ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

PRODUCTION, CHARACTERIZATION, AND OPTIMIZATION OF BRICKS MADE FROM A MIXED TANNERY SLUDGE AND MUNICIPAL WASTE INCINERATION BOTTOM ASH (MWIBA)

A Thesis in Environmental Engineering Stream

By
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A Thesis

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Engineering

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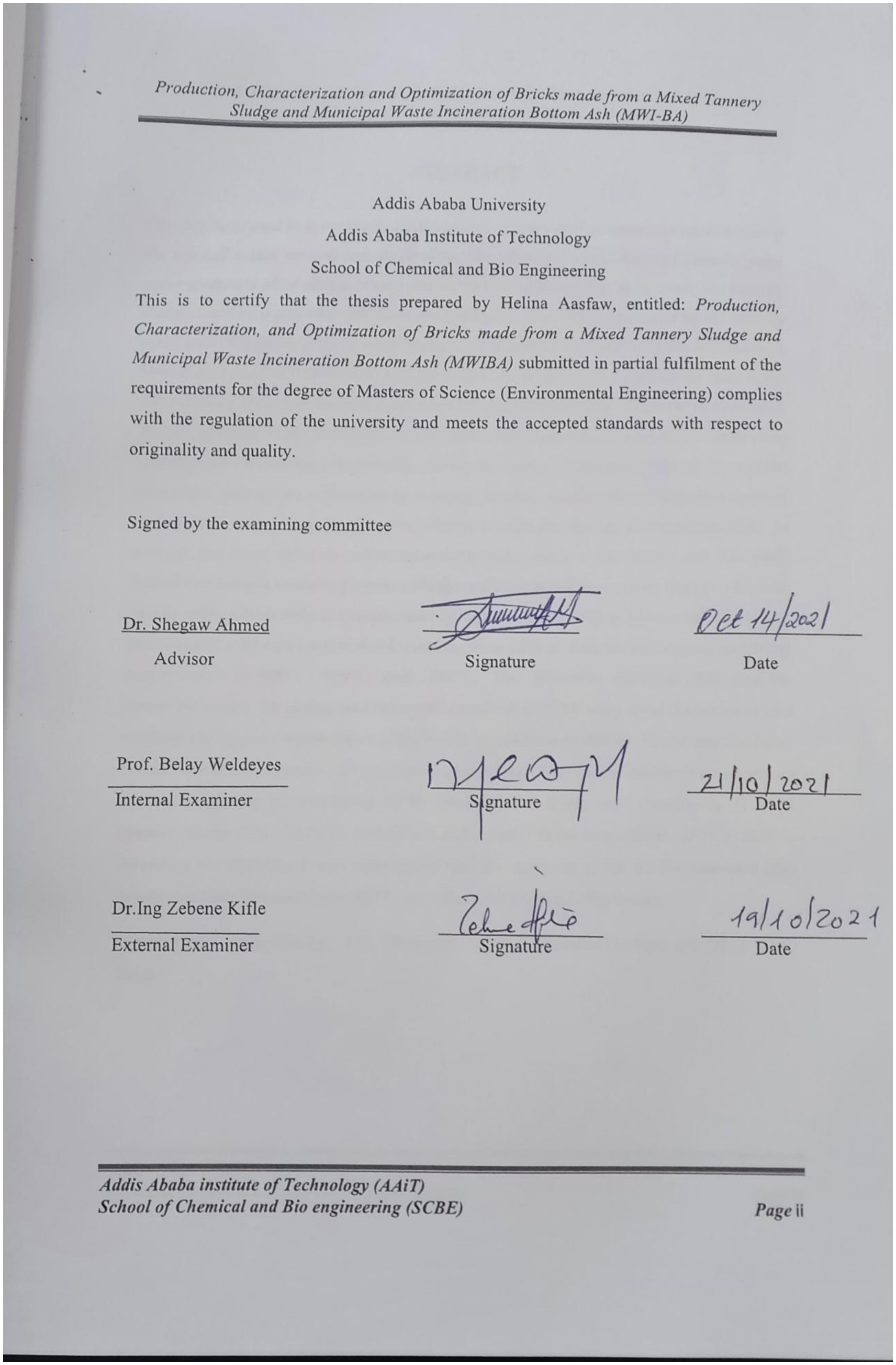

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This is to certify that the thesis prepared by Helina Aasfaw, entitled: *Production, Characterization, and Optimization of Bricks made from a Mixed Tannery Sludge and Municipal Waste Incineration Bottom Ash (MWIBA)* submitted in partial fulfilment of the requirements for the degree of Masters of Science (Environmental Engineering) complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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ABSTRACT

Clay has been used to make bricks for thousands of years and a continuous exploitation of the top soil makes the soil loss its fertility. The chemical composition of tannery waste water treatment plant sludge is very similar to that of brick clay. As a result, the tannery sludge could be a potential substitute for brick clay. The sludge produced by the tannery waste water treatment process must be disposed of in an environmentally friendly manner. Most sludge created in treatment systems across the world is released into an open dump site, resulting in carbon emissions and harmful heavy metal leaching into the environment. The use of sludge in the production of constructional materials is regarded the most cost-effective and environmentally friendly alternative among all disposal methods. One of the waste materials emanated from waste to energy facility, which contain high silica content, and might be incorporated with tannery sludge in brick production, is bottom ash (BA). As a result, this trend offers an environmentally friendly way to reuse bottom ash. The study looked into using a mixture of tannery sludge and bottom ash to partially replace clay soil. In this study, fifteen different proportions of tannery sludge (TS) to bottom ash (BA) were investigated, with replacement levels ranging from 10% to 30% for each waste and firing temperatures of 800°C, 900°C, and 1000°C. The Ethiopian standard (ES) and the American society for testing and materials standards (ASTM) were used to determine and evaluate the engineering qualities of the bricks. In addition to this the TS-BA amended clay bricks were also compared with the control clay bricks. After the production was optimized the best conditions for producing TS-BA amended clay bricks were found to be 11.69 % tannery sludge (TS), 10.16 % bottom ash (BA), and a firing temperature (FT) of 800°C. Based on the findings, it was determined that the majority of the TS-BA amended clay bricks met both Ethiopian and ASTM specifications for fired clay bricks.

***Key words**:* Tannery sludge (TS), Municipal waste incineration bottom ash (BA), Clay, Brick

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF EQUATIONS

LIST OF ACRONYMS

AAS	Atomic Absorption Spectrometry
ANOVA	Analysis of Variance
ASTM	American society for testing and materials association
BA	Bottom Ash
BBD	Box-Behnken design
CV	Coefficient of Variation
CS	Compressive Strength
EPA	Environmental Protection Agency
ES	Ethiopian Standard
FAAS	Flame Atomic Absorption Spectrometry
FT	Firing temperature
MWIBA	Municipal Waste Incineration Bottom Ash
RSM	Response surface method
TCLP	Toxicity characteristics leaching procedure
TS	Tannery Sludge
tpa	Tons per annum
USEPA	United States Environmental Protection Agency
WA	Water Absorption
XRD	X-ray Diffraction

CHAPTER 1 INTRODUCTION

1.1 Background

One of the major emerging environmental problems in the tanning industry is the disposal of chromium contaminated sludge produced as a by-product of wastewater treatment (Ahamed & Kashif, 2014). Usually, about 100-150 kg of sludge is generated per ton of hides/skins processed and this chromium-rich sludge has the potential to contaminate soil, surface water, and groundwater by generating leachate and pose a threat to the environment and natural resources if the sludge is not disposed of properly (Swarnalatha et al., 2006). Several trials have been reported in Bangladesh, Lithuania, India, and other parts of the world to use tannery sludge in various industrial and commercial manufacturing processes. Studies have been carried out on using tannery sludge in brick and cement mortar. Due to the similar mineralogical composition between brick clay and tannery sludge, the use of tannery sludge in brick production has been encouraged.

A couple of trials have been reported in this purpose. In a study that was conducted in Bangladesh, the researchers have manufactured bricks from clay to which tannery sludge was amended. The researchers evaluated the suitability of utilizing tannery sludge in the production of clay bricks. Different proportions (10, 20, 30, and 40 wt. %) of tannery sludge have replaced the clay. Each series was fired at different firing temperatures between 900 ℃ and 1000℃. The test results exhibited that water absorption increased and the compressive strength decreased with increasing tannery sludge contents and firing temperature.

However, 10% of tannery sludge by weight was concluded to be an optimum constituent for tannery sludge–amended brick. Moreover, the firing energy was confirmed to be saved up to 15-47% by incorporating 10-40% tannery sludge content. The study concluded that incorporating tannery sludge is promising to produce decent quality bricks that can fulfill all the requirements prescribed in ASTM standard (Juel et al., 2017a). In another study that was carried out in India, researchers blended tannery sludge with quarry dust and cement to make bricks. The study used tannery sludge as a partial replacement for clay at a 20%, and 30% by weight replacement level. The conclusion of the study indicated that 20% was the optimum tannery sludge addition to produce brick (Swarna & Venkatakrishnaiah, 2014).

Municipal waste incineration bottom ash should, also, be handled and disposed of in an environmentally sound manner. In Addis Ababa, Ethiopia, annually the waste to energy facility incinerates 420,000 tons of solid waste with residues of 100,400 tons of bottom ash. Several trials have been made in different countries to use bottom ash as an aggregate in concrete, road paving product, subgrade materials, and in some other industrial uses such as brick making. In Bangladesh, bricks were made from clay with different percentages of municipal waste incineration bottom ash. Various proportions (10, 20, 30, 40, and 50 wt. %) of bottom ash were used to replace the clay. The firing temperatures were ranged from 800 to 1100℃. Test results indicated that the compressive strength of the bricks was decreased as the proportion of bottom ash increased from 10-50% and the water absorption was increased when the proportion of bottom ash increased (Haque, O. 2011).

From the previous researchers, it is clear that tannery sludge and bottom ash could be used in the production of clay brick separately. In this study, both tannery sludge and bottom ash were used to partially replace the clay with a replacement level of 10-30% for each. Fifteen brick specimens were prepared with different proportions of tannery sludge and bottom ash in laboratory-controlled conditions and their suitability as an engineering material was assessed based on their engineering properties i.e., compressive strength and water absorption as well as its environmental implications. The constant consumption of clay and withdrawal of the topsoil for clay brick manufacturing cause generous exhaustion of virgin assets and this causes the agricultural soil to lose its fertility. So, substituting the clay with these wastes plays a vital role in terms of protection of the natural resource.

1.2 Statement of the problem

The development of the country into industrialization and population growth plays a vital role in the immense generation of waste from industries, households as well as commercials. For cities and countries with a high population density, the disposal of municipal wastes primarily solid wastes or incineration residues and sewage sludge specifically tannery sludge has been an issue of concern. The increase of municipal solid wastes has become a major problem in several countries including Ethiopia. An attractive method for this waste management is incineration because it can reduce the volume of waste by about 90%. However, the incineration process still leaves a large number of solid residues (i.e., bottom ash and fly ash) which require a huge disposal landfill.

The Reppi waste-to-energy facility located in Addis Ababa, Ethiopia is the first waste-to-energy facility in Africa. It produces electricity by incinerating municipal solid wastes collected from the capital. The facility was opened and begun operation in August 2018. The facility has a capacity of incinerating 420,000 tpa of solid waste with residues of 100,400 tpa of bottom ash and 15,210 tpa of fly ash. With the increase of municipal solid waste incineration, these by-products will soon have no place to store and can only be piled up or landfilled at will, which will take up land resources. After incineration, the heavy metals remain in fly ash and bottom ash and whenever they are in contact with soil or water, the environment will be polluted and people’s health will be threatened. According to the company’s personnel, currently, they are disposing of the bottom ash into the nearby water bodies. But in the future, they plan to use it as a landfill cover in the new sendafa landfill site.

However, the use of ashes in landfill cover may result in the release of inorganic salts and heavy metals into the environment. Ashes in contact with a liquid phase can result in mass transport of pollutants into a liquid phase and generate leachate. The potential environmental impact of ashes used in the construction of landfills regarding leaching is the contamination of soil, groundwater, and surface water bodies. Released heavy metals and salts from ashes could be taken up by plants and lead to contamination through the trophic chain (Travar et al., 2007).

In Ethiopia there are 34 tanneries that consume 20 million skins and 8 million hides in average per year. In tannery industries, they use chromium salt for their tanning process. Due to this, the sludge emanated from their waste water treatment plant is rich in chromium. In addition to this, the sludge contains high amount of organic matter so that there will be an emission of carbon when it is degraded through time. Currently, the factory's wastewater treatment plant, which treats the effluent of the factory, generates 1000 kg of sludge every week, and a pressure filter press is used to solidify the sludge and form a cake. At this time, the factory doesn't use its sludge for any other purpose. Instead, they dispose of their solid waste (dried cake) at Ayer Tena open dumpsite using their garbage trucks.

One of the methods of waste management is landfilling. But, to construct a landfill site that meet the specific environmental protection requirements needs high amount of investment cost. So, diverting the wastes into a useful product is important. As it is mentioned above, the disposal method used in each case causes a significant impact on the environment when these wastes are disposed to the open dump sites and water bodies. By its very nature tannery sludge contains an elevated concentration of heavy metals like Cr, Ni, Co, and Zn. Due to the use of basic chromium salts, dyes, and pigments. These poisonous chemicals and toxic waste products create air, water, and soil pollution which all severely impact the environment. So, there is a need to find out alternative ways to manage these wastes. On the other hand, the constant consumption of clay and withdrawal of the topsoil for ordinary brick manufacturing cause generous exhaustion of virgin assets and this causes the agricultural soil to lose its fertility. So, it is important to look for a potential substitute for clay, especially from waste.

Since tannery sludge has high amount of organic matter, it has high heating value. On the other hand, MWI-BA has high amount of silica content. So, during combustion or firing process of TS-BA amended clay brick, the sludge can be used as an energy source whereas the BA could be used as a source of silica. Thus, taking the nature and composition of tannery sludge and MWI-BA into consideration, they are mixed with clay soil in different proportions to make bricks.

1.3 Objectives

1.3.1 General Objective

The general objective of this research was to produce, characterize and optimize bricks made from a mixed tannery sludge (TS) and municipal waste incineration bottom ash (MWI-BA).

1.3.2 Specific Objectives

- To characterize the raw samples (Municipal Waste incineration Bottom Ash (MWIBA), Tannery Sludge (TS), and Clay).
- Production and characterization of bricks using
  - A mixed tannery sludge and municipal waste incineration bottom ash
  - Clay
- Optimization of the above production.

1.4 Research output

This study plays a vital role in the management and utilization of the tannery sludge and Municipal waste incineration bottom ash as a raw material for brick production. It also contributes to economic and environmental benefits by reducing the consumption of virgin materials required per unit produced, reduction in the waste disposal fee and avoidance of environmental contamination by the diversion of solid waste from landfills, and placement of waste in a sound, inert and useful medium and thereby contribute to sustainability.

CHAPTER 2 LITERATURE REVIEW

2.1 Research on bricks

Brick is perhaps the main construction component. The historical backdrop of brick-producing returns is 8000 years when the creation of the earliest sun-dried mud bricks was found (Hegazy et al., 2012). Brick has a place with a wide group of construction materials since it is principally utilized for the construction of external and internal dividers in buildings. Bricks have been principally manufactured from clay and shale for quite a long time. The constant extraction of clay and withdrawal of the topsoil for ordinary brick manufacturing cause generous exhaustion of virgin assets. Plus, the collection of unmanaged wastes has brought about landfill shortage just as genuine natural pollution.

Accordingly, engineers were obliged in tracking down a feasible answer for saving the virgin assets. In previous studies, Researchers went through assembling bricks from different wastes, for example, water treatment residual, bottom ash, granite sawing waste, paper sludge, straw fibers, fly ash, rice husk ash, and silica fume. Mechanical and physical properties (compressive strength and water absorption) of the bricks, which were manufactured from the previously mentioned wastes, were impressively encouraging; fulfilling, and qualified to be utilized in different building applications (Shakir et al., 2013).

The increasing demand for using a construction material that has a minimal cost, lightweight, and with no negative impact on the environment makes researchers look for a way to produce a material that meets the standard set for the construction materials and benefits the environment. Reusing wastes coming from industrial and agricultural activities for the production of construction materials become the best solution to avoid environmental pollution as well as the high cost of construction. Sludge created at wastewater treatment plants ought to be free from toxic chemicals and it should be controlled in an environmentally acceptable way.

The conventional act of releasing the sludge straightforwardly into a close-by stream is turning out to be unacceptable since it can disregard the admissible stream guideline. The release of sludge into the water body increases the concentration of aluminum in the water, aquatic organisms, and in human bodies.

The water treatment plant sludge is amazingly near brick clay in the chemical constituent. Along these lines, the sludge could be an expected substitute for brick clay. Among all removal alternatives, the utilization of sludge in producing constructional components is viewed as the most economic and environmentally sound choice (Hegazy et al., 2012). One of the most common industrial wastes, which contain high silica content, and might be incorporated with sludge in brick production, is Municipal waste Incineration Bottom Ash (MWIBA). Using Bottom ash as a construction material enables the utilization of a large number of waste by-products thereby reducing the adverse effects on the environment and the ever-increasing pressure on natural resources. The use of bottom ash could also lead to favorable properties to concrete and masonry units because of its silica content. The health risks from the use of ash in construction appear minuscule as compared to its advantages. So, this trend provides an environmentally sound manner to reuse municipal waste incineration bottom ash.

2.2 Overview of waste materials used in the production of brick

Due to the demand for bricks as building materials, many researchers have investigated the potential wastes that can be recycled or incorporated into fired clay bricks. Different types of waste have been successfully incorporated into fired clay bricks by previous researchers, even in high percentages. From the literature reviews related to the inclusion of waste materials, they vary from the most commonly used wastes such as the various types of fly ash and sludge, to sawdust, kraft pulp residues, paper, polystyrene, processed waste tea, tobacco, grass, spent grains, glass windshields, PVB-foils, label papers, phosphogypsum (waste used by phosphoric acid plants), boron concentrator and cigarette butts. The utilization of these wastes will help to reduce the negative effects of their disposal. However, the potential wastes can only be recycled if the properties and the environmental pollutant of the newly manufactured brick meet the specific requirements and comply with the relevant standards (Kadir & Mohajerani, 2011). In this review, wastes used in bricks will be discussed.

2.2.1 Sludge

Sludge is a waste material emanated from different sources such as sewage treatment plants, paper industries, tannery industries, and so on. Some studies were done to check the possibility of using sludge as a raw material for construction purposes. In previous studies, researchers tried to produce bricks from a municipal wastewater sludge mixing it with clay. 10% to 40% of sludge proportion was used with a firing temperature of 1080 °C. From this study, it was observed that the increased proportion of sludge affects the water absorption of the brick negatively (Tay, 1987).

Another study on the production of bricks from sewage sludge was conducted. In this study, 10% to 40% of dried sludge was used as a raw material with a firing temperature of 985°C and the brick was hand-molded. For the brick made with the addition of 40% sludge, the water absorption of the brick increases by up to 37% compared to the control brick whose water absorption is 23.6%, and the compressive strength is reduced to 2MPa against 15.8MPa for the control brick. From this study, the researchers concluded that the proportion of the sludge incorporated shouldn’t exceed 30% by weight due to its brittleness (Liew, Idris, Wong, et al., 2004).

Tannery sludge was another waste that was used as a raw material for brick making. In this study, tannery sludge and clay were mixed with different proportions (9%, 10%, 20%, and 30%) of tannery sludge and firing temperature (1000℃, 1100℃, and 1180℃). The paste was shaped in the mold using a hydraulic press. Tests were done to determine the properties of the brick. From the test result, the increment in the water absorption value was observed as the proportion of sludge increases. The compressive strength of the brick increased with a higher firing temperature and smaller sludge addition.

