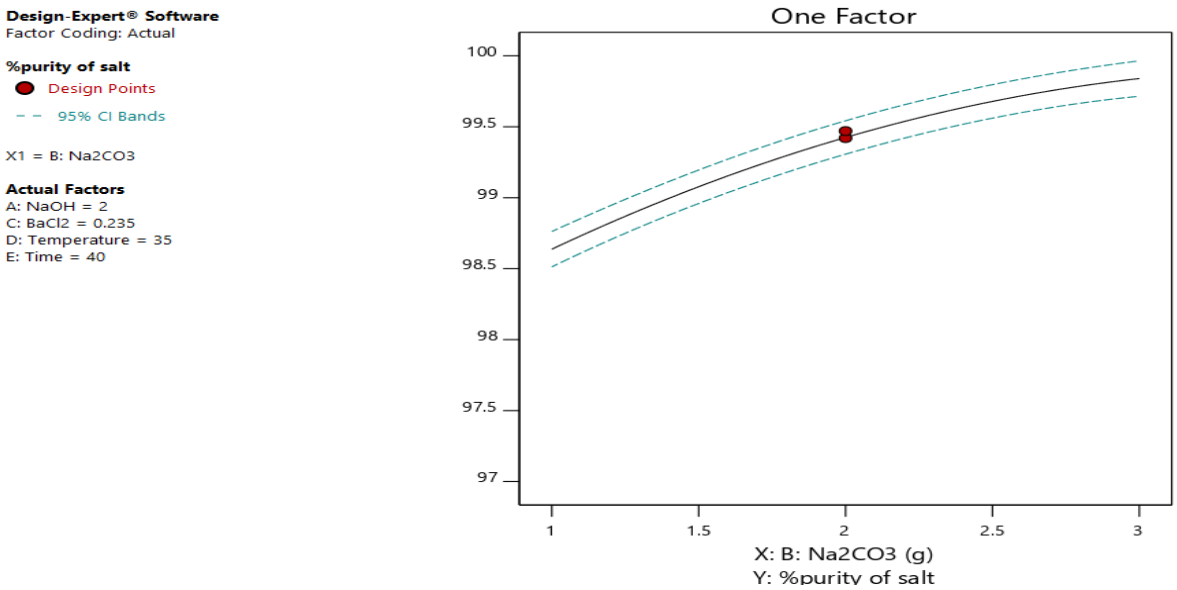

Figure B2: Effect of Na_2CO_3 on purity of salt

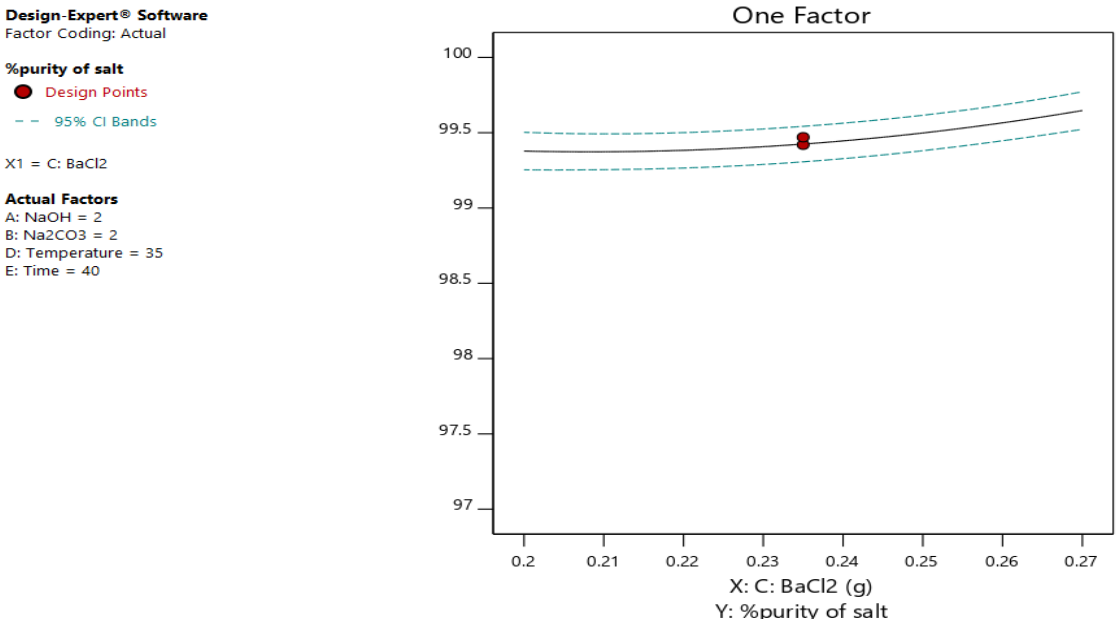

Figure B3: Effect of $BaCl_2$on purity of salt

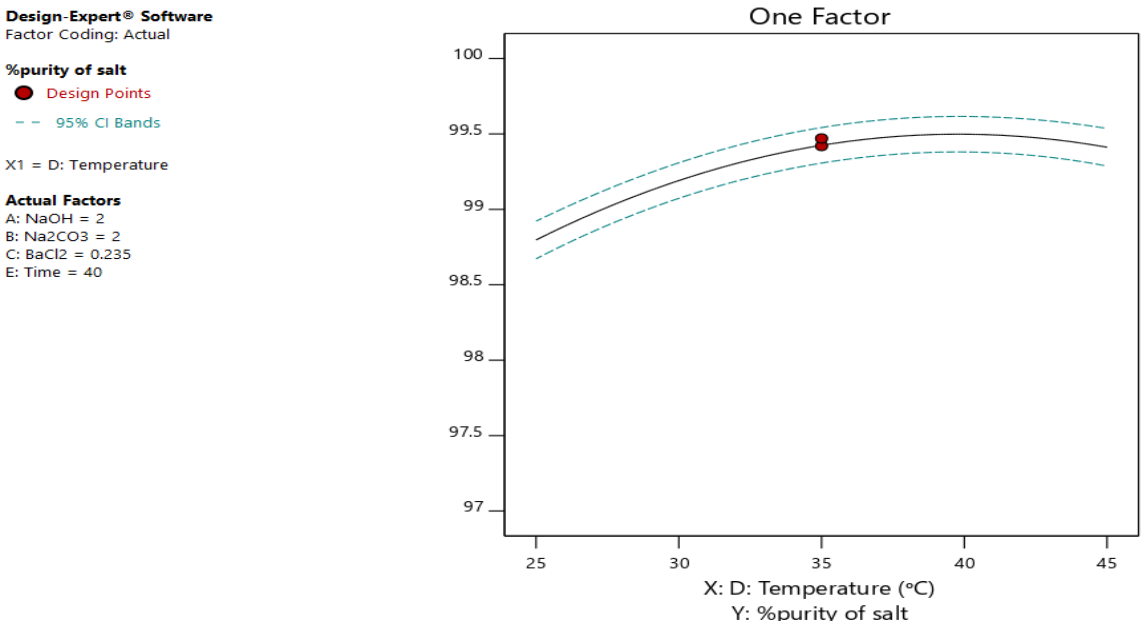