2.2.2 Fly ash

Numerous researchers worked on reusing fly ash for brick production. Various fly ash to clay ratios ranging from 1:10 to less than 1:1 and 40% to 100% fly ash was used in previous and most recent studies. One of the benefits of using fly ash is that it has a high calorific value ranging from 1,470 to 11,760 kJ/kg. Due to this, its firing energy saving is high. The test result of the fly ash brick indicated an improvement in plasticity, drying, and decreased crack formation. Different particle size distribution of fly ash also affects the properties.

Fine fly ash has been proved to be better than coarse fly ash. As the fine fly ash improves the mechanical properties. So, it is concluded that the addition of 10% fly ash is favorable in terms of energy saving. Nevertheless, other researchers recommended 40% of fly ash slag with 800 °C as the firing temperature to produce a good quality brick while saving energy usage in the manufacturing process (Kadir & Sarani, 2012).

2.2.3 Processed Waste Tea

Processed waste tea is another waste that was used in clay bricks. Different percentages of waste, 0%, 2.5%, and 5%, by mass, were combined with clay with a firing temperature of 900°C. The potential of processed waste tea in the unfired and fired clay body was studied due to its organic nature. The enhanced compressive strength results, compared to the control samples showed that the pore-forming of processed waste tea in the fired body and the binding in the unfired body has significant potential in both conditions of clay brick. From the test result, it was observed that with a higher percentage of processed waste tea, the water absorption, and compressive strength were increased. The organic nature of processed waste tea supplements the heat input of the furnace. Utilization of this waste enhances the physical and mechanical properties of the bricks and becomes the best option to produce environmentally sound bricks (Demir, 2006).

2.3 Municipal solid waste

The term "municipal solid waste" refers to the rubbish that accumulates in a municipality. Because the majority of this solid waste is generated without any sorting, it may be dangerous or harmless. In general, regardless of where municipal solid waste comes from, its influence on the ecosystem and various life forms pollutes the air, water, and land. Furthermore, the impact of municipal solid waste on land use, odors, and aesthetics has been factored into waste treatment system holistic considerations. In theory, the human race is responsible for all environmental contamination and, as a result, is the primary threat to nature's biodiversity. Global population expansion and rising consumer demand, particularly in fast-growing emerging and developing nations, have resulted in a significant increase in global production.

Most industrial facilities, on the other hand, have insufficient or non-existent environmental monitoring of their production processes, as well as insufficient or inadequate waste management and treatment capabilities. The global trend of increasing urbanization has resulted in an increase in waste generation from private habitation sites, private and public service facilities, as well as increased construction and demolition operations.

Due to the high population density of cities around the world, everyday consumption of products, and services is likewise high in metropolitan regions. Furthermore, the amount of municipal solid waste that accumulates is strongly related to the economic condition of the society in a specific country. In most countries around the world, municipal solid waste generation per capita has increased. Plastics, paper, glass, and metals are the four categories of solid waste with the greatest potential for recycling. Massive amounts of municipal solid waste pose a serious environmental threat as well as considerable socioeconomic difficulties (M. Saleh & Koller, 2019).

2.3.1 Composition of municipal solid waste

Because different waste kinds include varied levels of degradable organic carbon (DOC) and fossil carbon, waste composition is one of the most important factors impacting emissions from solid waste treatment. In different locations and nations, waste compositions, as well as the classifications used to collect data on waste content in MSW, differ greatly (Pipatti et al., 2006). Municipal solid waste is generated by private houses, hotels, offices, stores, education, and other institutions. Aside from specific types of hazardous trash, such as batteries, light bulbs, and fluorescent tubes, automotive components, expired pharmaceuticals and other pharmaceutical items, and a variety of chemicals, such as cleaning and cosmetic products, the lion's share of solid waste encompasses (M. Saleh & Koller, 2019):

- Organic (mainly food or horticulture) waste
- Cardboard
- Paper
- Plastics and other resins
- Textile rags
- Metal

- Glasses
- Demolition and construction debris

2.3.2 Management of municipal solid waste

Solid waste from homes, streets, and public places, as well as shops, offices, and hospitals, is referred to as municipal solid waste. Municipal or other governmental authorities are usually in charge of managing certain forms of waste. Although solid waste generated by industrial activities is not considered municipal waste, it must be considered when dealing with solid waste because it frequently finds up in the MSW stream (Zhu et al., 2008). The elements of a typical waste management system in a low- or middle-income country are as follows:

Waste generation

Waste generation refers to the process of identifying resources that are no longer useful and then discarding them or gathering them for disposal. What's vital to remember about trash generation is that there's an identification stage, and that this procedure differs from person to person. Waste generation is currently an activity that is difficult to control.

Waste handling and separation, storage and processing at the source

The operations related with managing wastes until they are deposited in storage containers for collection are referred to as waste handling and separation. The movement of loaded containers to the site of collection is also included in handling. Separation of waste components is a crucial stage in the processing and storage of solid waste at the point of generation. Because of public health concerns and aesthetic considerations, on-site storage is critical.

Collection

The collection includes gathering solid wastes and recyclable items as well as transporting these materials to a destination where the collection vehicle is emptied, such as a materials-processing facility, a transfer station, or a landfill, once they have been collected.

Transfer and transport

The functional aspect of transfer and transport consists of two steps: (1) the transfer of wastes from smaller collecting vehicles to bigger transport equipment, and (2) the subsequent transport of the wastes to a processing or disposal facility, frequently over great distances. Usually, the transfer takes place at a transfer station. Although motor vehicles are the most prevalent mode of trash transportation, rail cars and barges are also employed.

Separation, processing, and transformation of solid waste

Curbside collection, drop-off, and buyback centers are some of the methods and facilities now in use for recovering waste items that have been separated at the source. Materials recovery facilities, transfer stations, combustion facilities, and disposal sites are commonly used for the separation and processing of wastes that have been separated at the source, as well as the separation of commingled wastes. Transformation procedures minimize the volume and weight of waste that must be disposed of while also recovering conversion products and energy. A range of chemical and biological techniques can be used to convert the organic part of MSW. Combustion is the most widely employed chemical transformation technique in conjunction with energy recovery. Aerobic composting is the most widely utilized biological transformation method.

Disposal

Today, all solid wastes, whether they are residential wastes collected and transported directly to a landfill site, residue from solid waste combustion, compost, or other substances from various solid waste processing facilities, are ultimately disposed of by landfilling or land spreading. A sanitary landfill, on the other hand, is not a dump. It's a way to dispose of solid wastes on land or in the earth's mantle without endangering public health or causing nuisances.

2.3.3 Waste management hierarchy

The waste hierarchy ranks waste management methods according to environmental benefit. It places a high emphasis on preventing waste from occurring in the first place. When waste is generated, it is prioritized for re-use, followed by recycling, recovery, and finally disposal (*Guidance on Applying the Waste Hierarchy*, 2011).

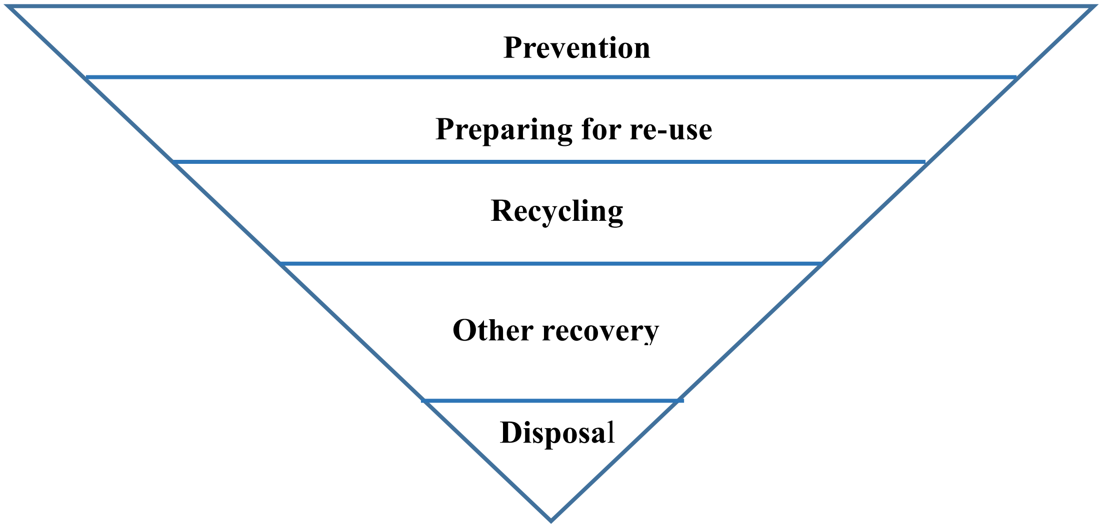


Figure 2.1 Waste management hierarchy

Prevention: using less material in design and manufacture. Keeping products for longer; reuse. Using less hazardous materials.

Preparing for re-use: checking, cleaning, repairing whole items or spare parts.

Recycling: turning waste into a new substance or product. including composting if it meets quality protocols.

Other recovery: incudes anaerobic digestion, incineration with energy recovery, gasification and pyrolysis which produce energy (fuels, heat and power) and materials from waste; some backfilling.

Disposal: Landfill and incineration without energy recovery.

Because preventing waste generation is the most important aspect of waste management, landfill disposal is only used as a last choice when no other options are available (African Clean Cities Platform (ACCP), 2019).

2.3.4 Municipal solid waste incineration

MSWI (municipal solid waste incineration) is the controlled combustion of trash at a facility designed specifically for this purpose. MSWI's main purpose is to minimize MSW volume and mass while also making it chemically inert in a combustion process so that no additional fuel is required (autothermic combustion). It also allows for the recovery of energy, minerals, and metals from the waste stream as a side effect. Incineration always leaves around 25% of residues in the form of slag (bottom ash) and fly ash (Mutz, D et.al., 2017). Incineration is the process of burning unprocessed (raw or leftover) MSW. A substantial amount of oxygen is necessary to properly oxidize the waste and allow combustion to take place. Incineration plants typically have combustion temperatures of over 850°C, and waste is transformed to carbon dioxide and water. Non-combustible materials (such as metals and glass) remain unaffected. Incineration with energy recovery is a well-known municipal waste treatment method (*Incineration of Municipal Solid Waste*, 2013).

2.3.4.1 Technology description

When flammable components in waste achieve the required ignition temperature and come into contact with oxygen, an oxidation reaction takes place. The reaction temperature ranges between 850 and 1450^{o}C, and the combustion process occurs in both the gaseous and solid phases, producing heat energy concurrently. A minimum calorific value of the waste is necessary to support a thermal chain reaction and self-sustaining combustion (so-called autothermic combustion), which means that no additional fuels are required. Exhaust gases are produced during incineration, and after being cleaned, they are released into the atmosphere via a flue, which is a conduit or canal. These flue-gases contain the bulk of the available fuel energy in the form of heat, as well as dust and gaseous air pollutants that must be eliminated through a flue-gas purification process. Excess heat from combustion can be used to generate steam for electricity generation, district heating/cooling, or process sector steam supply (Mutz, D et.al., 2017).

Advantages of incineration

Incineration is a cost-effective approach to minimize waste volume and landfill demand. Incineration plants can be built close to waste generation's center of gravity, lowering waste transportation costs. Using MSW incinerator ash for environmentally friendly construction not only provides a low-cost aggregate, but it also minimizes the requirement for landfill capacity. To maintain a sufficient slag quality, combustion of trash containing heavy metals and other contaminants should be avoided. (However, common home garbage contains trace quantities of heavy metals that do not readily leach in the field and consistently pass USEPA TCLP tests.) Before using slag, make sure it's in good shape.

Energy can be recovered for use as heat or power. Organic compounds eventually degrade into simpler carbon molecules such as CO_2 (carbon dioxide) and CH_4 (carbon monoxide) (methane). The balance between these two gases, as well as the reaction time frame, varies by option. The greatest technique to eliminate methane gas emissions from waste management procedures is incineration. Furthermore, waste-to-energy initiatives can be used to replace fossil fuel combustion (Mutz, D et.al., 2017).

Disadvantages of incineration

An incinerator facility requires both local and foreign cash throughout its operation, requiring large expenditures and significant operational costs. Waste generators will seek alternatives as a result of the rising costs of waste treatment. In addition, waste incineration is only feasible if specific conditions are met. In poor countries, the composition of garbage is frequently questioned in terms of its viability for auto combustion. The sophistication of an incineration facility necessitates the use of highly trained personnel (Mutz, D et.al., 2017).

2.3.4.2 Municipal solid waste incineration residues

Different solid and liquid residual materials, as well as gaseous effluents, are produced during the incineration process. On a wet basis, solids make up around one-fourth of the waste mass. The volume of leftovers is one-tenth of the total amount of garbage. Bottom ash, fly ash, air pollution control residues, and boiler and economizer ash are examples of MSWI residues (Sabbas et al., 2003).

2.3.4.2.1 Bottom ash

Bottom ash, often known as "incinerator bottom ash," is the principal remaining material after MSW incineration. This is the non-combustible waste feed ingredients that make up the leftover material in the combustion chamber. By weight, the bottom ash typically accounts for 20% to 30% of the initial waste feed, but only approximately 10% by volume. The bottom ash is ejected from the combustion chamber on a regular basis and subsequently cooled. The amount of ash produced is determined by how much waste is pre-treated before entering the incinerator (*Incineration of Municipal Solid Waste*, 2013). In section 2.5.2, I go over the details of bottom ash in greater depth.

2.4 Tannery waste water

Tannery wastewaters are complex, with high levels of organic, inorganic, and nitrogenous substances, as well as chromium, sulfides, suspended solids, and dissolved solids. Physical, chemical, biological, or a combination of these approaches are used to treat tannery wastewater. Tanneries are often thought of highly polluting industrial complexes that produce large amounts of high-strength effluent. The fill and draw style of operation connected with tanning processes, as well as the diverse procedures used for hide preparation, tanning, and finishing, all contribute to the variability of tannery wastewaters. The type of raw hides used and the desired features of the completed product defines these operations.

At least 300 kg of chemicals are added every ton of hides during the tanning process. Tannery effluent is one of the most dangerous pollutants produced by industry. Heavy metals, hazardous compounds, chloride, lime with high dissolved and suspended salts, and other contaminants are causing major concerns. Tanneries produce effluent with suspended particles, BOD, COD, and tannins, including chromium, in the range of 30-35L/kg skin/hide treated with variable pH (Durai & Rajasimman, 2011).

2.4.1 Treatment method for tannery waste water

Tannery wastewater treatment is a multi-stage procedure that purifies wastewater before it is discharged into a body of natural water, applied to land, or reused. Because each receiving body of water can only take a given number of contaminants without degrading, the goal is to decrease or remove organic matter, sediments, minerals, Chromium, and other pollutants. As a result, each effluent treatment plant must comply to discharge criteria, which are often established by the appropriate environmental authority as permitted levels of pollutants represented as BOD_5, COD, suspended solids (SS), Cr, total dissolved solids (TDS), and others for practical reasons (Itodo1, 2018). The following are the main phases of tannery wastewater treatment:

2.4.1.1 Preliminary treatment

In the case of common effluent treatment plants serving tannery clusters, such as those seen in developing nations, individual tanneries must typically have installed pre-treatment units. Before the effluent is discharged into the collection network, they must remove big particles, sand/grit, and grease, as well as drastically reduce the concentration of chrome and sulfides.

2.4.1.2 Physical-chemical treatment (primary)

The goal is to remove organic and inorganic solids that can settle via sedimentation, as well as materials that will float (scum) by skimming. During primary treatment, 25-50% of the biochemical oxygen demand (BOD_5), 50-70% of total suspended solids (SS), and 65% of oil and grease are eliminated. Primary effluent and sludge are the effluent and sludge produced by primary sedimentation.

2.4.1.3 Biological treatment (secondary)

Secondary treatment usually comes after primary treatment, with the purpose of removing biodegradable dissolved and colloidal organic waste via aerobic biological treatment techniques. Aerobic biological treatment involves aerobic microorganisms (mostly bacteria) metabolizing the organic content in the wastewater and creating additional microorganisms and inorganic end products in the presence of oxygen (principally CO_2, NH_3, and H_2O).Several aerobic biological processes are used for secondary treatment and the differences among them have to do primarily with the manner in which oxygen is supplied to the micro-organisms and with the rate at which organisms metabolize the organic matter.

2.4.1.4 Advanced treatment (tertiary)

Tertiary or advanced wastewater treatment is used to minimize residual COD loads and/or when previous treatment stages have failed to remove certain wastewater elements. Despite extensive physical-chemical and biological treatment in a well-designed wastewater treatment facility, the final effluent quality may not always meet the discharge restrictions. Recalcitrant COD, or chemicals that the microorganisms in the floc are unable to breakdown. Additionally, usually more difficult and expensive treatments, such as mineralization of organic compounds by oxidation with H_2O_2 in the presence of ferrous sulfate, are required in such circumstances (Fenton process and its derivatives). Ozonation is occasionally used to remove some of the leftover COD, rather than to kill potentially dangerous microorganisms (Buljan et al., 2011).

2.4.2 Tannery sludge management and disposal options

Because of the presence of chromium, sewage sludge from the tanning industry is a difficult-to-manage waste. In the case of tannery sludge, procedures such as anaerobic digestion, composting, agricultural usage, reclamation, and thermal processes that are routinely employed for the processing and management of municipal sewage sludge may be ineffective or even impossible to use. The tanning industry's sewage sludge has a higher concentration of chromium, which is both a hazardous component and an essential component for the correct functioning of higher organisms.

Most scientists previously believed that the fundamental form of chromium found in this sludge, Cr (III), was stable in the environment and had low toxicity. As a result, storage was the primary way of management. However, in the presence of manganese oxides, the limited mobility of this form of chromium in the environment can be changed, and it can turn into Cr (VI). When exposed to Cr (III) over an extended period of time, it can have damaging, mutagenic, and carcinogenic effects on mammalian cells, as well as damage the immune system.

Furthermore, chromium at the third oxidation stage may be more hazardous to many plants than Cr (VI), causing germination inhibition (Sobik-Szołtysek, 2019). Different approaches to tannery sludge management are reported in scientific literature. Some studies looked into the possibility of composting tannery waste, which was also mixed with other substrates, for use as fertilizer in agriculture. The fate of heavy metals found in tannery sludge, as well as their impacts on plant development and soil quality, are the key concerns associated with this approach, therefore tannery sludge disposal is still mostly based on incineration and landfilling (Alibardi & Cossu, 2016).

2.4.2.1 Landfilling

Sludge produced by tannery effluent treatment plants is difficult to use or dispose of safely around the world; landfill disposal should only be considered when no other feasible option is available. Unfortunately, properly built and constructed landfills are also unavailable in some places and/or poor countries (Unido, 2007). The biggest disadvantage of sludge landfilling is that it necessitates the creation of a new landfill location. In many nations, it will be illegal to deposit sludge with an organic content more than 5% in landfills. Sludge disposal on landfills is becoming less and less popular. Odor issues appear to be mostly caused by the discharge of sludge that has not been appropriately stabilized (Ahamed & Kashif, 2014).

2.4.2.2 Incineration

Incineration is the process of burning wastes directly in the presence of excess air (oxygen) at temperature of around 800 ^{0}C and above, releasing heat energy, inert gases, and ash. It is a waste treatment method that entails the burning of organic compounds found in waste. The inorganic ingredients of the waste produce the ash, which can take the form of solid lumps or particles carried by the flue gas. Before being released into the atmosphere, flue gases must be cleansed of gaseous and particulate contaminants.

The density and composition of the waste, as well as the relative percentages of moisture and inert materials, all of which contribute to heat loss, the ignition temperature, the size and shape of the constituents, the design of the combustion system, and so on, all influence net energy yield. In reality, approximately 65 to 80% of the energy content of organic matter can be recovered as heat energy, which can be used for direct thermal purposes or to generate electricity using steam turbine generators (Abajihad, 2012).

2.5 Raw materials for production of TS-BA amended clay bricks

The basics of brick production have not changed after some time. In any case, the progress in technology has made contemporary brick plants significantly more proficient and has enhanced the general quality of the products. The advancement of the brick industry depends on the complete knowledge of the production processes starting from the raw-material properties, firing temperature, and advanced kiln designs (Brick Industry Association, 2006). The difference in the quality of the brick is essentially caused by the variation of the raw material mineralogical composition, level of firing, and the distinction in the production technique.

2.5.1 Clay

Clay is a mineral material that is plentifully found in nature and it is considered to be one of the most significant components used for producing brick. It is an earthen mineral mass or fragmentary stone with the ability to be more plastic, which has the property of holding its shape when shaped and dried. Due to the chemical property and alteration of microstructure in clay, it obtains hardness and strength when it is fired to redness. Most flawless clay comprises kaolinite($2SiO_2.Al_2O_3.2H_2O$) with a little number of minerals like quartz, mica, feldspar, calcite, magnesite, and so forth (S.K Duggal., 2000).

The plastic property of the clay minerals come from their crystal nature. They are listed under the group of phyllosilicates due to their fine, or foliate shape. The small size, the foliate shape, the glassy nature, that allow them to interact with polar liquids like water, of the clay particles, and their chemical properties, make them have a plastic behavior. The crystals of these clay minerals typically have a thin, layered structure that enables them to absorb water and consequently to expand on wetting (Fernandes, 2019).

The kind and foundation of clay utilized in the production of bricks differ significantly upon the geological area of the production site. The principal distinction between clay body types is the silicon dioxide (SiO_2) content, aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) substance. The capability of clay to make a ceramic bond after firing is because of the content of silica in its particles.

After firing, this compound softens into a glassy form, which bonds the leftover particles to each other where they are in touch in a procedure known as sintering, which is depicted in Figure 2.3. The strength, toughness, and absorption of the subsequent item are subject to the state and nature of sintering inside the brick (Federico et al., 2005).

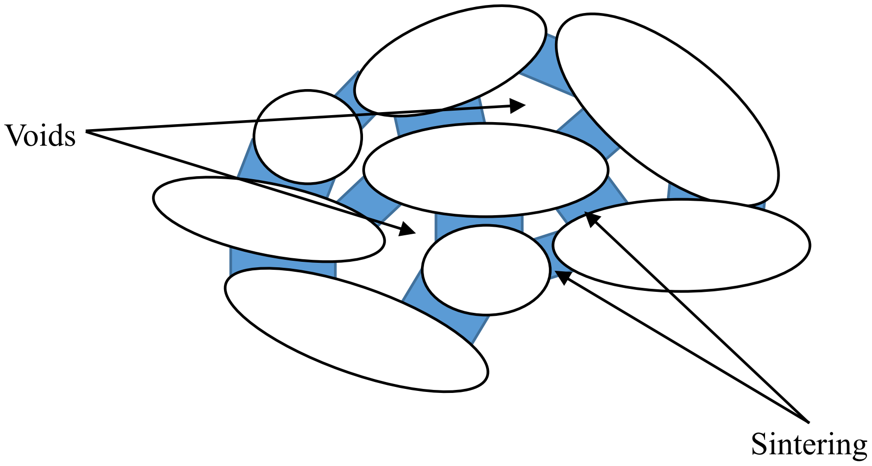


Figure 2.2 Sintering of clay particles

Types of Clay

Clay occurs in three principal forms, all of which have comparable compound pieces yet unique physical features.

- ✓ ***Surface clays***: surface clays might be the upthrusts of more seasoned stores or fresh sedimentary formation. As the name infers, they are found close to the outside of the earth.
- ✓ ***Shales***: shales are clays that have been exposed to higher pressing factors until they have almost solidified into slate.
- ✓ ***Fire clays***: fire clays are generally mined at more profound levels than other clays and have refractory characteristics.

The physical structures of surface and fire clays are different from shales however they have the same chemical composition. Each of the three sorts of clays is made out of silica and alumina with varying amounts of metallic oxides. Metallic oxides play a vital role in fostering particle fusions at lower temperatures. The color of the fired bricks is mostly affected by oxides of iron, magnesium, and calcium (Cengizler et al., 2012)**.**

Chemical composition of Clay

The major constituents of clay used for brick making are silica and alumina mixed in such quantity, that the clay turns out to be more plastic when water is added to it. It also contains a slight amount of lime, iron, manganese, sulfur, etc. (S.K. Duggal, 2005). silicon oxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3) or ferrous oxide (Fe_3O_4), potassium oxide (K_2O), titanium dioxide (TiO_2), sodium oxide (Na_2O), calcium oxide (CaO), and magnesium oxide (MgO) are metal oxides usually found in the clay bricks however, Manganese, magnesium, and calcium are found to be in lower amounts (Fernandes, 2019).

The color of the bricks differs highly based on the chemical composition of the clay and the operating conditions during firing. Due to different factors such as the nature of the clay minerals, the number of impurities (organic matter, lime, sand, etc.), and the concentration of iron oxides and hydroxides, the colors range from light beige to dark violet. Commonly, clays with a small concentration of iron compounds end up with yellowish bricks, however, clays with a high concentration of iron compound give red and violet bricks. The presence of limestone might bring about orange-tone bricks. In presence of a raised amount of organic matter, bricks become dark in color. other colors can also be acquired based on the proportion of the corresponding metallic oxide: red brick (5%-10% of Fe_2O_3), yellow brick (3%-10% of TiO_2), brownish brick (0.5%-4% of MnO_2), etc. (Fernandes, 2019).

Table 2.1 Standard chemical composition of a good clay soil

Analytes	**Proportions (%)**	**Remark**
SiO_2	50-60%	
Al_2O_3	20-30%	
Fe_2O_3	<7%	
CaO	10%	
Fe_2O_3	<7%	The sum of these ingredients is less than 20%
MgO	<1%	
Alkalis (NaOH, KOH, …)	<10%	
Carbon dioxide (CO_2)		Very small percentage
Sulfur trioxide (SO_3)		

Water (H_2O)		

Source: Duggal, 2000

The Functions of Various oxides of clay (S.K. Duggal, 2000).

Silica (SiO_2): it gives the brick the ability to hold its shape and durability, avoid shrinkage and warping. A surplus amount of silica makes the brick brittle and weak on burning. Although the presence of silica is necessary to reduce shrinkage in firing and to increase the refractoriness of low alumina clays, a huge amount of uncombined silica and sand is unwanted.

Alumina (Al_2O_3): Absorbs water and renders the clay plastic. If alumina exists more than the required amount, it produces cracks on drying. Clays having passing high alumina content are probably to be refractory.

Lime (CaO): usually occupy 10 percent of the clay. The effect of lime in clay brick are listed as follows:

- Decreases the shrinkage on drying.
- It makes the silica to be melted on firing and therefore helps to bind it.
- When it is found in the form of the carbonate, it reduces the point of fusion.
- An excess amount of lime results in the melting of brick and consequently causes the loses of shape.

Magnesia (MgO)**:** once in a while surpassing 1%, influences the color and makes the brick yellow in burning; it makes the clay mellow at a slower rate.

Ferric Oxide (Fe_2O_3)**:** the following characteristics are given by iron oxide.

- Gives red color on burning when an abundance of oxygen is accessible and dark brown or even black color when there is no sufficient amount of oxygen. However, an overabundance of ferric oxide makes the brick dark blue.
- Increase impermeability and sturdiness.
- In general, it lowers the fusion point of the clay, particularly if present as ferrous oxide.
- Gives strength and hardness.

2.5.2 Municipal Waste incineration Bottom Ash

BA is the major by-product residue of the MSWI process (85–95 wt. %). BA is a permeable, grayish, and coarse rock material containing glasses, ceramics, minerals, ferrous, and nonferrous materials, alongside modest quantities of organic carbon. The main compositions are oxides, hydroxides, and carbonates. From different spectroscopic evaluations, the main compositions of BA (>10 wt. %) were found to be SiO_2, CaO, Fe_2O_3, and Al_2O_3, whereas Na_2O, K_2O, MgO, and TiO_2 are present in small quantity (0.4–5.0 wt. %). Therefore, oxides are principal. From all the aforementioned oxides, the percentage of SiO_2 in BA is predominant, accounting for up to 49% (Cho et al., 2020). BA consists of a considerable concentration of heavy metals such as Zn, Pb, Cu, Ni, Cr, and Cd.

The weight of BA is insignificant compared with natural sands and aggregates (Dugenest et al., 1999). Incombustible materials collected at the outlet of the combustion chamber can also be considered as BA. Since BA contains a high amount of silica, it can be recycled to be used as secondary aggregate for civil engineering and construction. Consequently, nowadays, 50% of BA is recycling by some European countries to use as a raw material for the construction material industry or road construction (Giro-Paloma et al., 2017). The property of BA is principally controlled by the method of incineration used and the three T'S (temperature, time, and turbulence) (Yafee, 2011). The pH value of BA fell in the range of 10.5 to 12.2. This is due to the hydroxide formation of Calcium oxide (Chandler, A.J., et.al 1997).

2.5.2.1 Characteristics of Municipal Waste Incineration Bottom Ash

Even though the nature of the waste materials charged into the combustion chamber differs from one place to another, bottom ashes from incineration of waste usually have the same property (Hansson, 2017). This section provides an overview of the physical and chemical properties of municipal waste incineration BA.

- ### Physical Properties of Municipal Waste Incineration Bottom Ash

Particle Morphology of Bottom Ash

The physical and chemical properties of BA are mainly controlled by the particle morphology of the bottom ash (Solid & Incinerator, 2011). The shape of a municipal waste incineration bottom ash is most likely irregular and angular with a permeable microstructure formed from the heating and cooling during incineration. The porous nature of BA is responsible for the irregular shape, high specific surface area combined with high absorption characteristics (Lynn et al., 2016).

Absorption

Absorption is utilized to figure the change of weight of an aggregate because of the absorption of water into penetrable pore spaces inside aggregate particles. Bottom ash is a profoundly permeable aggregate; in this way, it will in general retain water (Chandler et al., 1997). In concurrence with the morphological properties, high water absorption results have been accounted for MWIBA, ranging from 2.4 to 15.0%, with an average of 9.7%. The absorption properties of the material are considerably higher than normal sand which is regularly 1-3%. Further contrast of fine and coarse parts of MWIBA showed that the fine portion commonly had higher absorption values because of the larger specific surface area (Lynn et al., 2016).

- ### Chemical Properties of Municipal Waste Incineration Bottom Ash

Chemical Compositions of MWIBA

The leaching property of bottom ash depends mostly on its mineralogical characteristics. Bottom ash has various mineral phases. Although quartz (SiO_2), calcium carbonates ($CaCO_3$), and lime (CaO) are considered to be the major constituents of bottom ash, magnesium carbonate, barite, or gypsum are also present in a minor amount. All these inorganic compounds are important components of agricultural lands but they are dumped inappropriately with organic solid waste (Chimenos et al., 1999). Based on the previous researches on analysis of MWIBA samples, the main oxides present in MWIBA are listed below.

Table 2.2 Chemical composition of Municipal waste incineration bottom ash

Analytes	**Municipal waste incineration bottom ash (%)**	
	1	2
SiO_2	37.5	34.92
CaO	22.2	27.39
Al_2O_3	10.3	6.98
Fe_2O_3	8.10	6.72
SO_3	2.40	7.49
MgO	1.90	2.90
Na_2O	2.90	0.52
K_2O	1.40	2.02
P_2O_5	2.40	7.43

[1] *(Lynn et al., 2016)*

[2] *(Solid & Incinerator, 2011)*

Organic content

The measure of unburned organic materials in MWIBA is 0.2-5% (Hansson, 2017). Residual organic matter leftover in MWIBA after the burning process can prompt adverse consequences on density, stiffness, and expanded risk of degradation over the long run. The amount of organic matter can be measured by loss on the ignition test by comparing the difference in mass of the sample before and after ignition (Lynn et al., 2017).

Heavy metal composition

Based on the kind of waste received, the innovation of the incinerator, and the working states of the incinerator, the inorganic content of BA differs among incinerators. But the number of heavy metals fluctuates within certain ranges regardless of the origin. The range of heavy metal composition is shown in Table 2.3. In the table, the elemental constituents are grouped as the elements of potential environmental concern (i.e., recognized as toxic or hazardous elements). It is acknowledged that the total metal content of the ash is not related to the potential environmental impact exerted by the material in its use or the disposal site. Metals are typically considered of concern once they are released into the environment by leaching (Astrup et al., 2016).

Table 2.3 Ranges for the heavy metal content of Municipal waste incineration bottom ash

Element	Concentration range (mg/kg) (minimum to maximum)
Cd	0.30-70.0
Cu	190-25,000
Cr	20.0-3,400
Ni	7.00-4,300
Pb	75-14,000
Zn	10-20,000

Source: *(Astrup et al., 2016)*

- **Leaching behavior of Municipal Waste Incineration Bottom Ash**

The presence of heavy metals in MWIBA bottom ash and its leaching into groundwater have been an issue for quite a while since it was landfilled. Numerous nations are taking on source decrease strategies by restricting the poisonous trace metals in various items. The heavy metals normally present in MWIBA ash are cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). Heavy metals are more accumulated in fly ashes than bottom ashes except for Cu, Cr, and Pb because of their low volatilities. Along these lines, because of the substantial metals in it; leaching tests should be done to assess the environmental impact (Joseph et al., 2018).

2.5.3 Tannery Sludge

Tannery sludge is a waste that radiates from the leather processing industry and this waste should be wisely managed. nitrogen, ammonia, sulfides, calcium compounds, chromium (III) salts (especially sulfates) as well as high chromium content are the chemical composition of inorganic substances usually presented in tannery sludge (Malaiškiene et al., 2019). The properties of the tannery sludge are extremely dependent on the technology of tanning and the method of sewage waste treatment. Due to the limited treatment choice of tannery sludge, it is mostly landfilled. Its property limits biological treatment and the horticultural utilization of most potential items acquired from its processing is exceptionally confined. Its incineration brings about producing unsafe ash as well as implies the danger of chromium oxidation and discharge of gaseous heavy metals during the process (Industrial and Municipal Sludge Emerging Concerns and Scope for Resource Recovery2019, Pages 61-81).

2.5.3.1 Characteristics of Tannery Sludge

The composition of tannery sludge differs from country to country based on the tanning process applied and the type of chemicals used. But chromium has been the main constituent in the sludge. Some of the sludge have a higher size compared with soil. The main components of tannery sludge are Fe_2O_3, SO_3, CaO, and SiO_2. The clay that is used for brick manufacturing consisted of similar components present in the tannery sludge but in different quantities (Juel et al., 2017b).

Table 2.4 The basic properties and metal content of tannery sludge

Properties	Tannery sludge
pH	7.5±0.2
Moisture Content	70±8.34
Organic Content	28.75±3.68
Total heavy Metal Content (mg/kg)	
Cr	19,229±6303
As	1.8±0.3
Pb	63.8±5.6
Cd	<0.01
Ni	139.5±1.91
Cu	385.7±170
Zn	250.6±68

***Source**: (Juel et al., 2017b)*

- **Chemical composition of Tannery Sludge**

Tannery sludge composition can vary from country to country depending on the tanning processes applied and the chemicals involved.

Table 2.5 Chemical composition of tannery sludge

Analytes	Tannery Sludge (%)
SiO_2	3.55
CaO	26.26
Al_2O_3	0.48
Fe_2O_3	34.32
SO_3	28.71

MgO	1.69
TiO_2	0.41
MnO	0.20
ZnO	0.08

Source: *(Juel et al., 2017b)*

2.6 Method of Brick Production

The production process has six general phases.

- Mining and storage of raw materials
- Preparing raw materials
- Molding the brick
- Drying
- Firing and cooling

2.6.1 Mining and storage of raw materials

Surface clays, shales, and some fire clays are mined using power equipment in open pits. The clay or shale mixtures are then transported to storage rooms at the facility. The storage of significant quantities of raw materials required for many days of plant operation ensures continuous brick manufacturing regardless of weather conditions. To make combining the clays easier, several storage spaces are usually used. Blending produces more consistent raw materials, aids in color control.

2.6.2 Preparation

Sorting, crushing, sieving, and proportioning are all part of the preparation process. Sorting entails removing roots, stones, and other contaminants before laying the material out to dry. Crushing entails pulverizing the clay's hard lumps, and sieving involves removing any particles larger than 1mm (Okunade, 2008).

2.6.3 Molding

It is the process of shaping the brick from the prepared clay into the desired shape. Molding can be done by hand or with a machine. The soft mud (hand molding), stiff mud (machine molding), or dry press method are all options for brick molding (molding using a maximum of 10 percent water and forming bricks at higher pressures). The soft mud method is used to make fire-brick.

The dry-press process is used to make roofing, floor, and wall tiles. All structural clay products, on the other hand, are made using the stiff-mud procedure (Duggal, 2008, P.20).

- *Soft-Mud Process* – For clays that contain too much water to be extruded by the stiff-mud process, the soft-mud or molded procedure is ideal. Clays are blended with 20 to 30% water and then molded into bricks. The molds are lubricated with either sand or oil to prevent the clay from sticking, resulting in “sand-struck” or “oil-struck” brick. Hand-made brick can be made in this fashion.
- *Stiff-Mud Process* – To induce plasticity, water in the range of 10 to 15% is introduced into the clay in the stiff-mud or extrusion process. The tempered clay goes through a de-airing chamber after pugging. De-airing the clay removes air holes and bubbles, increasing its workability and plasticity, resulting in greater strength. The clay is then extruded through a press to form a clay column. Textures or surface coatings can be applied to the clay column as it exits the press. The individual bricks are subsequently cut out of the clay column using an automated cutter.
- *Dry-Press Process* – This method works well with clays that have a low plasticity. Clay is combined with a small amount of water (up to 10%), then pushed into steel molds by hydraulic or compressed air rams at pressures ranging from 500 to 1500 psi (3.4 to 10.3 MPa).

2.6.4 Drying

Depending on the manner of manufacture, green bricks contain 7–30 percent moisture. The purpose of drying is to remove moisture in order to reduce shrinkage and save fuel and time during the burning process. The drying shrinkage is determined by the clay's pore spaces and the mixing water. Sand minimizes shrinkage, increases porosity, and allows for faster drying. Within three to four days, the moisture content is reduced to roughly 3% under exposed settings. As a result, the green bricks' strength is improved, and they may be handled securely.

2.6.5 Firing

The firing of clay may be divided into three main stages.

Dehydration (149℃ to 982℃): this is also known as the water smoking stage. During dehydration:

- The clay loses its plasticity as the water that has been held in the pores after drying is forced out.

- Some of the carbonaceous materials is consumed in the combustion process.
- A portion of sulfur is distilled from pyrites.
- Hydrous minerals like ferric hydroxide are dehydrated, and
- The carbonate minerals are more or less de-carbonated.

Quick heating produces cracking or bursting of the bricks. On the other hand, if alkali is contained in the clay, slower heating of clay forms scum on the surface of the bricks.

Oxidation (538℃ to 982℃): The remaining carbon is removed during the oxidation process, and the ferrous iron is converted to ferric iron. Only when all of the carbon has been removed is the sulfur removed. Because of its affinity for oxygen, sulfur prevents iron from oxidizing. As a result, in order to avoid black or spongy cores, oxidation must continue at a rate that allows these changes to take place before the heat softens the clay and closes its pores. Sand is frequently added to raw clay to create a more open structure and so allow gases created during combustion to escape.

Vitrification (871℃ to 1316℃): Temperatures ranging from 871°C to 1316°C are used to transform the bulk into a glass-like material. When exposed to heat, clay, unlike metal, softens slowly and melts or vitrifies gradually. The clay is vitrified to become a hard, solid mass with a low absorption rate. The vitrification period can be subdivided further into:

- *Incipient fusion*: at which the clay has softened sufficiently to cause adherence but not enough to close the pores or cause loss of space.
- *Complete Vitrification*: when extensive fluxing occurs and the mass becomes tight, solid, and non-absorbent.
- *Viscous Vitrification/fusion*: When the clay mass breaks down and becomes molten, a deformed shape result. The key to the firing process is to keep the kiln temperature

controlled enough to allow for incipient fusion and partial vitrification while avoiding viscous fusion.