Figure B4: Effect of temperature on purity of salt

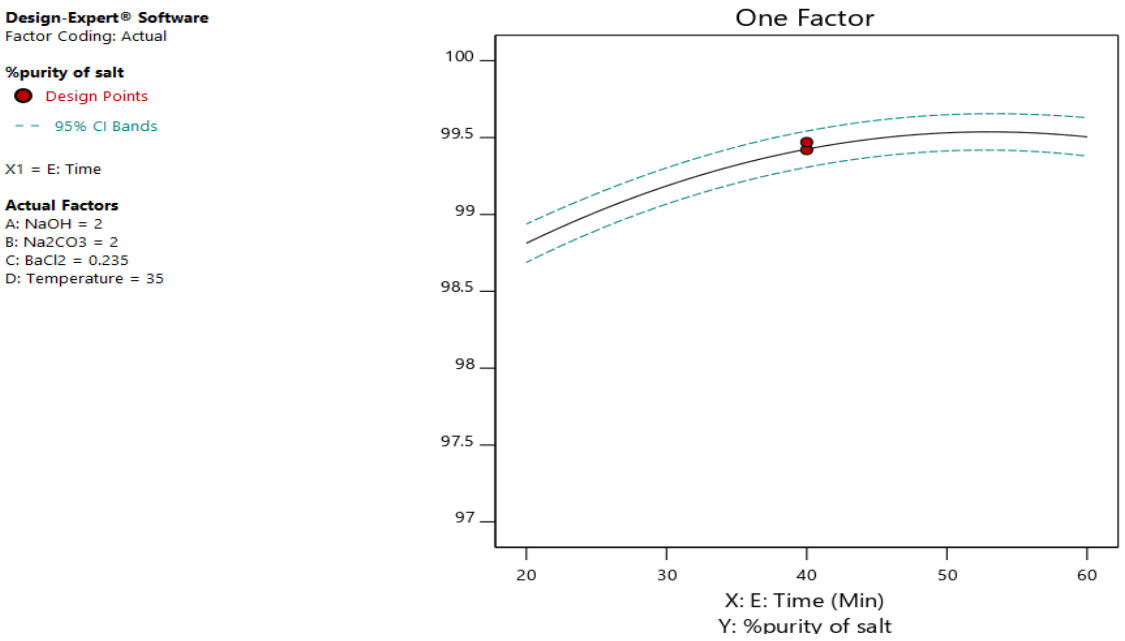

Figure B5: Effect of temperature on purity of salt

Appendix C: Individual and intreraction effect Plots of process variable on salt of Dobi