Clay products are typically vitrified to the point of viscosity. Bricks, on the other hand, are burned to complete vitrification in order to obtain maximum hardness and toughness. The rate of temperature change must be carefully monitored and is determined by the raw materials used as well as the size of the brick being manufactured. Temperature sensors are typically installed in kilns to manage firing temperatures at various stages.

2.6.6 Cooling

The cooling process begins after the temperature has reached its maximum and has been maintained for a specified period of time. In tunnel kilns, cooling time rarely exceeds 10 hours, and in periodic kilns, cooling time ranges from 5 to 24 hours. Because the rate of cooling has a direct effect on color, cooling is an important stage in brick manufacturing. (Brick Industry Association, 2006).

2.7 Standard tests of bricks

Clay bricks have a number of characteristics that are significant in determining strength and durability. The qualities are tightly linked to the quality of the raw clay and are clearly correlated to the manufacturing conditions (Fernandes, 2019). Most manufacturers combine different clays to achieve the desired raw material and fired brick properties. This enhances the finished product's overall performance (Brick Industry Association, 2006).

2.7.1 Compressive strength

The compressive strength of clay bricks is an important property that allows for the assessment of the material's ability to withstand compressive loads in the structure. The raw material's properties, as well as the manufacturing process, have a significant impact on the compressive strength value. (Fernandes, 2019). The compressive strength has great importance for two reasons. Firstly, with higher compressive strength, other properties like flexure, resistance to abrasion, etc., also improve. For two reasons, compressive strength is quite important. To begin with, stronger compressive strength improves other qualities such as flexure, abrasion resistance, and so on.

Second, while other qualities are more difficult to assess, compressive strength is straightforward. Compressive strength generally decreases as porosity increases, although strength is also impacted by clay composition and firing. (Okunade, 2008).

2.7.2 Water absorption

Pores make up a major portion of the brick's volume, and when the bricks are exposed to rain or water, the waters are penetrated. The quality of the raw clay, the presence of additives or impurities, the amount of water used, and the firing temperature all influence the size and distribution of the pores. The capacity of the fluid to be held and circulated within the brick is then determined by water absorption, favoring degradation and a drop in mechanical strength. When temperature drop below 0°C, the water inside the pore freezes, causing delamination, disintegration, and cracking on the surface.

Furthermore, when soluble salts are present, water tends to react with them, resulting in efflorescence. The volume increase induced by the crystallization of the salts is largely an aesthetic deterioration of the brick surface (Fernandes, 2019). The qualities of the clay, the technique of production, and the degree of burning all influence water absorption. Lower absorption levels are associated with greater firing temperatures for a particular clay and technique of manufacturing. Although manufacturing and firing procedures can influence absorption, these attributes are mostly determined by the properties of the raw materials (Brick Industry Association, 2006).

2.8 Standard specification for clay bricks

Compressive strength and water absorption are the physical property requirements for burnt clay bricks in most specifications. Furthermore, the minimum compressive strength and maximum water absorption are utilized together to forecast the clay bricks' durability. In the construction sector, specifications are an important aspect of quality assurance and control. The concerned parties must carefully specify the products and construction criteria in order to achieve quality workmanship and appropriate performance. To manage the quality of specified items, reference standards should be employed. In light of these facts, various countries have developed standard criteria for burnt clay bricks that include definitions and classifications (classification based on: - dimensions, size, durability, efflorescence, compressive strength, and water absorption). Clay bricks are categorized based on these physical characteristic standards (Belayneh, 2013).

The physical and mechanical qualities of clay bricks are used to categorize them in various specifications. Clay bricks, for example, are graded based on their compressive strength and water absorption, according to ASTM C 62-97a. Similarly, the Ethiopian standard specification for Clay Bricks - Solid Clay Bricks (ES 86:2001) classifies bricks based on their physical and mechanical qualities.

2.8.1 Ethiopian standard specification for clay bricks (ES: 86:2001)

Table 2.6 Ethiopian standard for the classification of bricks

Class	Minimum Compressive Strength (MPa)		Maximum Water Absorption (%)	
	Average of five bricks	Individual brick	Average of five bricks	Individual brick
A	20	17.5	21	23
B	15	17.5	22	24
C	10	7.5	No limit	No limit
D	7.5	5.0	No limit	No limit

Source: *ES 86:2001*

2.8.2 The American society for testing and materials; Standard specification for building brick (ASTM C 62-04)

Table 2.7 ASTM standard for the classification of bricks

Designation	Minimum Compressive Strength (MPa)		Maximum Water Absorption (%)	
	Average of five bricks	Individual brick	Average of five bricks	Individual brick
Grade SW	20.7	17.2	17.0	20
Grade MW	17.2	15.2	22.0	25.0
Grade NW	10.3	8.6	No limit	No limit

Based on ASTM specification:

Grades classify brick according to their resistance to damage by freezing when wet. Three grades are covered and the grade requirements are shown above in Table 2.7.

- **Grade SW** (Severe Weathering): Brick intended for use where high and uniform resistance to damage caused by cyclic freezing is desired and where the brick may be frozen when saturated with water.
- **Grade MW** (Moderate Weathering): Brick intended for use where moderate resistance to cyclic freezing damage is permissible or where the brick may be damp but not saturated with water when freezing occurs.
- **Grade NW** (Negligible Weathering): Brick with little resistance to cyclic freezing damage but which are acceptable for applications protected from water absorption and freezing.

With a view to the above, this research is aimed at finding out the way for effective utilization of Tannery sludge, MWIBA, and clay in the development of bricks. Sample collection, sample preparation, sample and product characterization, leaching test, and the calculation for energy saving during firing of TS integrated clay bricks are all included in this study. For the optimization of production conditions, design expert software (Response surface, Box-Behnken design) will be used in the experimental design. The Box-Behnken approach makes it simple to detect probable interactions between parameters in a short period of time with a limited number of experiments.

CHAPTER 3 MATERIALS AND METHODS

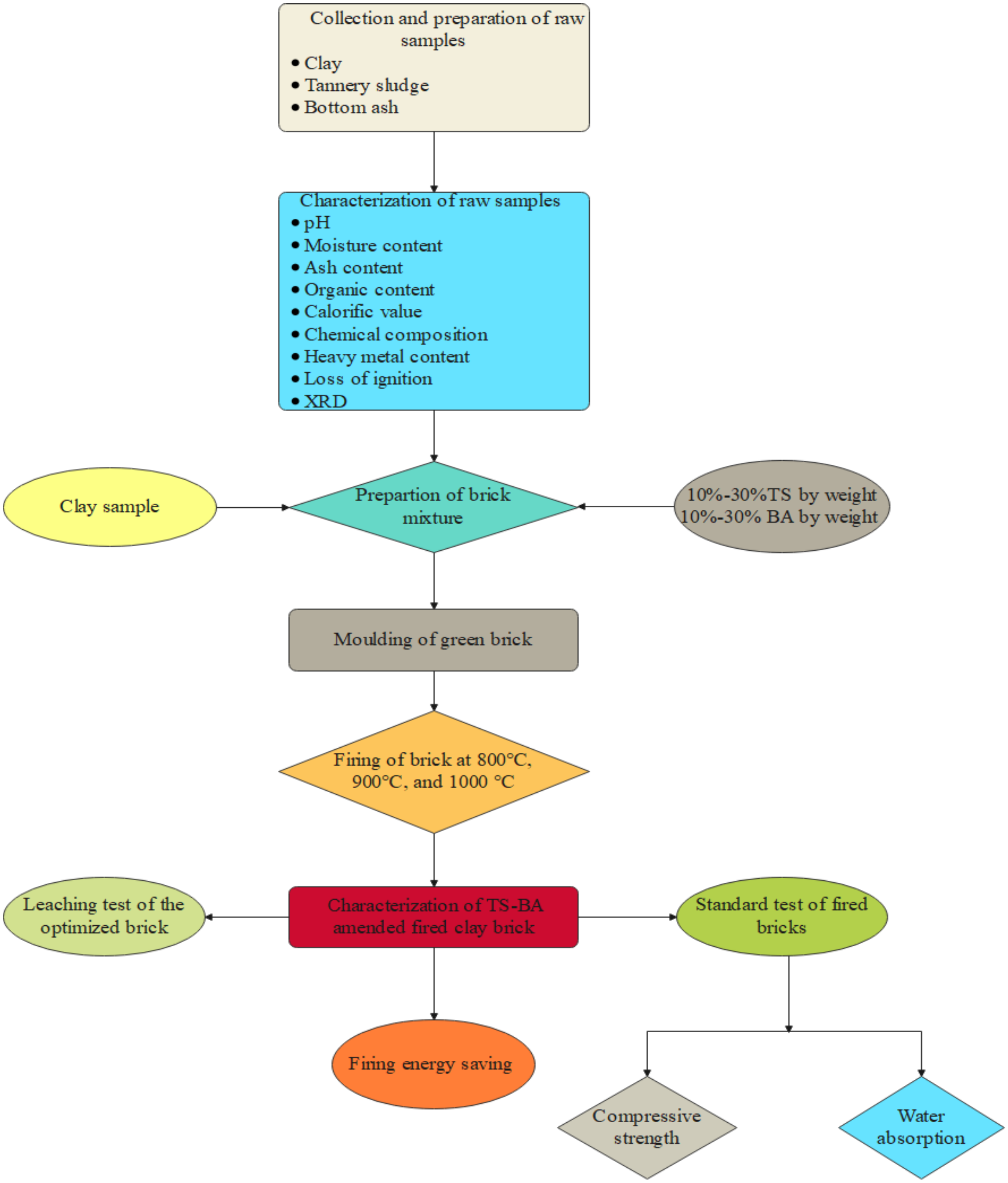


Figure 3.1 Flow chart of the experiment

3.1 Characterization of raw samples

The physicochemical characteristics of the raw samples which encompasses the pH, moisture content, ash content, organic content, calorific value, chemical composition, heavy metal content determination, and loss on ignition were determined based on the standard test methods.

3.1.1 Materials

The main raw samples, which are tannery sludge (TS), municipal waste incineration bottom ash (BA), and clay, were tested for the following parameters. Analytical grade chemicals (65%HNO_3 and 37% HCl) were also used.

- **Equipment and Instruments**

The following equipment and instruments were used for the characterization of raw samples.

Table 3.1 List of equipment and instruments used in characterization of raw samples

Equipment/Instrument	Model	Use
Spatulas		To spread and lift sample
Balance	Ohaus RD35LM Ranger high-resolution Bench Scale	To measure the mass of the sample
Aluminum foil		To hold sample
Drying Oven	Electric Thermostatic Drier 202-0A	To dry the samples
Jaw crusher	5657 HAAN	Size reduction (1st)
Attrition Mill	DIETZ-motoron kg 7311with 5657 HAAN mill	Size reduction (2nd)
Laboratory Sieve	Retsch, AS200	To screen and separate the sample from any foreign matter
Plastic bag	Falcon	To contain and transport samples
Crucible		To heat samples to a very high temperature
Tong		to handle the hot crucible
Desiccator		To preserve samples from moisture

Vortex mixer	Stuart SA8	To mix the sample with distilled water
pH meter	JENWAY 3505	To measure the acidity or alkalinity of the sample
Measuring Cylinder		To measure volume
Pipette	ACURA 825/835	To measure out or transfer small quantities of acid
Round bottom flask		As a reactor during digestion
Fume hood		Prevent the release of hazardous substances into the general laboratory space by controlling and then exhausting hazardous and/or odorous chemicals.
Thermometer		To measure the temperature of the oil
Oil bath	IKA® HBR 4 Heating Baths	To heat the solution
Temperature controller	Polyscience 9106A12E	To provide consistent temperature to the condenser
Condenser		To condense acid evaporated during digestion
Atomic absorption spectroscopy (AAS)		To read the concentration of heavy metals
Complete silicate analyzer		Used for identification of the chemical composition of the samples
Filter paper (0.45 µm pore size)	Whatman 7404-009 Nylon Membrane Circle	Used for the filtration process
Measuring Scale		To measure the dimensions of the Brick
Adiabatic Oxygen Bomb Calorimeter	1241EF, PARR MOLINE ILLINOIS, USA	To determine the calorific value of the sample
Flame atomic absorption spectrometry (FAAS)		To read the concentration of heavy metals leached out from the brick sample

- **Chemicals and Reagents**

In this experimental works, the following chemicals, reagents and heat transfer fluid were used to conduct a pH, leaching and compressive strength tests.

Table 3.2 List of chemicals and reagents used in characterization of raw samples

Chemicals and Reagents	Use
Distilled Water	Used for mixing samples to measure the pH of the sample
Plaster of Paris (Gypsum)	To coat/cap the bearing surfaces of the brick
Glacial acetic acid	To extract toxic heavy metals
65% HNO_3	To digest samples
37% HCl	To digest samples
Thermal Oil	As a heat transfer fluid

3.1.2 Methods

The method used for this research consists of the collection, preparation, and characterization of raw samples. preparation of the brick mixture, brick making, and testing of the produced brick.

3.1.2.1 Collection and preparation of raw samples

The clay sample was obtained from a local brick manufacturing plant, the Ethio-Brick factory, which is a private limited company (PLC) located in Addis Ababa, Ethiopia. The Tannery Sludge was collected from Abyssinia Tannery Factory located in Kality, near Bihere Tsege Public Park, Addis Ababa, Ethiopia. From which 1 ton of tannery sludge is generating weekly. The sludge was collected from the pressure filter press unit found in the factory's wastewater treatment plant. The other sample, which is, municipal waste incineration bottom ash was obtained from the Reppi waste-to-energy facility located at the outskirt of Addis Ababa, from which about 275 tons of municipal waste incineration bottom ash is generating daily. All of the samples were collected in February.

All of the samples were dried at 105 ℃ for 24hr to remove moisture. To get a uniform particle size, the samples were crushed and sieved in such a way that the sample did not contain larger particles. The pulverized samples were weighted, and preserved in an airtight plastic bag for the next step. Clay samples were prepared by mixing 75% white and 25% red soil samples as per the commercial brick standard composition.

Table 3.3 Analytical methods for raw samples characterization

Parameters	Standard test Method
For raw Tannery sludge, Bottom Ash and Clay	
pH	ASTM-D4972-01
Moisture Content	ASTM-D2216
Ash Content	ASTM-D2974
Organic Content	ASTM-D2974
Calorific Value	ASTM-D5865
Chemical Composition	Complete silicate and sulfur analysis
Heavy Metal content	EPA 3050B

3.1.2.2 pH determination

10 g of sample was taken and dried by air then sieved through a 2mm sieve to remove the courser fraction of the sample. Next to that, the sieved sample was placed into a glass container and 10 mL of distilled water was added. Later it was mixed thoroughly with the vortex shaker for 30min and let to stand for an hr. Finally, the pH meter was immersed into it and the pH was read.

3.1.2.3 Proximate analysis of the raw samples

The proximate analysis consists of the determination of moisture content, ash content, Organic matter, and calorific value.

- **Water Content (Moisture Content) determination**

To determine % water content of the samples, first the mass of the clean and dry aluminum foil was determined and recorded. Then the moist specimen was placed on the aluminum foil container and the mass of the foil and the moist sample was determined using balance and the value was recorded. Then, the aluminum foil with the moist sample was placed in the drying oven for about 24 hours. The mass of the sample was measured every four-hour interval. The temperature of the drying oven was maintained at 105℃. After the material has dried to a constant mass, the container was removed from the drying oven and allowed to cool to room temperature inside the desiccator for 30 min. Finally, the mass of the container and the oven-dried sample was determined using the same type of balance used previously.

The water content of the material was calculated as follows:

$$W = \frac{(Mcws - Mcs)}{(Mcs - Mc)} * 100 = \frac{Mw}{Ms} * 100 \text{………………………. Equation 3.1}$$

Where:

W = Water content, %,

Mcws = Mass of container and wet specimen, g,

Mcs = Mass of container and oven dry specimen, g,

Mc = Mass of container, g,

Mw = Mass of water, g, and

Ms = Mass of solid particles, g.

- **Ash content determination**

The mass of the porcelain dish was determined and 2g of the oven-dried test specimen from the moisture determination was placed in the dish. Next to that, then, the mass of the dish and the sample were determined, it was placed in a muffle furnace.

The muffle furnace's temperature was gradually brought to 750℃ and the specimen was held inside the furnace until it was completely ashed for about 2 hours. Subsequently, the container was removed and placed in a desiccator to be cooled. Finally, the mass of the porcelain with the ash was measured. The ash content was calculated as follows:

$$\text{Ash content (\%)} = \frac{Wpwa - Wp}{Ws} * 100 \ldots\ldots\ldots\ldots\ldots \text{Equation 3.2}$$

Where:

W_{pwa} = weight of porcelain with ash

W_p = weight of porcelain

W_s= weight of specimen

- **Organic matter determination**

The amount of organic matter present in the specimen was calculated by deducting the ash content from 100. Organic Matter content was calculated as follows:

$$\text{Organic content, \%} = 100 - AC \ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 3.3}$$

Where:

AC = Ash content, %

- **Calorific value determination**

The calorific value of the sample, which was dried at 105℃, was determined using an adiabatic oxygen bomb calorimeter. The result of the calorific value was used for the estimation of energy saving due to the incorporation of tannery sludge with in the clay brick. The test was conducted at the geological survey of Ethiopia.

3.1.2.4 Chemical composition

The chemical compositions of the raw samples were identified using complete silicate and sulfur analysis. The major and minor elements are expressed as oxides in percentage. Using $LiBO_2$ FUSION, HF attack, GRAVIMTRIC, COLORIMETRIC, and AAS method, the percentage oxide composition was determined. The analysis has been done at the Geochemical Laboratory, Geological Survey of Ethiopia.

3.1.2.5 Heavy metal determination

For heavy metal analysis, first, a round bottom flask was soaked with 10% of HNO_3 for 24 hours. Next, the flask was rinsed with distilled water and dried in a hot air oven for 90 min. Then, a 2 g lightly ground dried sample was taken and transferred into a digestion flask.

After that, the sample was digested with acid (HNO_3: HCl = 1:3 vol. ratio) for 24 hours in the fume hood at ambient temperature. Later, the flask was placed in an oil bath whose temperature was maintained at 95 ℃ for 2.5 hours. Finally, the solution was diluted with distilled water and filtered through a 0.45 µm filter paper. The filtrate was collected for the determination of the concentration of heavy metals. These are Cr, Pb, Cd, Ni, Cu, Co, and Zn. The reading was performed at JIJE LABOGLASS PLC using FAAS.

3.1.2.6 X-ray diffraction (XRD)

X-Ray Diffraction (XRD) analysis of the phase composition of the BA was accomplished by D8 ADVANCE BRUKER diffractometer. The instrument was operated at 40kV and 15mA (Cu-kα, λ=1.540593-1.544414 Å) using a scan range of 10-60° with a step size of 0.02°. The speed of scanning was set at 10 deg/min. This XRD analysis was performed at the college of natural science, department of chemistry, AAU.

3.1.2.7 Loss of ignition

Weight loss on ignition was obtained by heating 1 g of dry sample into a crucible with a heating rate of 3.08℃/minute up to a temperature of 950°C, maintaining this temperature for two hours. After that, the crucible was cooled and stored in a desiccator to determine the weight loss (Mora-Basto et al., 2019).

3.2 Production and characterization of bricks

The brick samples were made by mixing the three raw samples based on a respective ratio. Physicochemical characteristics of the bricks such as percentage of water absorption and compressive strength were performed as per the standard test methods. Moreover, heavy metal leach-ability test was also conducted for the optimized sample.

3.2.1 Materials

The main raw samples used for the brick-making purpose are tannery sludge (TS), municipal waste incineration bottom ash (BA), and clay.

- **Equipment and Instruments**

The following equipment and instruments were used for the production and characterization of produced bricks.