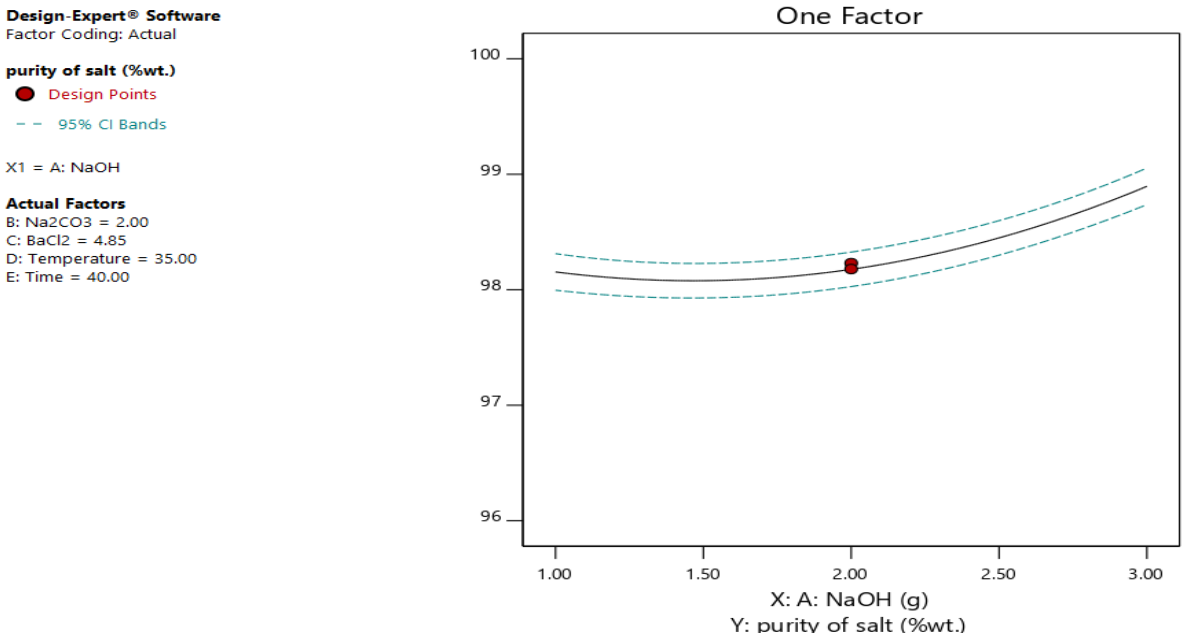

Figure C1: Effect of NaOH on purity of salt

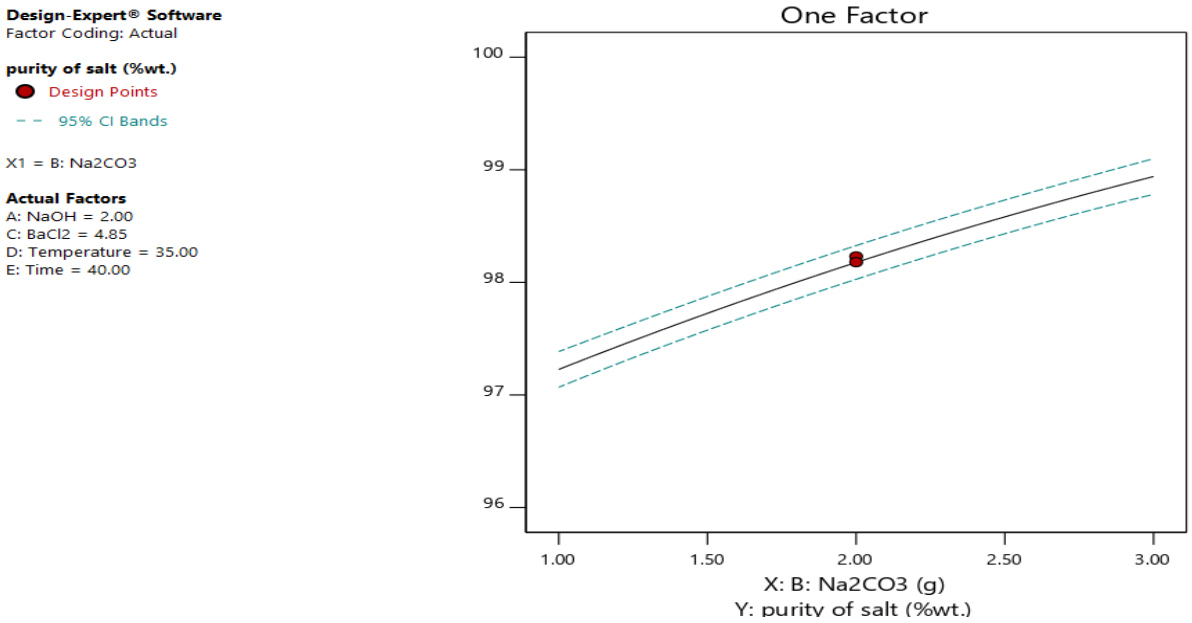

Figure C2: Effect of Na_2CO_3 on purity of salt

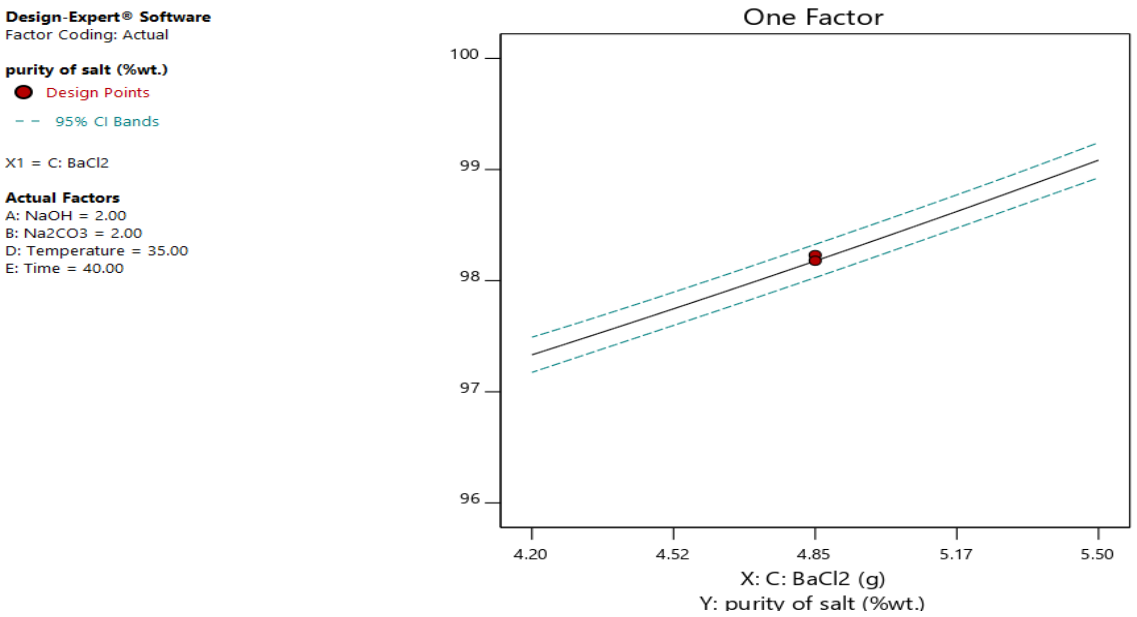

Figure C3: Effect of $BaCl_2$ on purity of salt

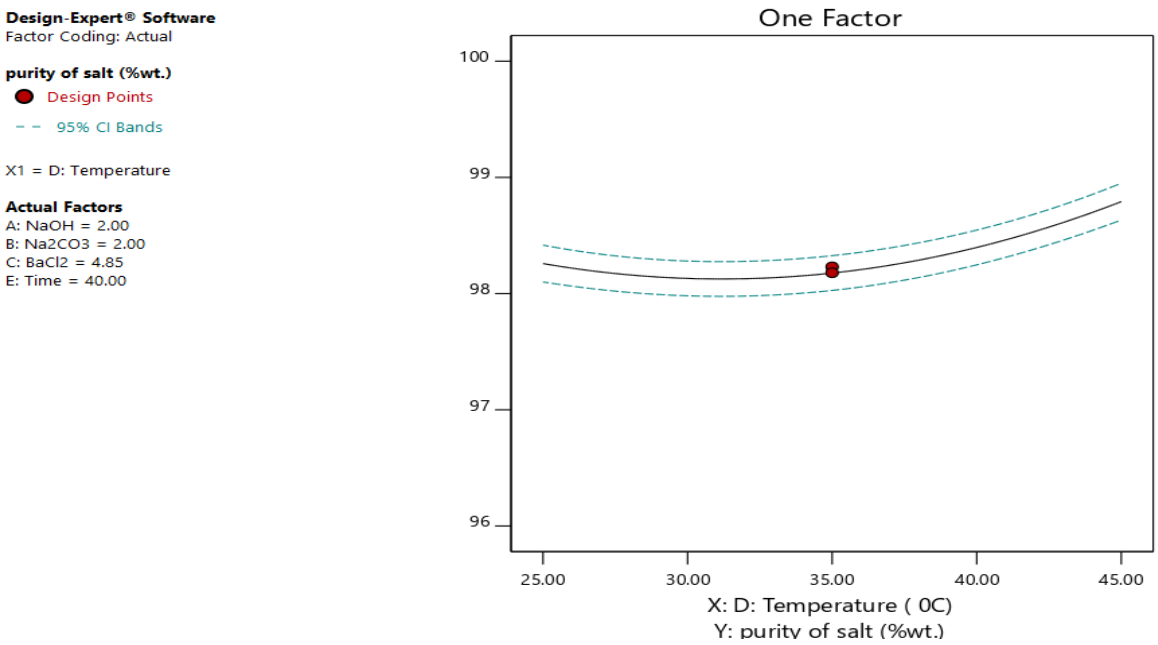

Figure C4: Effect of temperature on purity of salt

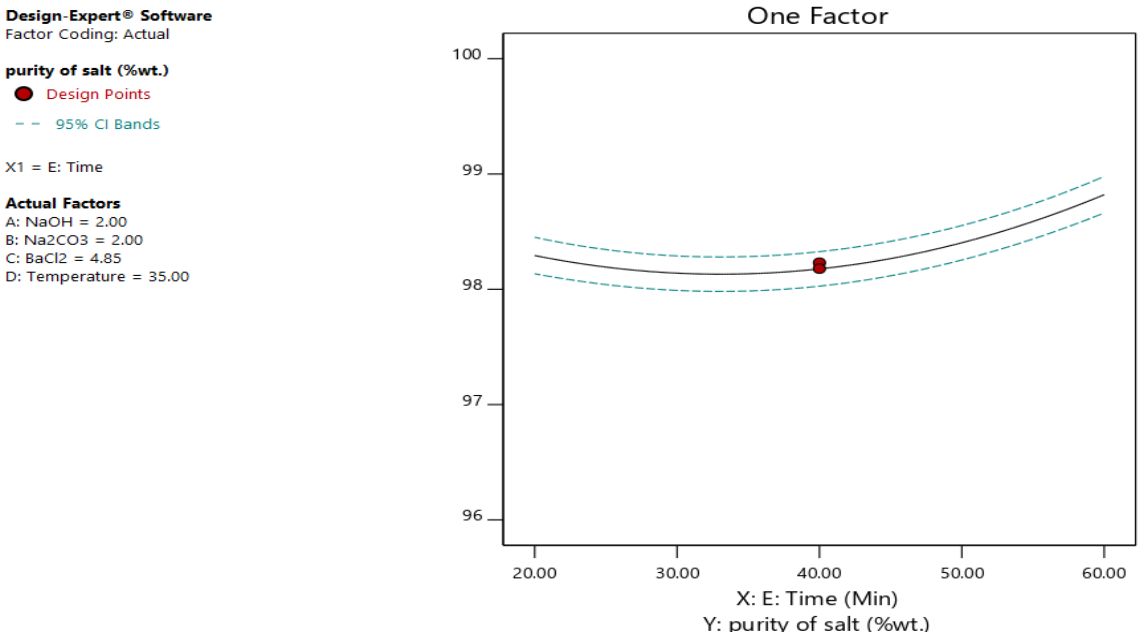

Figure C5: Effect of time on purity of salt