Table 3.4 List of equipment and instruments used in production and characterization of bricks

Equipment/instrument	Model	Use
Rectangular steel mold	-	To make bars of bricks
Compression testing machine	AUTOMAX 5 50- C4652	To measure the compressive strength of the bricks
Plastic bucket	-	To hold the brick samples and the water during testing the water absorption of the bricks

3.2.2 Method

In this production process, TS, and BA were used to replace brick clay partially with different replacement ratios. The mixtures of each batch were homogenized in a mixing bowl and 350-450ml of water was added to make the mixture plastic. Then, the plastic mixtures were passed into individual molds and given manual compaction to form bars of bricks. After a week of air drying in an open-air at the laboratory, the prepared bricks were subjected to heating at a rate of 5℃$/min$ up to the design temperature of 800, 900, and 1000℃ for 2hr and 50min - 3 hours.

15 brick samples (length, 10cm; width, 10cm; height, 5cm) of the TS-Clay-BA mixture in varying proportions were prepared in the laboratory and three reference bricks were also made from 75% white clay and 25% red clay at three different firing temperature for each response. After the completion of the burning process, the furnace was switched off and the bricks had not been removed until they become cool to room temperature. The prepared bricks were then taken to the laboratory for the determination of physical and mechanical properties.

Table 3.5 Analytical methods for product characterization

Parameters	Standard test method
Water absorption (%)	ASTM C67-03
Compressive strength (MPa)	ASTM C67-03

3.2.2.1 Box-Behnken experimental design

The experiments were designed according to the Box-Behnken method with the selected three important TS-BA-Clay brick production parameters: %Tannery Sludge, %Bottom Ash, and Firing Temperature. The required responses such as water absorption and compressive strength were optimized after studying the influences of these independent parameters and their interaction effects. The factors and levels are given in Table 3.6. The factors, i.e., tannery sludge, bottom ash, and firing temperature were designed as A, B, and C, respectively. The level of firing temperature was set to be in the range of 800℃ - 1000℃ by considering the point at which vitrification, important stage in brick production, starts.

Table 3.6 Experimental levels of selected variables for Box-Behnken design

Abbreviation	Variables	Units	Levels		
			-1 (Low)	0 (Medium)	+1 (High)
A	Tannery sludge	%	10	20	30
B	Bottom ash	%	10	20	30
C	Firing temperature	℃	800	900	1000

According to BBD the total number of experiments can be calculated as:

$$N = K^2 + K + Cp \ldots\ldots\ldots\ldots\text{ Equation 3.4}$$

Where K is a number of factors, and Cp is a central replication point (Kassahun, 2017).

A second-order polynomial equation was used to find the relationship between the independent variables and the response. For the three chosen factors, the equation can be written as:

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \varepsilon \ldots\ldots\text{Equation 3.5}$$

where β0 is a constant, A, B, and C are the independent variables, β_is are the coefficients for linear effect, β_{ij}s are the coefficients for cross-product interaction effect, β_{ii}s are the coefficients for quadratic interaction effect, and ε is the random error. The regression analysis and estimation of these coefficients were performed with a statistical software package Design-Expert® version 12 (Stat Ease, Inc.). The adequacy of the model equations was evaluated using analysis of variance (ANOVA).

Quality of fit of the model equations and their statistical significance were expressed using F-test, coefficient of determination (R^2), prediction coefficients of determination (Pred R^2), adjusted coefficients of determination (adj-R^2), and coefficients of variation (CV). To visualize the relationship between the experimental variables and responses, 3D plots were generated from the models. Each of the independent variables was studied at three levels (-1, 0, +1) (Table 3.6), with fifteen (15) experimental runs as shown in Table 3.7.

Table 3.7 Box-Behnken design of different production conditions

Run	**Factors**		
	A[1]	**B**[2]	**C**[3]
1	10 (-1)	10(-1)	900
2	10(-1)	30(+1)	900
3	20(0)	20(0)	900
4	20(0)	30(+1)	800
5	30(+1)	10(-1)	900
6	30(+1)	20(0)	1000
7	10(-1)	20(0)	1000
8	10(-1)	20(0)	800
9	20(0)	30(+1)	1000
10	30(+1)	20(0)	800
11	20(0)	20(0)	900
12	30(+1)	30(+1)	900
13	20(0)	10(-1)	1000
14	20(0)	10(-1)	800
15	20(0)	20(0)	900

[1] *%age Tannery Sludge*

[2] *%age Bottom Ash*

[3] *Firing Temperatures*

3.2.2.2 Investigation on the effect of brick production parameters

To determine optimum brick production conditions (%age of sludge, %age of BA, and firing temperature) a series of performance tests (%age water absorption, and compressive strength) were done with the prepared fifteen (15) brick samples based on the standard test method of ASTM C67-03.

3.2.2.3 Percentage of water absorption

The brick sample was dried in a ventilated oven at 110 °C for 24 h. After drying, the samples were cooled at room temperature. The dried and cooled brick was submerged, without preliminary partial immersion, in distilled water at 27 °C for 24 hours. Then the surface water of the brick was wiped off with a damp cloth, and the weight of the brick was taken within 5 minutes after removing the brick from the bath. Water absorption of the sample was calculated using the following equation.

$$\text{Water absorption, \%} = \frac{100(Ws-Wd)}{Wd} \text{………………Equation 3.6}$$

Where:

Wd = dry weight of the specimen, and

Ws = Saturated weight of the specimen after submersion in water

3.2.2.4 Compressive strength

The dimensions of the brick were measured and its area was calculated. Then paste of gypsum was made by mixing the gypsum powder with water and the paste was placed on both sides of the brick surface with 15 min intervals and leveled well. So that, the uneven surface in the brick will be eliminated. After capping both sides, the bricks were placed in a compression machine. Finally, the ultimate failure load was observed.

The compressive strength of each specimen was calculated as follows:

$$\text{Compressive strength, C} = \frac{W}{A} \text{……………. Equation 3.7}$$

Where:

C = Compressive strength of the specimen, $\frac{\mathrm{N}}{\mathrm{mm\^{}2}}$

W = Maximum load, N, and

A = average of the areas of the upper and lower bearing surfaces of the specimen, mm^2

3.2.2.5 Environmental aspects of TS-BA amended clay brick

Other than testing the compressive strength, and water absorption of the brick, the environmental safety of the bricks also needs to be verified by the leaching tests. The leaching tests were carried out to investigate the levels of possible leachates of heavy metals from the produced bricks. In this study leaching test follows the USEPA SW-846 Methods 1311 standard test method. Based on this test method, the dried sample was sieved through a 9.5 mm sieve mesh and an acetic acid solution (0.57% v/v) was prepared. Next, 75 g of sample was weighed and placed in a 2 L PE bottle, and acetic acid was added to the samples at a constant ratio of liquid: solid (20:1 w/w). Then the PE bottle was sealed and placed in a rotary agitator, whose speed of rotation was 30 rpm, for 18 hours at 25℃. Later, the leachate was filtered with a 0.6 µm membrane filter. Finally, the concentration of all metals in the leachate was analyzed using flame atomic absorption spectrometry (FAAS). The leachate analysis was conducted at the Ethiopian construction design and supervision works corporation.

3.2.2.6 Energy saving during firing of tannery sludge incorporated clay brick

Brick production industries are considered to be one of the highest energy-consuming sectors and have a large negative impact on the environment related to energy use so, savings in energy consumption by incorporating tannery sludge may lead to sustainable brick production. The firing energy saved due to incorporating sludge can be calculated using the following equation derived by (Mohajerani et al., 2016).

Energy used for control clay brick, $Q_1=q*m_1$

Energy used for TS-MWIBA brick, $Q_2=q*m_2-CV*m_3$

Energy saved, $Q_1-Q_2=q*m_2-(q*m_2-CV*m_3)$

Energy saved, $\Delta E(\%) = \frac{Q1-Q2}{Q1}*100\%$

$$= \frac{q*m1-(q*m2-CV*m3)}{q*m1} \ldots\ldots \text{ Equation 3.8}$$

Where:

q= 3MJ Kg^{-1} energy used for brick making

m_1= mass of clay in control clay brick (kg)

m_2= mass of clay in TS-BA brick (kg)

m_3= mass of TS in TS-BA brick (kg)

CV= Calorific value of TS

3.3 Optimization of the production

From the Box-Behnken experimental design, numerical optimization was used to optimize the production. Depending on the experiment result, constraints and goals for the brick production parameters and responses were set. The solution with the highest desirability was chosen and in order to verify the optimization results, the selected parameters were validated in the laboratory with suggested values.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Characteristics of raw Samples

4.1.1 Proximate analysis

Table 4.1 Results for the Physical-chemical characteristics of raw samples

Properties	**Clay Soil**		**Tannery sludge**	**Bottom Ash**
	White Soil	Red Soil		
pH	7.83	7.63	6.900	11.1
Moisture Content (%)	23.1	10.79	68.27	16.4
Ash Content (%)	95.0	80.0	55.00	92.5
Organic Content (%)	5.00	20.0	60.00	5.00
Loss on Ignition (%)	7.05	9.39	52.79	4.78
Calorific Value (Cal/gm)	-	-	2691.2	-

Table 4.1 shows the physical-chemical parameters of clay, sludge, and bottom ash. The pH values of dried white clay and red clay are 7.83 and 7.63, respectively. The pH of the tannery sludge was measured to be 6.9. The bottom ash sample, on the other hand, is in the basic range, with a pH of 11.12. However, according to Ethiopian environmental protection standards, the pH of waste should be between 6.5 and 8.0 to be disposed so that BA could not disposed of directly to the environment. The presence of $Ca\ (OH)_2$ in the bottom ash makes it to be alkaline. Calcium carbonate is decomposed into calcium oxide (CaO) and carbon dioxide (CO_2) during the burning of waste items containing $CaCO_3$ at a temperature of 900°C. During quenching at the furnace exit, CaO is hydrated and forms $Ca\ (OH)_2$.

The sludge sample, white clay, and red clay all had moisture content of 68.27%, 23.1%, and 10.79%, respectively. With a moisture content of 16.4%, the bottom ash had a lower moisture content than the white clay and sludge at the time of collection. The weather and the amount of time it takes to dry before collection determine the moisture content of the sample. The ash content of the white clay, red clay, tannery sludge, and bottom ash samples was determined to be 95%, 80%, 55%, and 92.5%, respectively.

The organic content of sludge, white clay, red clay, and bottom ash was 60%, 5%, 20%, and 5% respectively. When compared to the rest of the raw samples, the sludge had a high organic content (60%). This is due to the presence of proteinaceous particles in the sludge from liming and unhairing procedures. As a result, the sludge's loss on ignition increases to 52.79%, making the product lighter than the control brick. Since the waste to energy facility incinerates the wastes at high temperatures, the organic content of the bottom ash was found to be low (5%) in comparison to the sludge.

The presence of organic matter reduces the quality of the brick by forming pores during the firing process. The pores created by burning of organic matter are responsible for high water absorption. On the other hand, the presence of organic matter raises the calorific value of the sludge, which is related to energy savings during combustion. A sample with a higher calorific value requires less energy for firing.

4.1.2 Heavy metal content result

The heavy metal content of the raw samples is described in Table 4.2. The main component of tannery sludge was discovered to be chromium metal. The other heavy metals contained in the sludge were discovered to be in the following order: Cr > Zn > Ni > Co > Cu > Cd > Pb. The principal component of bottom ash was discovered to be Zink metal. Other heavy metals contained in the bottom ash were found in the following order: Zn > Cu > Ni > Pb > Co > Cr > Cd. As can be seen from the result, all of the tested parameters surpassed the regulation limit set by the USEPA for waste disposal.

Table 4.2 Heavy Metal Composition of raw samples

Analytes (ppm)	**Clay Soil**		**Sludge**	**Bottom Ash**
	White Soil	Red Soil		
Cu	70.20	58.00	8.00	1011.6
Zn	130.20	114.20	308.6	2045.4
Pb	42.80	24.00	<0.01	86.20
Co	42.60	67.00	16.00	57.60
Ni	49.80	49.80	48.20	132.00
Cd	-	-	0.012	0.645
Cr	-	-	1246.9	14.04

The composition of tannery sludge and bottom ash might vary from place to place due to the variety of the tanning process, chemicals, and kind of waste involved. Despite this, chromium has remained the most prevalent ingredient, as seen by tannery sludge. For example, Juel et al. (2017b) found 19,229 mg/kg Cr in Tannery Sludge.

4.1.3 Chemical composition result

Table 4.3 shows the chemical compositions of the raw samples. In the sludge sample, the primary components were SiO_2, CaO, Al_2O_3, and Fe_2O_3, whereas the main components in the bottom ash sample were SiO_2, Al_2O_3, CaO, Fe_2O_3, P_2O_5, SO_3, MgO, and NaO.

Table 4.3 Chemical composition of the raw samples

Analytes (%)	**Clay Soil**		**Sludge**	**Bottom Ash**
	White Soil	**Red Soil**		
SiO_2	59.5	46.54	27.24	46.28
Al_2O_3	21.85	24.66	4.10	17.58
Fe_2O_3	4.82	13.00	1.08	7.44
CaO	<0.01	<0.01	7.36	13.56
MgO	0.08	0.60	<0.01	1.32
Na_2O	1.62	<0.01	<0.01	1.28
K_2O	0.62	<0.01	<0.01	0.52
MnO	0.08	0.14	<0.01	0.12
P_2O_5	0.13	0.30	0.67	3.76
TiO_2	0.22	0.86	0.09	0.52
LOI	7.05	9.39	52.79	4.78

The content of SiO_2 is relatively high, according to the findings. Furthermore, the content of fluxing agents K_2O and MgO was minimal, indicating that a high level of densification would be impossible (Mora-Basto et al., 2019). The clay used to make bricks had similar components to those found in sludge and bottom ash, but in different amounts. As a result, tannery sludge and bottom ash can partially replace clay and used as a raw material for brick production. The amount of Fe_2O_3 was relatively low in the tannery sludge consequently the color of the brick with high proportion of sludge became dark. When it comes to CaO, it's content was higher than that of the clay so that during drying of the green bricks, the size of the bricks did not shrink that much.

4.1.4 XRD result

The mineralogical composition of municipal waste incineration bottom ash was determined using XRD analysis. The investigation of the peaks obtained by the XRD revealed the presence of quartz (SiO_2), calcite ($CaCO_3$), hematite (Fe_2O_3), and bauxite (Al_2O_3).

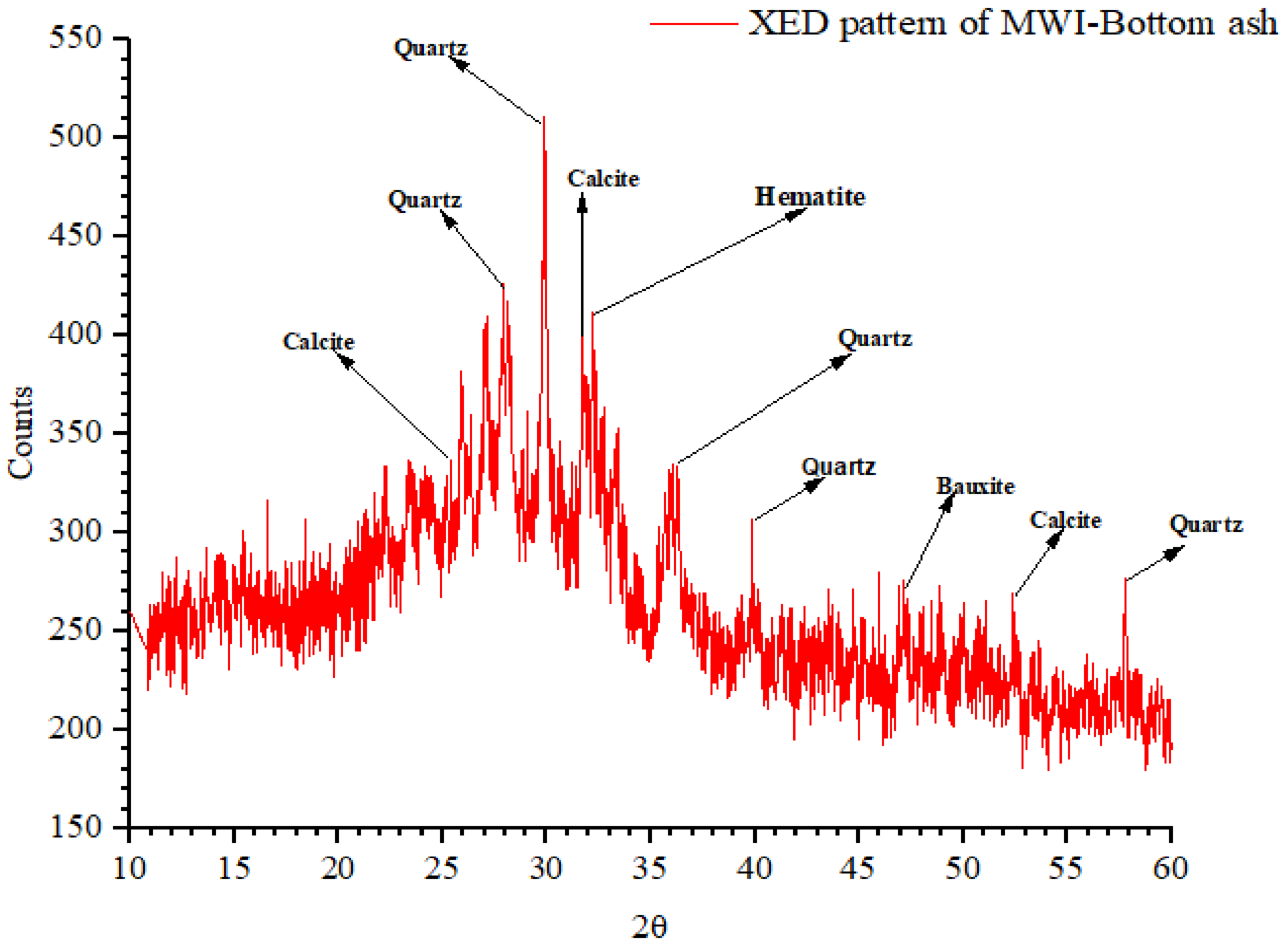


Figure 4.1 X-ray diffraction patterns for municipal waste incineration bottom ash

4.2 Performances of bricks prepared using different production conditions

4.2.1 Statistical analysis on brick production

A Box-Behnken design was used to determine a minimum % age water absorption and a maximum compressive strength. A total of 15 experimental runs were carried out using the relationships in Table 3.4, including the central point that assesses process stability and inherent variability. To model and optimize experiments, % tannery sludge (A), % bottom ash (B), and firing temperature (C) were used as independent variables. The experimental responses employed were water absorption and compressive strength. Table 4.4 shows how the responses were entered into the design layout. The major statistical analyses of the production process are summarized below, including model generation, model fitness test, and ANOVA analysis. The design matrix for three variables is varied at three levels (+1, 0, -1).

A second-order model with interaction terms effective on water absorption and compressive strength of different bricks was developed using the response surface design method. To avoid a systematic inaccuracy, the experiments were carried out in a random order, as is customary. Both quadratic terms were effective on both responses, according to the analysis of variance. Table 4.4 displays the results of the analysis of variance (ANOVA) for the response surface quadratic model for water absorption.

The P-values were utilized to determine the significance of each of the coefficients, which is required to comprehend the pattern of mutual interactions between the test variables. The higher the significance of the corresponding coefficient, the larger the magnitude of the F-test value and the smaller the magnitude of P-values. The model terms are significant if the P value is less than 0.05. A, B, C, AC, BC, and C^2 are significant model terms in this situation. The coefficient of determination, R^2, was used to express the model equation's fitness. Analysis of variance was used to determine the model's suitability. The developed correlation has an R-squared value of 0.9954. It means that the experimental factors analyzed account for 99.54 % variation in the percentage of water absorption.

The ANOVA revealed that the linear effects of tannery sludge and bottom ash, the quadratic effect of firing temperature, the linear effect of firing temperature, and the interaction effect between tannery sludge and firing temperature had the highest to lowest effects on the % age WA, respectively ($P \leq 0.01$), followed by the interaction effect between bottom ash and firing temperature ($P \leq 0.05$).

The interaction effect between tannery sludge and bottom ash, and the remaining two quadratic effects of tannery sludge and bottom ash had no impact on the WA. The significant terms were thus included in the final models. The lack of fit test yielded a P-value of 0.1242 and an F-value of 7.21, indicating that the lack of fit is not significant when compared to the pure error on the WA, implying that the model fits well.

For this study, the R^2 for the two responses i.e., WA, and CS, was found to be 0.9954, and 0.9891 respectively. These imply that the models were adequate to predict the response in the experimental range with 99.54, and 98.91% variability. The Pred R^2 shows that the model equations for WA and CS give good predictions with 93.25, and 90.57 % variability, respectively. In addition, the adj-R^2 of water absorption (98.73%), and CS (96.95%) were in a reasonable agreement with Pred R^2 values. Adeq precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The adeq ratio for water absorption and Compressive strength is 36.1 and 21.858 respectively, which indicates an adequate signal and the possibility of using this model to navigate the design space.

Table 4.4 Design expert output (ANOVA) for the water absorption of the TS-BA amended clay bricks

Response 1: Water absorption (%W. A)

ANOVA for Response Surface Quadratic Model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	391.4	9	43.49	121.54	<0.0001	Significant
Linear effect						
A	155.5	1	155.5	434.56	<0.0001	
B	147.06	1	147.06	410.99	< 0.0001	
C	21.95	1	21.95	61.33	0.0005	
Interaction effect						
AB	1.09	1	1.09	3.05	0.1411	
AC	17.56	1	17.56	49.06	0.0009	
BC	5.31	1	5.31	14.85	0.0120	
Quadratic effect						
A^2	0.1953	1	0.1953	0.5459	0.4932	
B^2	0.1828	1	0.1828	0.5108	0.5067	
C^2	41.31	1	41.31	115.46	0.0001	
Residual	1.79	5	0.36			
Lack of Fit	1.64	3	0.5459	7.21	0.1242	Not significant
Pure error	0.15	2	0.076			
Cor total	393.19	14				
Std. Dev	0.6		**R^2**		0.9954	
Mean	24.53		**Adjusted R^2**		0.9873	
C.V	2.44		**Predicted R^2**		0.9325	
PRESS	26.54		**Adeq Precision**		36.1040	

For compressive strength (Table 4.5), the variables with largest to smallest effects on the compressive strength were the linear effect of bottom ash, the linear effect of tannery sludge, the interaction effect between tannery sludge and firing temperature, the quadratic effect of firing temperature, the linear effect of firing temperature, followed by the interaction effect between tannery sludge and bottom ash respectively. As the quadratic effect of tannery sludge and the quadratic effect of bottom ash, the interaction effect between bottom ash and firing temperature gave an insignificant effect ($P > 0.05$) on the compressive strength.

Table 4.5 shows the compressive strength's coefficient of determination (R^2), adjusted coefficient of determination (adj R^2), and predicted coefficient of determination (Pred R^2). High R^2 values meant that all quadratic models were very good at fitting the data under the conditions of the experiment, and adjusted R^2 values meant that the predicted and experimental values of the model were in good agreement. The predicted and experimental values of the two responses and the graph of the predicted values, obtained using the developed correlation, versus actual values are shown in **Appendix B.**

Table 4.5 Design expert output (ANOVA) for the compressive strength of TS-BA amended clay bricks

Response 2: Compressive strength (C.S)

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares-Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	18.44	9	2.05	50.53	0.0002	Significant
Linear effect						
A	5.38	1	5.38	132.66	<0.0001	
B	7.62	1	7.62	188.04	< 0.0001	
C	2.57	1	2.57	63.26	0.0005	
Interaction effect						
AB	0.51	1	0.51	12.61	0.0164	
AC	0.57	1	0.57	14.06	0.0133	
BC	0.014	1	0.014	0.36	0.5772	
Quadratic effect						
A^2	0.00031	1	0.00031	0.00765	0.9337	
B^2	0.017	1	0.017	0.43	0.5431	
C^2	1.72	1	1.72	42.31	0.0013	
Residual	0.2	5	0.041			
Lack of Fit	0.095	3	0.032	0.58	0.6809	Not significant
Pure error	0.11	2	0.054			
Cor total	18.64	14				
Std. Dev	0.20		**R^2**		0.9891	
Mean	8.63		**Adjusted R^2**		0.9695	
C.V. %	2.33		**Predicted R^2**		0.9057	
PRESS	1.76		**Adeq Precision**		21.858	

Table 4.6 shows the second-order polynomial models for water absorption and compressive strength. According to Kumar et al. (2008), when the regression coefficient has a positive value, the response will be raised, and when the regression coefficient has a negative sign, the response will be decreased. The results revealed that increasing tannery sludge and bottom ash with a lower firing temperature resulted in a smaller Water absorption and a greater Compressive strength. The interaction effect between tannery sludge and firing temperature and the interaction effect between bottom ash and firing temperature affect the water absorption negatively.

Table 4.6 Second-order polynomial model for water absorption and compressive strength

Response	**Second-order polynomial model**
Water absorption	Coded: $Y = 26.07+4.41A + 4.29B + 1.66C + 2.09AC+1.15BC – 3.35C^2$ Actual: $= -214.82–1.64A – 0.802B +0.5537C + 0.0021AC +0.001153BC- 0.00034C^2$
Compressive strength	Coded: $Y = 8.3–0.82A-0.98B + 0.57C + 0.36AB + 0.38AC+ 0.68C^2$ Actual: $= 71.07 - 0.497A - 0.12B - 0.126C+0.0036AB + 0.000377AC + 0.000068C^2$

Y = Coded value of response, A = coded value of Tannery sludge (%), B = Coded value of Bottom ash (%), C = Coded value of firing temperature (℃)

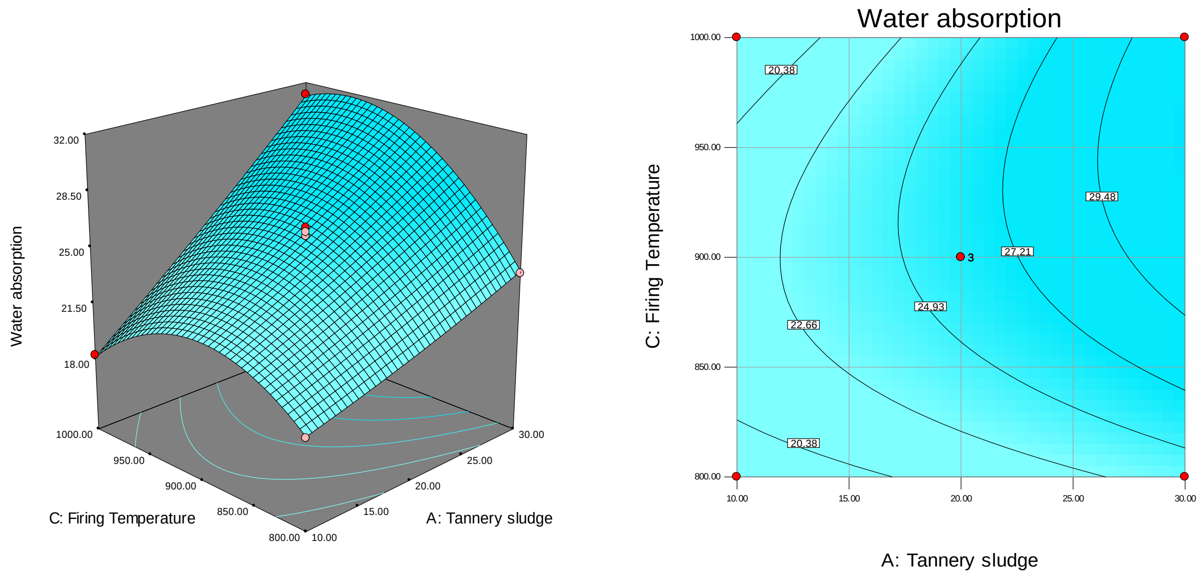
4.2.2 Interaction effects on the water absorption of the brick

The water absorption of the brick determines its long-term durability. The less water that gets into brick, the longer it will last and the more resistant it will be to the environment. As a result, the interior structure of the brick must be sufficiently dense to prevent water penetration (Weng et al., 2003). The water absorption test results of the control clay brick declined as the firing temperature was increased. The water absorption of 100 % clay bricks burnt at 800°C, 900°C, and 1000°C was determined to be 14.7%, 13.4%, and 8.56%, respectively. As a result, it can be stated that raising the firing temperature improves water absorption for waste-free control bricks. The water absorption test results for TS-BA bricks, on the other hand, ranged from 187.89% to 36.2%.

Five different bricks with a mixing ratio (A: B) of 10:10 with a firing temperature of 900°C, 20:10, and 10:20 with a firing temperature of 1000°C, and 10:20 and 20:10 with a firing temperature of 800°C achieved water absorption of less than 23%, meeting the requirements of ES 86:2001 and ASTM C 62-04 for clay bricks. along with the two standards, these bricks were categorized as Class A and Grade SW, respectively. The water absorption of one brick was between 23% and 24%, whereas the water absorption of the second brick was between 24% and 25%. Referring to ES 86:2001 and ASTM C 62-04, these bricks are designated as class B and Grade MW and class C and Grade MW, respectively. The remaining eight bricks have a water absorption greater than 25% and are categorized as class C and Grade NW, respectively.

The experimental data gathered from the interactions of the independent variables' responses were evaluated. Figure 4.2 depicts the three-dimensional response surface plot as well as the contour plot for water absorption. The interaction effect of tannery sludge and firing temperature on the water absorption of the brick (Fig. 4.2a) revealed that a minimum water absorption was achieved at 1000°C and 10% tannery sludge content, and a maximum water absorption was achieved at 1000°C and 30% tannery sludge content. The ANOVA shows that tannery sludge is the most significant term, followed by firing temperature. Increased tannery sludge tends to increase the brick's water absorption. The effect of tannery sludge can be explained by the fact that increasing tannery sludge lowers the quantity of silica in the brick mixture, which gives the bricks their resilience. The water absorption rises from 18.23 % to 21.91 % when the firing temperature is increased from 800°C to 900°C while retaining the tannery sludge at 10%.

However, as the firing temperature goes from 903°C to 1000°C, the value of water absorption begins to fall. This is due to the fact that vitrification begins at 871°C, which is the temperature at which the mass is transformed into a glass-like substance. Furthermore, the tannery sludge contains a high amount of organic matter, 60 % (Table 4.1), and as the firing temperature rises with the tannery sludge, the water absorption rises as well, due to the burning of the organic matters, which has the ability to create pore spaces in the brick that favor water absorption. Juel et al., observed that a large amount of sludge and a higher firing temperature resulted in higher water absorption, while a smaller amount of tannery sludge and a higher firing temperature resulted in reduced water absorption.



(A) (B)

Figure 4.2 3D Response surface (A) and contour (B) plots of the interaction between tannery sludge and firing temperature on water absorption

With a three-dimensional response surface plot and contour plot holding tannery sludge constant at 20%, the effect of bottom ash and firing temperature on the % age WA of the brick is depicted in Fig. 4.3. The smallest water absorption was recorded as 18.7% when the firing temperature and amount of bottom ash were kept at 800°C and 10%, respectively, as shown in the three-dimensional plot. As the quantity of bottom ash added raised from 10% to 30%, the brick's water absorption increased from 18.7% to 24.9%.

Bottom ash has an angular and uneven shape with a porous microstructure created from the heating and cooling process during incineration; as stated by Lynn et al., 2016. Its irregularity and porosity cause considerable water absorption. More precisely, when we moved diagonally from the bottom to the top, the water absorption increased from 18.43% to 26.35%, while the firing temperature and amount of bottom ash increased from 800°C to 900°C and 10% to 20%, respectively.

Water absorption increases from 26.35 % to 29.5 % as the firing temperature and amount of bottom ash rise from 900°C to 1000°C and 20% to 30 %, respectively. This conclusion coincides with, Haque, O. 2011, in that a larger amount of bottom ash resulted in higher water absorption, but not with the firing temperature. As stated by Haque, O. 2011, Increasing the firing temperature minimizes water absorption. The disagreement might be occurred due to the type of waste materials charged into the incinerator, as well as the heating and cooling methods utilized during incineration. Another possible explanation might be that the porous structure of the bottom ash influenced the response considerably than the firing temperature.

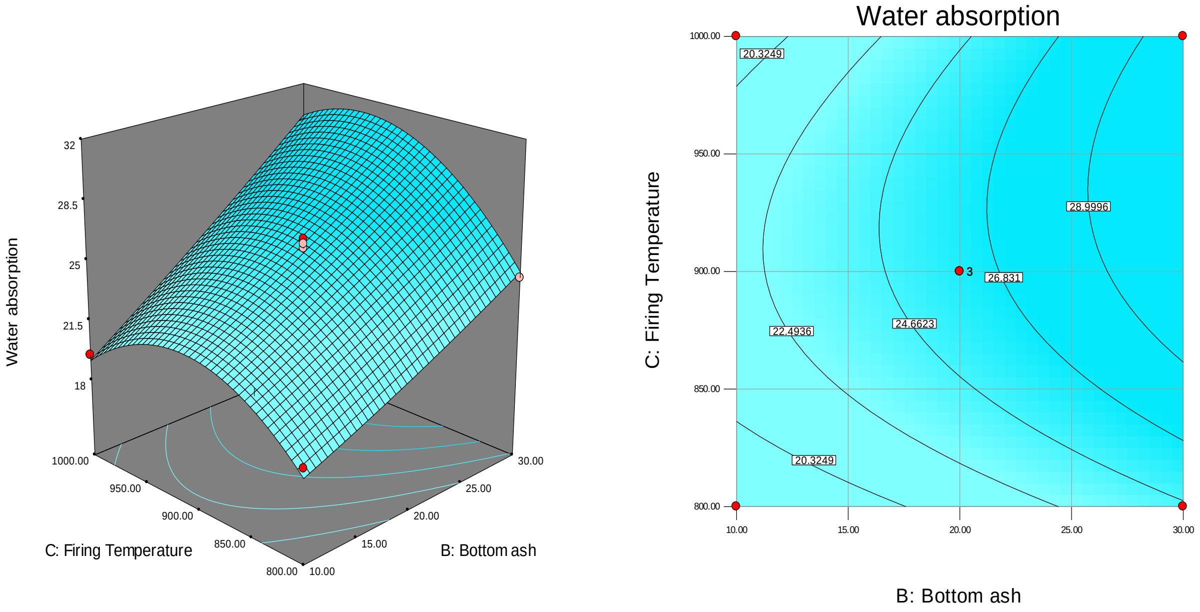


Figure 4.3 3D Response surface (A) and contour (B) plots of the interaction between Bottom ash and Firing Temperature on water absorption.

4.2.3 Interaction effects on the compressive strength of the brick

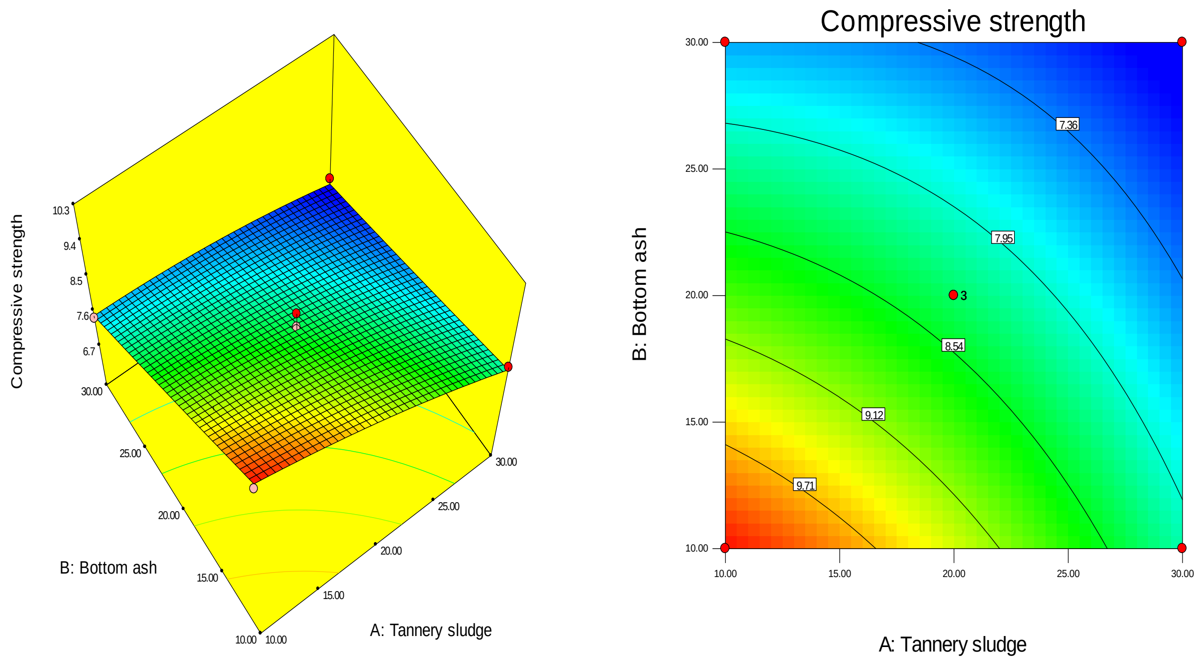
The compressive strength test is an essential factor in defining the engineering quality of a building material. The ability of a material to resist forces at failure is its strength. The compressive strength test result of the control clay brick improved as the firing temperature was increased. The compressive strength of 100% clay bricks fired at 800°C, 900°C, and 1000°C is 17.78MPa, 24.2MPa, and 27.5MPa, respectively. According to the ES 86:2001 and ASTM C 62-04 criteria, all the three control bricks were classified as Class A and Grade SW bricks respectively.

However, depending on the content of TS, BA and firing temperature, the compressive strength of TS-BA incorporated bricks ranged from 6.91 to 10.38Mpa. The sludge and bottom ash contents are inversely proportional to compressive strength, but the firing temperature is directly proportional. The compressive strength of eleven of the fifteen TS-BA integrated brick samples ranged from 8.14 to 10.38 MPa. All of them were categorized as Class C as maintained by ES 86:2001. However, referring to ASTM C 62-04, only six of them met the requirements to be designated as Grade NW bricks. The remaining four bricks had compressive strengths ranging from 6.91 to 7.45 MPa and were classified as Class D bricks along with ES 86:2001, yet they failed to meet any of the ASTM's requirements.

The experimental data gathered from the interactions of the independent variables' responses were evaluated. Figure 4.4 displays the three-dimensional response surface plot and the contour plot for the brick's compressive strength. The two interaction effects had a significant impact on the bricks' compressive strength. Those were, the interaction between tannery sludge and bottom ash (AB), and the interaction between tannery sludge and firing temperature (AC).

The interaction effect between tannery sludge and bottom ash is depicted in Fig. 4.4a. as shown in the 3D surface plot, the maximum compressive strength was attained when the amount of tannery sludge and bottom ash were kept at 10% each while the firing temperature was kept at 900°C. Referring to the 3D plot, the brick's compressive strength was observed to be reduced from 8.26MPa to 8.15MPa and from 8.26MPa to 7.45MPa when the percentage of tannery sludge and bottom ash increased respectively.

From these results, it was discovered that the amount of bottom ash had a greater impact on compressive strength than tannery sludge. The existence of a high amount of calcite in bottom ash was confirmed by XRD analysis, and this $CaCO_3$ decomposes into CaO and CO_2 at 900°C and above. The strength of the bricks may be affected by the calcination procedure (Chimenos et al., 1999).