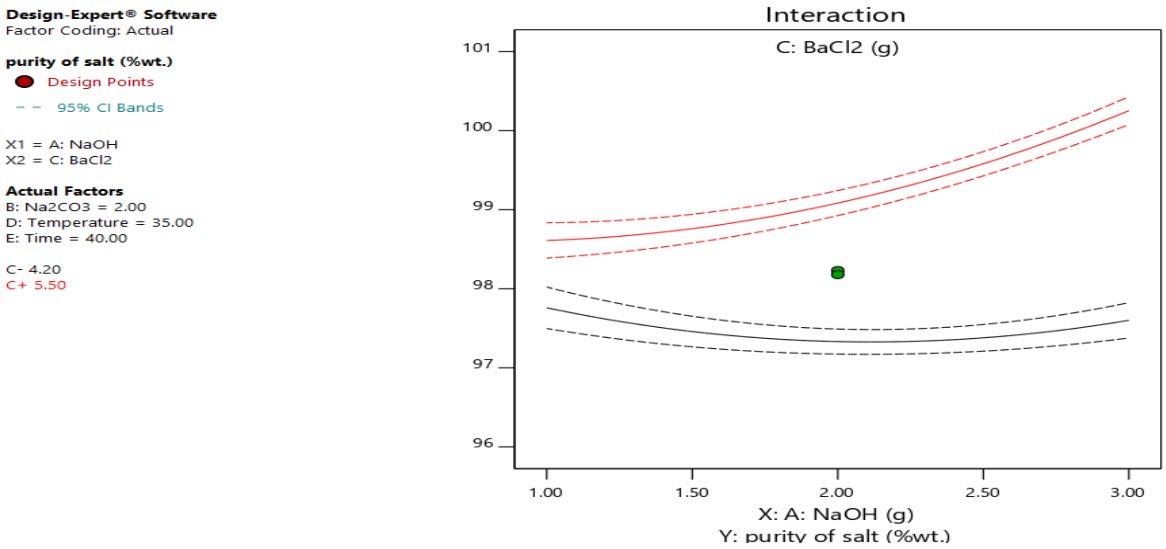

Figure C6: Interaction effect of NaOH and $BaCl_2$ on purity of salt

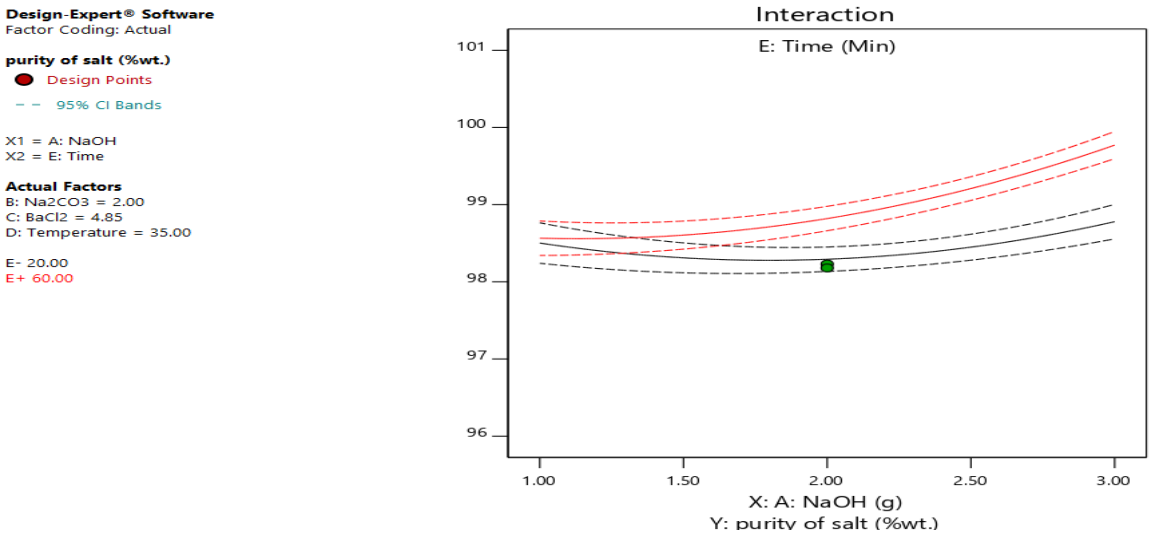

Figure C7: Interaction effect of NaOH and time on purity of salt

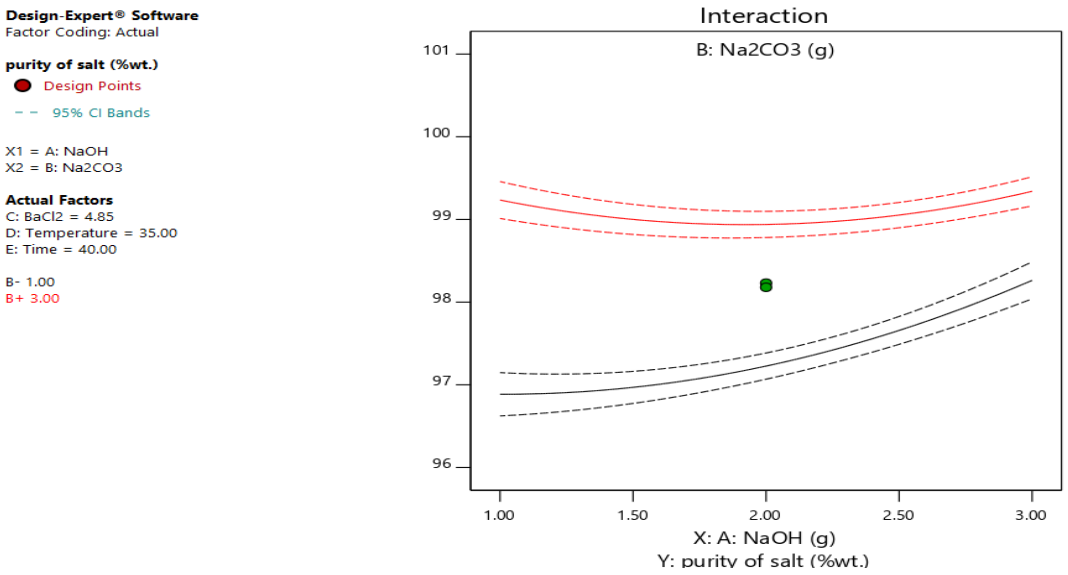

Figure C8: Interaction effect of Na_2CO_3 and Na_2CO_3 on purity of salt

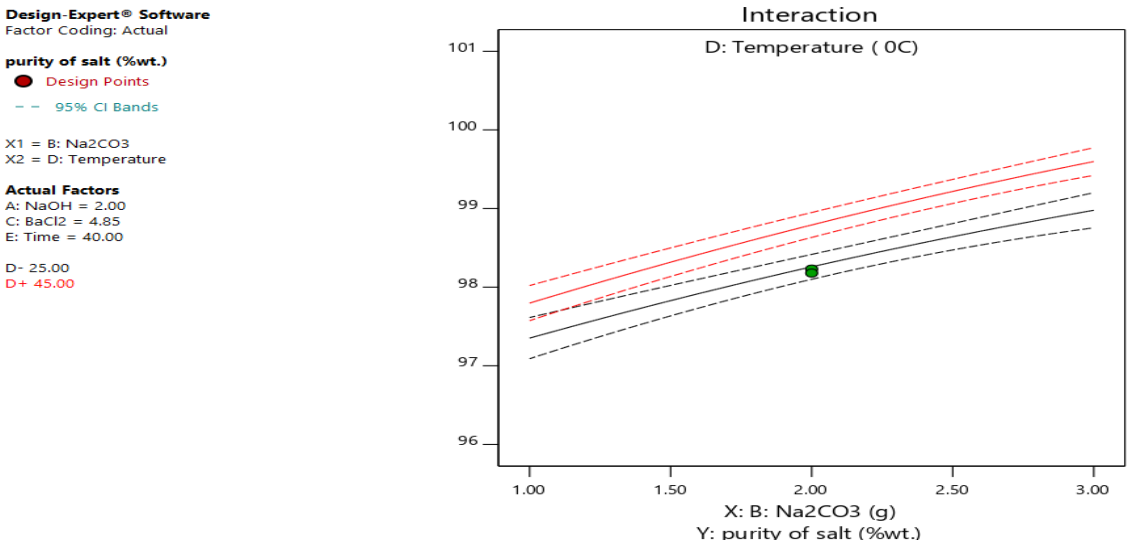

Figure C9: Interaction effect of Na_2CO_3 and temperature on purity of salt