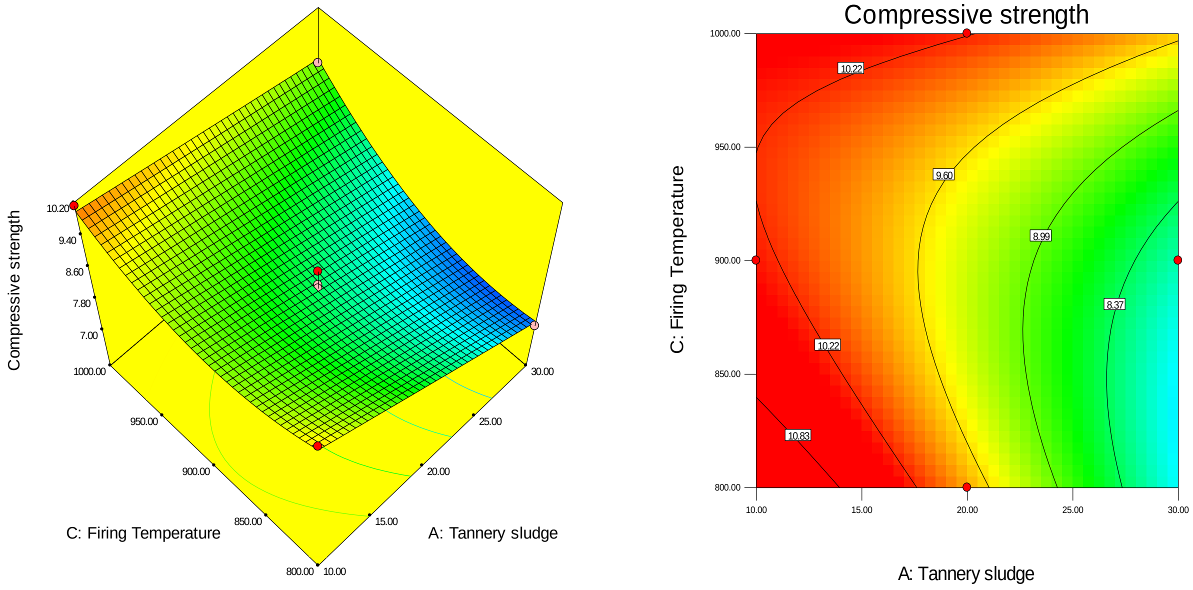


(A) (B)

Figure 4.4 3D Response surface (A) and contour (B) plots of the interaction between Tannery sludge and Bottom ash on compressive strength

In Fig. 4.5, the influence of tannery sludge and firing temperature on the compressive strength of the brick is depicted using a three-dimensional response surface plot and a contour plot, with a constant 10% bottom ash. The greatest compressive strength was achieved at a firing temperature of 1000°C and a 20% tannery sludge content and the minimum compressive strength was recorded at a firing temperature of 800°C and a 30% tannery sludge content. The compressive strength of the bricks decreased from 8.33 to 7.10 MPa as the tannery sludge content raised from 10% to 30%, while it increased from 8.33 to 10.12 MPa when the firing temperature rose from 800°C to 1000°C.

This is most likely due to the burning of organic materials and the compaction of bricks. This research supports the findings of the previous research of (Juel et al., 2017). The brick's compressive strength was maximized resulting in a high firing temperature and a small proportion of tannery sludge.



(A) (B)

Figure 4.5 3D Response surface (A) and contour (B) plots of the interactions between Tannery sludge and firing temperature on compressive strength

4.2.4 Optimal brick production parameters to prepare a high-performance brick

Preliminary findings suggest that the bricks' water absorption and compressive strength fluctuate depending on the experiment conditions, reaching values of 17.89% and 10.38 MPa, respectively, under a certain production condition. At a firing temperature of 1000°C, 20% tannery sludge content, and 10% bottom ash, the maximum compressive strength was achieved. In terms of the other response, the lowest water absorption was achieved at 900°C firing temperature, 10% tannery sludge content, and 10% bottom ash content. However, one of the goals of this study is to find the best brick production condition for maximum compressive strength and minimal water absorption. Table 4.7 shows the constraints that were used to optimize the production parameters. A total of twenty-nine solutions were discovered.

Three brick samples were made in the laboratory using the same optimum conditions as the solution with the highest desirability. The validation result for tannery sludge-bottom ash incorporated brick is shown in Table 4.8.

Table 4.7 Optimization constraints and solutions for a TS-BA amended clay brick production parameters

Constraints

Name	Goal	Lower limit	Upper limit
TS	Is In range	10	30
BA	Is in range	10	30
FT	Minimize	800	1000
WA	Minimize	17.89	36.2
CS	Maximize	6.91	10.38

Solutions

Number	TS	BA	FT	WA	CS	Desirability	
1	10.62	11.26	800.00	16.96	10.69	1.000	Selected
2	10.93	12.18	800.00	17.21	10.53	1.000	
3	11.40	10.70	800.00	16.94	10.64	1.000	
4	11.07	11.84	800.00	17.16	10.55	1.000	

Table 4.8 Validation result for tannery sludge-bottom ash incorporated brick

Parameters	Model predict	Experimental result
Tannery sludge (%)	10.62	11.00
Bottom ash (%)	11.26	12.00
Firing temperature (℃)	800.00	800.00
Water absorption (%)	16.96	17.56±0.2
Compressive strength (MPa)	10.69	10.72±0.08

4.3 Environmental aspects of TS-BA amended clay brick

Heavy metal leaching can be a problem because waste materials with high quantities of heavy metals are integrated into clay bricks. It is vital to ensure that heavy metal leaching from the bricks does not exceed the maximum allowed level. Table 4.9 shows the concentration of metals leached out from the brick. As illustrated in Table 4.9, the concentration of Cr leached out from the brick is in minuscule levels, and the rest metals were found to be below the detection limit.

The metals may be trapped inside the burnt bricks due to a silicate-based Physical-chemical containment mechanism and the fusing of ash residue within a glassy matrix after the bricks have been exposed to high temperatures (Liew, Idris, Samad, et al., 2004). Hexavalent chromium (Cr^{+6}), the most toxic species of chromium, is reduced to trivalent chromium (Cr^{+3}) at high temperatures (800°C or higher), and $CaCrO_4$ becomes the dominant crystalline phase in coexistence with magnesium chromite ($MgCr_2O_4$), in which chromium is found as Cr(III), and chromium mobility is limited as these compounds are insoluble (Juel et al., 2017b).

Table 4.9 Leaching test result of optimized TS-BA amended clay brick fired at 800℃

Metals	Optimized brick sample Heavy metal Content (ppm)	USEPA regulatory limit (ppm)
Chromium (Cr)	0.24	5
Lead (Pb)	ND	5
Nickel (Ni)	ND	11
Copper (Cu)	ND	100
Zinc (Zn)	ND	500

ND: Not detected

4.4 Energy saved through the incorporation of TS in clay brick

The calorific value of the tannery sludge employed in this investigation is 11.26 MJ/Kg. The amount of energy saved during the firing of a TS-BA incorporated clay brick was determined using Eq.1. The results showed that for '10% TS,' an estimated 46.16% of energy would be saved and for '20% TS,' an estimated 80.26% of energy would be saved. Although increasing the amount of tannery sludge in a brick affects its quality (compressive strength and water absorption), bricks with a higher tannery sludge content can effectively save energy. The tannery sludge employed in this study had a 60% organic content, which could help with heat input to the furnace and minimize the amount of energy needed for firing.

Table 4.10 Energy saved during firing at 1000℃

Sludge Content (%)	M_1 (Kg)	M_2 (Kg)	M_3 (Kg)	**Energy saved** (%)
10	0.600	0.5171	0.05171	46.16
20	0.600	0.4749	0.09498	80.26

M_1= Mass of control brick

M_2= Mass of TS-BA brick

M_3= Mass of TS in TS-BA brick

q= $3 MJKg^{-1}$

$$\%\textbf{Energy saved} = \frac{qM1 - (qM2 - qM3)}{qM1}$$

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Raw samples obtained from Abyssinia tannery and Reppie waste to energy facility were classified as hazardous wastes owing to the presence of toxic heavy metals in both wastes at concentrations exceeding the permissible limits set by the USEPA regulatory limit. As a result, dumping these pollutants into the environment without treatment causes significant environmental damage. These wastes, on the other hand, can be used to make a construction material as their chemical compositions are quite similar with that of the clay used in brick production.

The major goal of this study was to employ both wastes as raw materials and produce brick by substituting them for a portion of clay soil and the specific objectives were characterization of the raw samples, to test the performance of the produced bricks, to study the interaction effects of production parameters, to optimize the operating parameters, to conduct a leaching test to check the toxicity of the brick, and to check the effect of incorporating tannery sludge with in clay brick in terms of energy saving.

In this study, laboratory tests and analysis were performed to assess the chemical properties of the collected raw samples and fifteen TS-BA amended and three control (100%) clay brick samples were made and their properties investigated to evaluate their responses (water absorption and compressive strength) under different mixing proportion and firing temperature, to observe the interaction effects of the independent variables, and finally to optimize the production parameters to determine their suitability to be used as a clay substitute to produce bricks for construction purpose.

According to the results of a complete silicate analysis, the waste materials have the same chemical makeup as clay, but in different amounts. As a result, it may be inferred that these waste materials can partially replace clay soil in the production of bricks. From the three raw samples, tannery sludge has a high calorific content (calculated at 11.26MJ/Kg). So, integrating it into the brick mixture can minimize the energy needed to produce bricks.

The water absorption of the bricks increases as the TS and BA increase with the firing temperature. When TS and BA were increased, the compressive strength of the bricks fell, but raising the firing temperature helped the bricks attain high compressive strength. However, TS-BA incorporated bricks were found to meet both Ethiopian and ASTM specifications for fired bricks used in construction. The optimum recipe for TS-BA incorporated bricks is 10.62% TS, 11.26% BA, and a firing temperature of 800°C. The concentrations of heavy metals leached out of the optimized sample are negligible and far below the USEPA standards regulatory limit. As a result, other than their potential use as raw materials for brick production, it is concluded that including these waste materials in brick production can limit the release of particularly dangerous heavy metals into the environment.

By introducing 10-20% TS into the brick mix, the firing energy savings of the TS-BA incorporated clay bricks were calculated to be in the range of 46.16 % -80.26 %. As a result of combining TS and BA with clay, a high-quality, environmentally friendly brick is produced that meets Ethiopian and ASTM criteria for physical and mechanical qualities of fired bricks. The overall results lead to the conclusion that tannery sludge and municipal waste incineration bottom ash can be used as a raw material for producing environmentally sound construction materials.

5.2 Recommendations

- The incorporation of TS and BA in significant proportions should be investigated further.
- Further research on the use of fluxing chemicals to improve the brick's durability.
- More research into the use of TS and BA to make other building materials is needed.
- Further research into the potential of extracting and recovering useful metals from BA.
- Further study on the compositional analysis of the TS and BA amended clay brick.
- Other production parameters influencing the qualities of the bricks must be identified.

REFERENCES

Abajihad, Z. (2012). Assessment of Tannery Solid Waste Management and Characterization-A Case of Ethio-Leather Industry Private Limited Company (ELICO). *Unpublished D.Phil. Thesis. Ethiopia: Addis Ababa University, School of Engineering.*

African Clean Cities Platform (ACCP). (2019). *Basics of municipal solid waste management*.

Ahamed, M. I. N., & Kashif, P. M. (2014). Safety Disposal of Tannery Effluent Sludge : Challenges To Researchers- a Review. *International Journal of Pharma Sciences and Research (IJPSR)*, *5*(10), 733–736.

Alibardi, L., & Cossu, R. (2016). Pre-treatment of tannery sludge for sustainable landfilling. *Waste Management*, *52*, 202–211.

Astrup, T., Muntoni, A., Polettini, A., Pomi, R., Van Gerven, T., & Van Zomeren, A. (2016). Treatment and Reuse of Incineration Bottom Ash. In *Environmental Materials and Waste* (pp.607-645). Academic Press.

Rand, T., Haukohl, J., & Marxen, U. (2000). *Municipal Solid Waste Incineration: requirments for a successful project (Vol. 462). World Bank Publications*.

Belayneh, A. T. (2013). *Effects of Firing Temperature on Some Physical Properties of Burnt Clay Bricks Produced Around Addis Ababa (*unpublished Master's Thesis*).* Addis Ababa University,Addis Ababa, Ethiopia.

Brick Industry Association. (2006). Technical notes on brick construction: Manufacturing of Brick. *Brick Industry Association*, *December*, 1–7.

Cengizler, H., Cicek, T., & Tanriverdi, M. (2012). A Brief Overview of Fly Ash Brick Production. In *Proceeding XIII. Int. Miner. Process. Symp.* (pp. 983-992).

Chimenos, J. M., Segarra, M., Fernandez, M. A., & Espiell, F. (1999). *Characterization of the bottom ash in municipal solid waste incinerator*. *Journal of hazardous materials*, *64*(3), 211-222.

Cho, B. H., Nam, B. H., An, J., & Youn, H. (2020). Municipal solid waste incineration (MSWI) ashes as construction materials-a review. *Materials*, *13*(14), 1–30.

Mutz, D., Hengevoss, D., Hugi, C., & Gross, T. (2017). Waste-to-Energy Options in Municipal Solid Waste Management A Guide for Decision Makers in Developing and Emerging Countries. *Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH*.

Demir, I. (2006). *An investigation on the production of construction brick with processed waste tea. Building and Environment*, *41*(9), 1274–1278.

Department For Environment, Food, and Rural Affairs. (2013). *Incineration of Municipal Solid Waste*.

Department For Environment, Food, and Rural Affairs. (2011). *Guidance on applying the waste hierarchy*

Dugenest, S., Casabianca, H., & Grenier-Loustalot, M. F. (1999). Municipal solid waste incineration bottom ash: Physicochemical characterization of organic matter. *Analusis*, *27*(1), 75–81.

Durai, G., & Rajasimman, M. (2011). Biological treatment of tannery wastewater - A review. *Journal of Environmental Science and Technology*, *4*(1), 1–17.

Federico, L. ., Chidiac, S. E., & Drysdale, R. G. (2005). The use of waste material in the manufacturing of clay brick. In *Proceedings of the 10th Canadian Masonry Symposium, Banff, Alta* (pp. 8-12).

Fernandes, F. M. (2019). 1 – Clay bricks. In *Long-term Performance and Durability of Masonry Structures: Degradation Mechanisms, Health Monitoring and Service Life Design*. Elsevier.

Giro-Paloma, J., Ribas-Manero, V., Maldonado-Alameda, A., Formosa, J., & Chimenos, J. M. (2017). Use of municipal solid waste incineration bottom ash and crop by-product for producing lightweight aggregate. In *IOP Conference Series: Materials Science and Engineering*, (Vol. 251, No. 1, p. 012126). IOP Publishing.

Hansson, L. (2017). *Characterization of bottom ash from municipal solid waste incineration as a possible element in concrete Investigation of the compressive strength and leaching properties* (Master's thesis).

Hegazy, B. E. D. E., Fouad, H. A., & Hassanain, A. M. (2012). Brick manufacturing from water treatment sludge and rice husk ash. *Australian Journal of Basic and Applied Sciences*, *6*(3), 453–461.

Haque, O. (2011). *Feasibility study of manufacturing fired brick from municipal solid waste incinerator Ash.*

Itodo1, A. (2018). Introduction To Treatment. *Journal of Water Technology and Treatment Methods*, *1 Issue: 1*, 8.

Joseph, A. M., Snellings, R., Van den Heede, P., Matthys, S., & De Belie, N. (2018). The use of municipal solidwaste incineration ash in various building materials: A Belgian point of view. *Materials*, *11*(1),141.

Juel, M. A. I., Mizan, A., & Ahmed, T. (2017). Sustainable use of tannery sludge in brick manufacturing in Bangladesh. *Waste Management*, *60*, 259–269.

Kadir, A. A., & Mohajerani, A. (2011,July). Bricks: An excellent building material for recycling wastes - A review. In *Proceedings of the IASTED International Conference on Environmental Management and Engineering (EME 2011*), *Calgary, AB, Canada* (pp. 4-6)

Kadir, A. A., & Sarani, N. A. (2012). An overview of wastes recycling in fired clay bricks. *International Journal of Integrated Engineering*, *4*(2), 53–69.

Kassahun, S. K. (2017). *Photocatalysis of titanium dioxide nanoparticles for drinking water disinfection under vis-LEDs and sunlight illumination Photocatalysis of titanium dioxide nanoparticles for drink* (Doctoral dissertation, Addis Ababa University Addis Ababa, Ethiopia).

Liew, A. G., Idris, A., Samad, A. A., Wong, C. H. K., Jaafar, M. S., & Baki, A. M. (2004).

Reusability of sewage sludge in clay bricks. *Journal of Material Cycles and Waste Management*, *6*(1), 41–47.

Liew, A. G., Idris, A., Wong, C. H. K., Samad, A. A., Noor, M. J. M. M., & Baki, A. M. (2004). Incorporation of sewage sludge in clay brick and its characterization. *Waste Management and Research*, *22*(4), 226–233.

Lynn, C. J., Dhir OBE, R. K., & Ghataora, G. S. (2016). Municipal incinerated bottom ash characteristics and potential for use as aggregate in concrete. *Construction and Building Materials*, *127*, 504–517.

Lynn, C. J., Ghataora, G. S., & Dhir OBE, R. K. (2017). Municipal incinerated bottom ash (MIBA) characteristics and potential for use in road pavements. *International Journal of Pavement Research and Technology*, *10*(2), 185–201.

M. Saleh, H., & Koller, M. (2019). Introductory Chapter: Municipal Solid Waste. *Municipal Solid Waste Management*.

Malaiškiene, J., Kizinievič̂, O., & Kizinievič̂, V. (2019). A study on tannery sludge as a raw material for cement mortar. *Materials*, *12*(9).

Mohajerani, A., Kadir, A. A., & Larobina, L. (2016). A practical proposal for solving the world's cigarette butt problem: Recycling in fired clay bricks. *Waste Management*, *52*, 228–244.

Mora-Basto, R. L., Torres-Sánchez, D. A., Chaparro-García, A. L., & Sánchez-Molina, J. (2019). Physicochemical and mineralogical properties of clays used in ceramic industry at North East Colombia. *Dyna (Colombia)*, *86*(209), 97–103.

Okunade, E. A. (2008). Engineering properties of locally manufactured burnt brick pavers for agrarian and rural earth roads. *American Journal of Applied Sciences*, *5*(10), 1348–1351.

Pipatti, R., Sharma, C., & Yamada, M. (2006). Chapter 2: Waste generation. Compositon and Management data. *IPCC Guidelines for National Greenhouse Gas Inventories*, *5*(2), 23.

Sabbas, T., Polettini, A., Pomi, R., Astrup, T., Hjelmar, O., Mostbauer, P., Cappai, G., Magel, G., Salhofer, S., Speiser, C., Heuss-Assbichler, S., Klein, R., & Lechner, P. (2003).

Management of municipal solid waste incineration residues. *Waste Management*, *23*(1), 61–88.

Shakir, A. A., Naganathan, S., & Mustapha, K. N. (2013). Properties of bricks made using fly ash, quarry dust and billet scale. *Construction and Building Materials*, *41*, 131–138.

Sobik-Szołtysek, J. & Wystalska, K. (2019). Sludge from tannery industries. In *Industrial and Municipal Sludge(pp. 31-46): Emerging Concerns and Scope for Resource Recovery*. Elsevier Inc.

S.K. Duggal. (2000). Building materials, Third edition, Motilal Nehru institute of technology Allahabad (U.P.), New age international (p) Ltd. publishers, New Delhi.

Swarna, M. A., & Venkatakrishnaiah, R. (2014). Manufacturing of Bricks Using Tannery Effluent sludge. *International Journal of Recent Development in Engineering and Technology*, *3*(4), 33–36.

Swarnalatha, S., Ramani, K., Karthi, A. G., & Sekaran, G. (2006). Starved air combustion-solidification/stabilization of primary chemical sludge from a tannery. *Journal of Hazardous Materials*, *137*(1), 304–313.