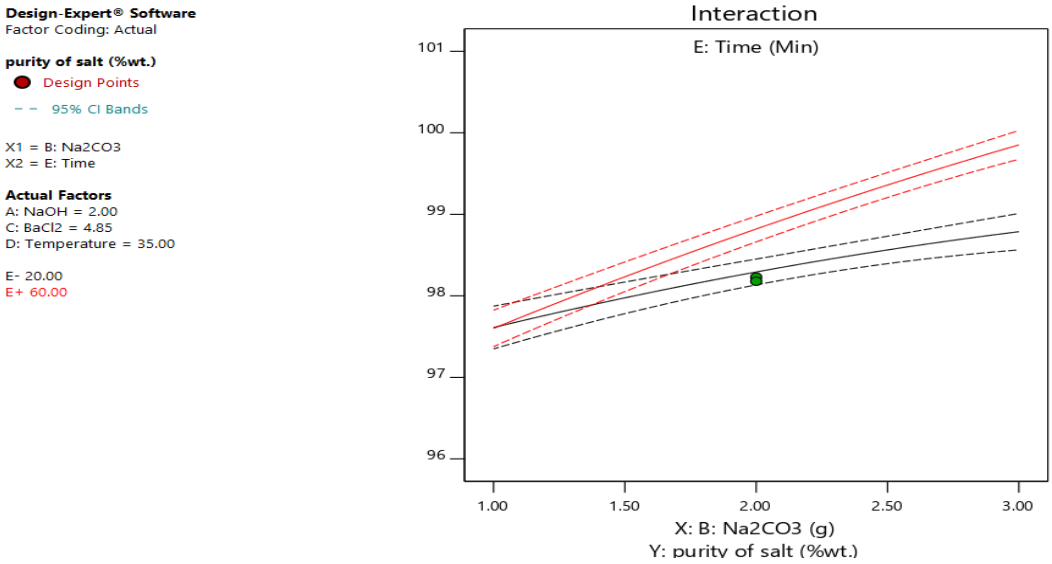

Figure C10: Interaction effect of Na_2CO_3 and time on purity of salt

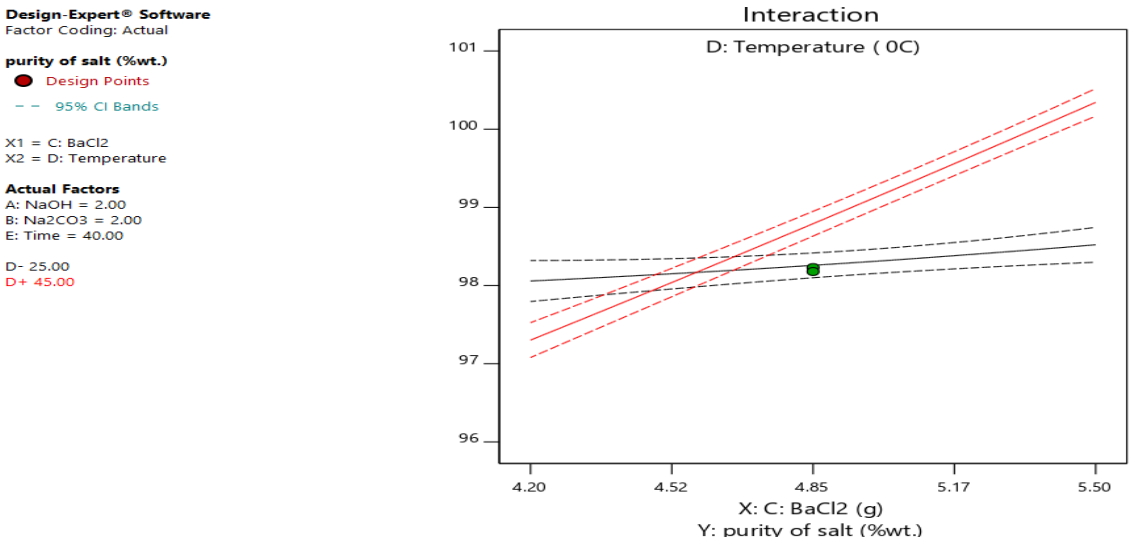

Figure C11: Interaction effect of $BaCl_2$ and temperature on purity of salt

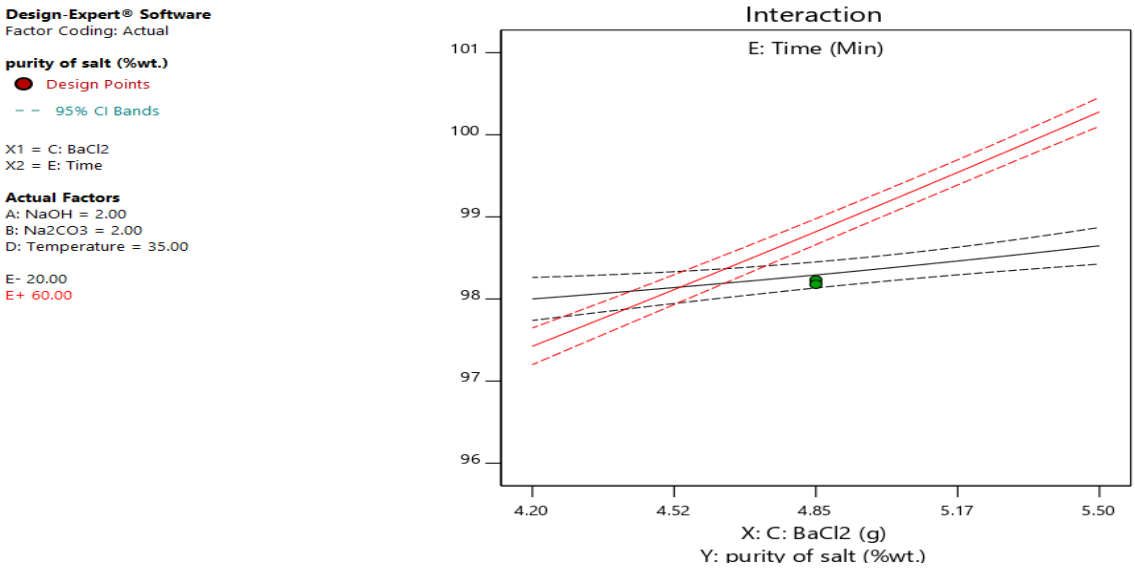

Figure C12: Interaction effect of $BaCl_2$ and time on purity of salt

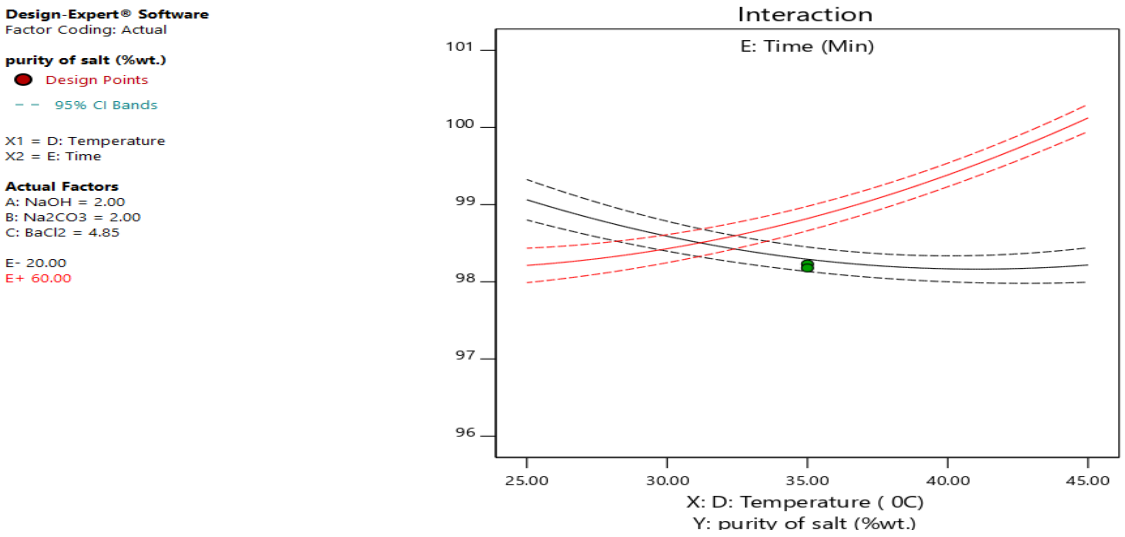

Figure C13: Interaction effect of temperature and time on purity of salt

Appendix D:Laboratory equipment and samples photo

Figure D1: Salt sample of a) Dobi b) Afdera

Figure D2: a) gravimetric precipitation of sulphat b) chemical treatment purification.

Figure D3: chloride test of salt samples using $AgNO_3$ and KCr_3 indicator

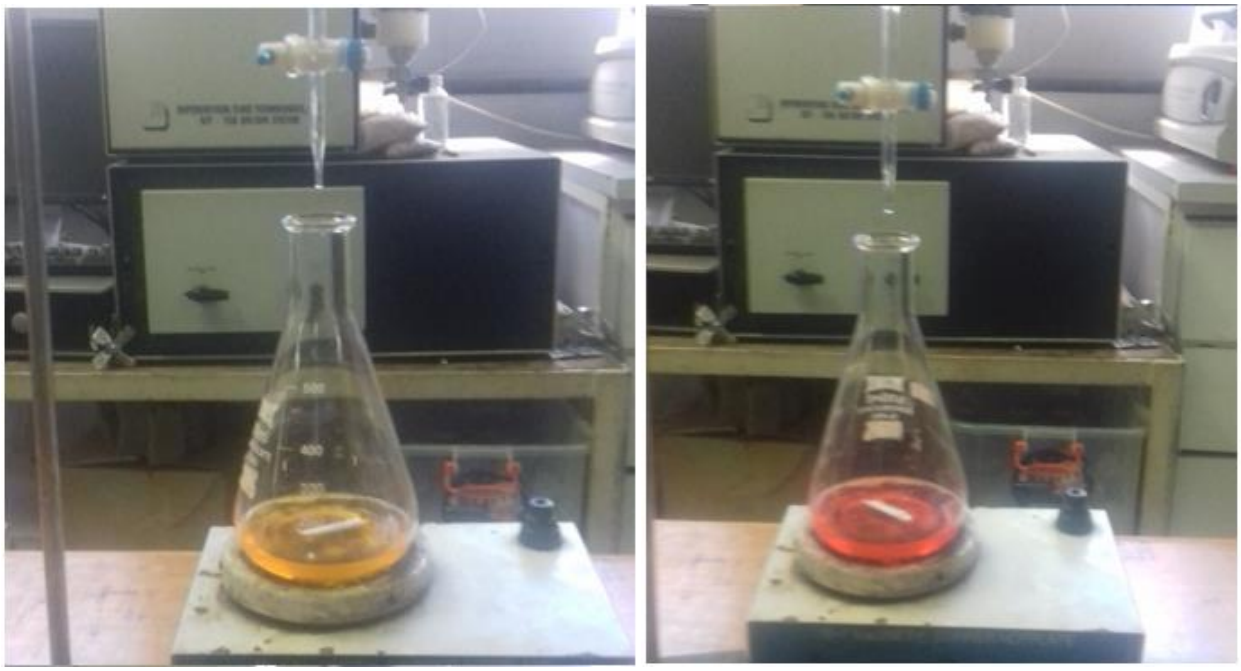

Figure D4: alkalinity test of salt using methyl orange indicator

Figure D5: a) filtration of salt solution b)Flame atomic absorption spectrometer

Appedix E: Methods of Analysis (AOAC)

Analysis of Moisture Content (AOAC1999)

1. Dry the empty dish and lid in the oven at 105°C for 3hr and transfer to desiccator to cool. Weigh the empty dish and lid.
2. Weigh about 3 g of sample to the dish. Spread the sample with spatula.
3. Place the dish with the sample in the oven for 3 hr at 105°C.
4. After drying, transfer the dish with partially covered lid to the desiccator to cool. Reweigh the dish and its dried sample.

Determination of Alkalinity (AOAC 1998)

1. Soak the flasks with nitric acid solution overnight.
2. Wash the flasks by carbon dioxide free distilled water.
3. Weigh 20g of sample.
4. Dissolve the sample in one liter of double de-ionized water and filtered the solution.
5. Pour 50ml of the filtrate to the flask and add 2ml of methyl orange indicator.
6. Titrate the solution with 0.1N hydrochloric acid.