Tay, J. (1987). Bricks Manufactured from Sludge. *Journal of Environmental Engineering*, *113*(2), 278–284.

Travar, I., Andreas, L., Tham, G., & Lagerkvist, A. (2007). Environmental impact of ashes used in a landfill cover construction. *Proceedings Sardinia Margherita Di Pula*, 1–5.

Unido. (2007). *pollutants in tannery effluent. international scenario on environmental regulations and compliance*.

Weng, C. H., Lin, D. F., & Chiang, P. C. (2003). Utilization of sludge as brick materials. *Advances in Environmental Research*, *7*(3), 679–685.

Muntasir, S. Y. (2015). *Physical and chemical characteristics analysis of bottom ash and boiler tappings coming from the Burnaby Incinerator (Doctoral dissertation, University of British Columbia).*

Zhu, D., Asnani, P. U., Zurbrügg, C., Anapolsky, S., & Mani, S. (2008). *Improving Municipal Solid Waste Management in India : A Sourcebook for Policymakers and Practitioners.*

APPENDICES

Appendix A: Experimental Results

Table A-1 Moisture Content of Clay, Bottom Ash and Tannery Sludge

Sample	**M_{cws}**	**M_{cs}**	**M_c**	**M_{cws} - M_{cs}**	**M_{cs}- M_c**	**Moisture Content (%) = $(\frac{Mcws - Mcs}{Mcs - Mc}) * 100$**
White Clay	510.52	416.7	10.52	93.82	406.18	23.1
Red Clay	508.6	459.9	8.6	48.7	451.3	10.8
Bottom Ash	208.3	180.13	8.3	28.17	171.83	16.4
Tannery Sludge	179.4	97	9.4	82.4	87.6	94.1

M_{cws} = mass of container with wet sample (g)

M_{cs} = mass of container and oven dry sample (g)

M_c = mass of container (g)

Moisture Content (%) = $(\frac{Mcws - Mcs}{Mcs - Mc}) * 100$

Table A-2 Ash Content of Clay, Bottom Ash and Tannery Sludge

Raw sample	**W_{pwa}**	**W_p**	**W_s**	**W_{pwa}- W_p**	**Ash Content (%)**
White Clay	24.1	22.2	2	1.9	95
Red Clay	25.4	23.8	2	1.6	80
Bottom Ash	22.8	20.9	2	1.9	95
Tannery Sludge	31.2	30.1	2	1.1	55

W_{pwa} = weight of porcelain with ash (g)

W_p= weight of porcelain (g)

W_s = weight of sample (g)

$$\textbf{Ash Content (\%)} = \left(\frac{\mathbf{Wpwa-Wp}}{\mathbf{Ws}}\right) * \mathbf{100}$$

Table A-3 Organic Content of Clay, Bottom Ash and Tannery Sludge

Sample	Ash Content (%)	Organic Content (%)
White Clay	95	5
Red Clay	80	20
Bottom Ash	95	5
Tannery Sludge	55	45

Organic Content % = 100 - Ash Content (%)

Table A-4 Energy saved during firing at 1000℃

Sludge Content (%)	M_1 (Kg)	M_2 (Kg)	M_3 (Kg)	**Energy saved** (%)
10	0.600	0.5171	0.05171	46.16
20	0.600	0.4749	0.09498	80.26

M_1= Mass of control brick

M_2= Mass of TS-BA brick

M_3= Mass of TS in TS-BA brick

q= 3MJKg^{-1}

$$\%\boldsymbol{Energy\ saved} = \frac{qM1 - (qM2 - qM3)}{qM1}$$

Table A-5 Water absorption of bricks calculation

Firing temperature	**%TS**	**%BA**	**m_1**	**m_2**	**Water absorption (%)**
800℃	20	10	499.5	592.9	18.7
	10	20	501.5	596.3	18.9
	30	20	478.9	591.4	23.49
	20	30	499.3	619.6	24.09
900℃	10	10	487.1	574.28	17.89
	10	30	477.7	603.2	26.3
	20	20	474.8	599.9	26.35
	20	20	470.3	592.9	26.06
	20	20	476.2	599.2	25.8
	30	30	443.1	603.6	36.2
	30	10	463.8	583.1	25.7
1000℃	20	30	478.3	619.4	29.5
	10	20	517.1	611.38	18.23
	20	10	474.9	567.5	19.5
	30	20	420.5	551.7	31.2

$$\%\boldsymbol{Water\ absorption} = \frac{(\boldsymbol{m2} - \boldsymbol{m1})}{\boldsymbol{m1}} * \mathbf{100}$$

Table A-6 Compressive strength of bricks calculation

Firing temperature	**%TS**	**%BA**	**Weight load (KN)**	**Area (mm^2)**	**Compressive strength (MPa)**
800℃	20	10	76.14	8100	9.40
	10	20	78.651	8100	9.71
	30	20	57.51	8100	7.10
	20	30	59.292	8100	7.32
900℃	10	10	83.268	8100	10.28
	10	30	61.722	8100	7.62
	20	20	69.174	8100	8.54
	20	20	69.336	8100	8.56
	20	20	65.772	8100	8.12
	30	30	55.971	8100	6.91
	30	10	65.934	8100	8.14
1000℃	20	30	69.174	8100	8.54
	10	20	81.972	8100	10.12
	20	10	84.078	8100	10.38

30	20	73.062	8100	9.02

$$\boldsymbol{Compressive\ strength} = \frac{\boldsymbol{Force}\ (\boldsymbol{N})}{\boldsymbol{Area}(\boldsymbol{mm^2})}$$

Appendix B: Experimental Design Outputs

Table B-1 Design Summery for brick production

File Version	12.0.3.0		
Study Type	Response Surface	**Subtype**	Randomized
Design Type	Box-Behnken	**Runs**	15
Design Model	Quadratic	**Blocks**	No Blocks

Factor	**Name**	**Units**	**Type**	**Min**	**Max**	**Low Coded**	**High Coded**	**Mean**	**Std. Dev.**
A	TS	%	Numeric	10	30	-1	+1	20	7.303
B	BA	%	Numeric	10	30	-1	+1	20	7.303
C	FT	℃	Numeric	800	1000	-1	+1	900	73.03

Response	**Name**	**Units**	**Obs.**	**Analysis**	**Min**	**Max**	**Mean**	**Std. Dev.**	**Ratio**	**Model**
R1	WA	%	15	Polynomial	17.89	36.2	24.527	5.12	2.023	Quadratic
R2	CS	MPa	15	Polynomial	6.91	10.38	8.629	1.115	1.502	Quadratic

Table B-2 Computer output from design-expert for fitting a model to the %age Water absorption response

Response 1: water absorption
Warning: The Cubic model is aliased.
Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	9023.85	1	9023.85			
Linear vs Mean	324.50	3	108.17	17.32	0.0002	
2FI vs Linear	23.96	3	7.99	1.43	0.3045	
Quadratic vs 2FI	**42.93**	**3**	**14.31**	**40.00**	**0.0006**	**Suggested**
Cubic vs Quadratic	1.64	3	0.55	7.21	0.1242	Aliased
Residual	0.15	2	0.076			
Total	9417.04	15	627.8			

"Sequential Model Sum of Squares": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Lack of Fit Tests

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Linear	68.53	9	7.61	100.59	0.0099	
2FI	44.57	6	7.43	98.13	0.0101	
Quadratic	**1.64**	**3**	**0.55**	**7.21**	**0.1242**	**Suggested**
Cubic	0.000	0				Aliased
Pure Error	0.15	2	0.76			

"Lack of Fit Tests" want the selected model to have an insignificant lack-of-fit.

Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	2.50	0.8253	0.7777	0.6443	113.85	
2FI	2.36	0.8863	0.8009	0.4717	207.72	
Quadratic	**0.60**	**0.9954**	**0.9873**	**0.9325**	**26.54**	**Suggested**
Cubic	0.28	0.9996	0.9973			Aliased

"Model Summary Statistics": focus on the model maximizing the **adjusted R^2** and the **predicted R^2**.

Table B-3 Computer output from design-expert for fitting a model to the CS response

Response 2: Compressive Strength

Warning: The Cubic model is aliased.

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	1116.81	1	1116.81			
Linear vs Mean	15.57	3	5.19	18.58	0.0001	
2FI vs Linear	1.10	3	0.37	1.48	0.2922	
Quadratic vs 2FI	**1.77**	**3**	**0.59**	**14.59**	**0.0066**	**Suggested**
Cubic vs Quadratic	0.095	3	0.032	0.58	0.6809	Aliased
Residual	0.11	2	0.054			
Total	1135.45	15	75.70			

“Sequential Model Sum of Squares”: Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Lack of Fit Tests

Source	Sum of Square	df	Mean Square	F-value	P-value	
Linear	2.96	9	0.33	6.10	0.1488	
2FI	1.87	6	0.31	5.77	0.1552	
Quadratic	**0.095**	**3**	**0.032**	**0.58**	**0.6809**	**Suggested**
Cubic	0.000	0				Aliased
Pure Error	0.11	2	0.054			

“Lack of fit tests”: The selected model should have an insignificant lack of fit.

Model Summary Statistics

Source	Std.Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	0.53	0.8352	0.7902	0.6704	6.14	
2FI	0.50	0.8939	0.8144	0.5335	8.70	
Quadratic	**0.2**	**0.9891**	**0.9695**	**0.9057**	**1.76**	**Suggested**
Cubic	0.23	0.9942	0.9594			Aliased

“Model Summary Statistics”: Focus on the model maximizing the **Adjusted R^2** and the **Predicted R^2**.

Table B-4 Experimental design data for the brick production process

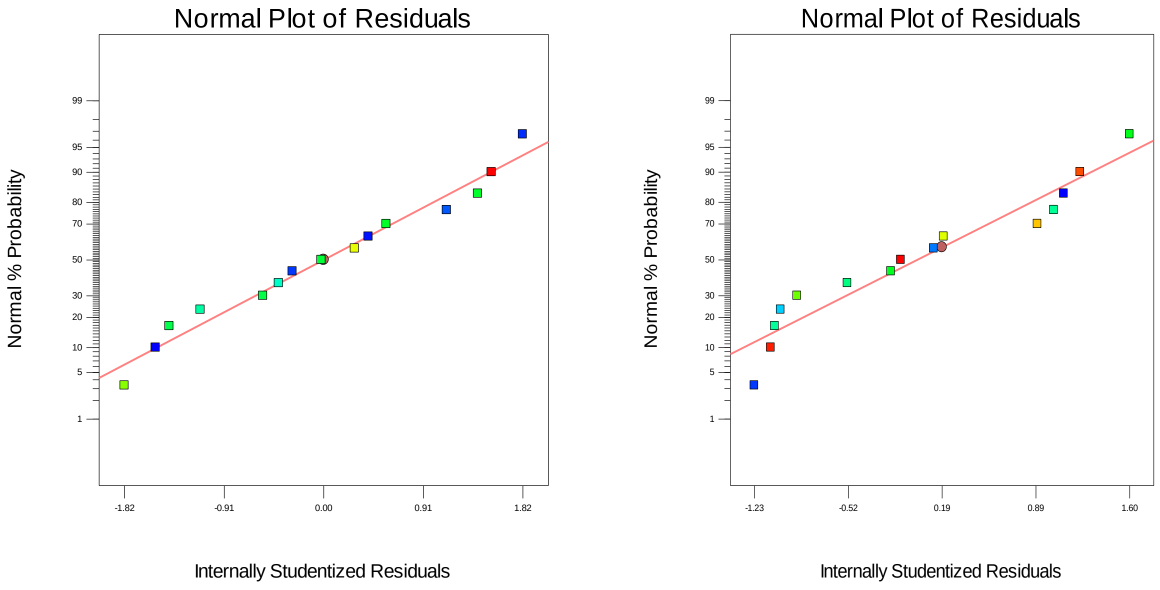
Run	**A: Tannery Sludge**	**B: Bottom Ash**	**C: Firing Temperature**	**Water Absorption**	**Compressive strength**
	(%)	(%)	(°C)	(%)	(MPa)
1	30	20	800	23.49	7.10
2	20	30	800	24.09	7.32
3	10	10	900	17.89	10.28
4	20	30	1000	29.50	8.54
5	30	10	900	25.70	8.14
6	20	20	900	26.35	8.21
7	20	10	800	18.70	9.40
8	20	20	900	26.06	8.56
9	20	20	900	25.80	8.12
10	30	30	900	36.20	6.91
11	10	20	1000	18.23	10.12
12	10	30	900	26.30	7.62
13	20	10	1000	19.50	10.38
14	30	20	1000	31.20	9.02
15	10	20	800	18.90	9.71

Table B-5 Experimental and predicted values of %age Water absorption

Standard Order	**Run Order**	**Actual Value**	**Predicted Value**	**Residual**	**Leverage**	**Internally Studentized Residuals**	**Externally Studentized Residuals**
6	1	23.49	23.61	-0.12	0.750	-0.410	-0.373
10	2	24.09	24.43	-0.34	0.750	--1.124	-1.163
1	3	17.89	18.35	-0.46	0.750	-1.534	-1.885
12	4	29.50	30.04	-0.54	0.750	-1.818	-2.793
2	5	25.70	26.12	-0.42	0.750	-1.408	-1.622
14	6	26.35	26.07	-0.27	0.333	0.573	0.530
9	7	18.70	18.16	0.54	0.750	1.818	2.793
13	8	26.06	26.07	-0.010	0.333	-0.020	-0.018
15	9	25.80	26.07	-0.27	0.333	-0.553	-0.510
4	10	36.20	35.74	0.46	0.750	1.534	1.885
7	11	18.23	18.11	0.12	0.750	0.410	-0.373
3	12	26.30	25.88	0.42	0.750	1.408	1.622
11	13	19.50	19.16	0.34	0.750	1.124	1.163
8	14	31.20	31.12	0.085	0.750	0.284	0.256
5	15	18.90	18.99	-0.085	0.750	-0.284	-0.256

Table B-6 Experimental and predicted values of Compressive Strength

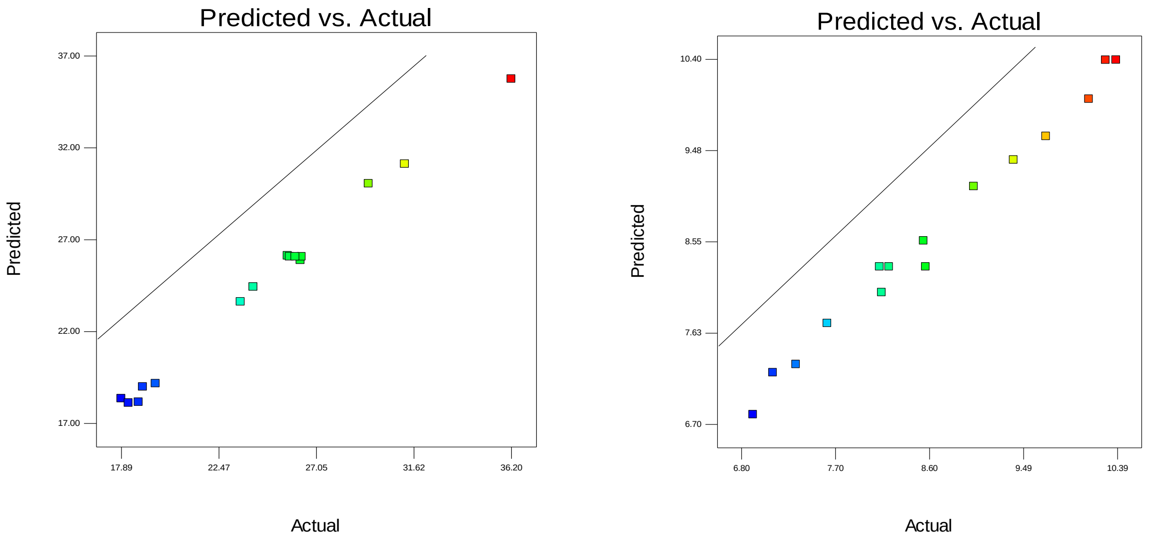
Standard Order	Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals
6	1	7.10	7.22	-0.12	0.750	-1.2290	-1.316
10	2	7.32	7.31	0.012	0.750	0.124	0.111
1	3	10.28	10.39	-0.11	0.750	-1.105	-1.137
12	4	8.54	8.56	-0.020	0.750	-0.199	-0.178
2	5	8.14	8.04	0.10	0.750	1.030	1.039
14	6	8.21	8.30	-0.087	0.333	-0.527	-0.485
9	7	9.40	9.38	0.020	0.750	0.199	0.178
13	8	8.56	8.30	0.26	0.333	1.602	2.053
15	9	8.12	8.30	-0.18	0.333	-1.075	-1.096
4	10	6.91	6.80	0.11	0.750	1.105	1.137
7	11	10.12	10.00	0.12	0.750	1.229	1.316
3	12	7.62	7.72	-0.10	0.750	-1.030	-1.030
11	13	10.38	10.39	-0.013	0.750	-0.124	-0.111
8	14	9.02	9.11	-0.091	0.750	-0.906	-0.887
5	15	9.71	9.62	0.091	0.750	0.906	0.887



(A) (B)

Figure B-1 Normal probability plots (A) Response: Percentage Water Absorption

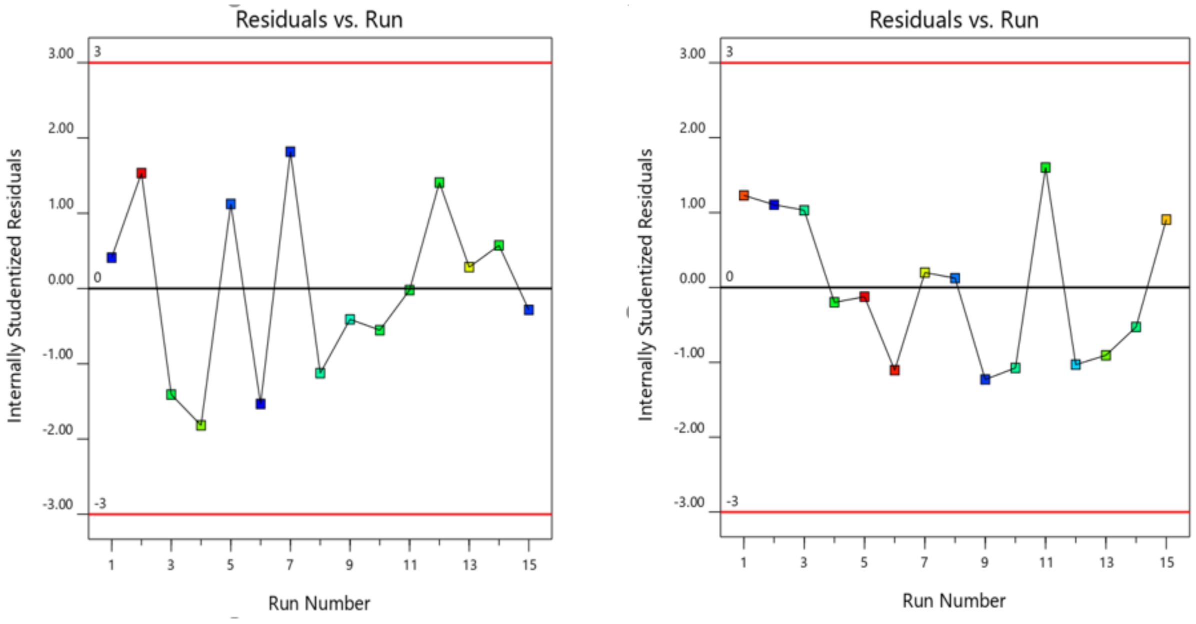
(B) Response: Compressive Strength



(A) (B)

Figure B-2 Predicted vs. Actual plots (A) Response: Percentage Water Absorption

(B) Response: Compressive strength



(A) (B)

Figure B-3 Residual vs. Run plots (A) Response: %Water Absorption

(B) Response: Compressive strength

Appendix C: Experimental Pictures

Raw Tannery Sludge

1st Size reduction

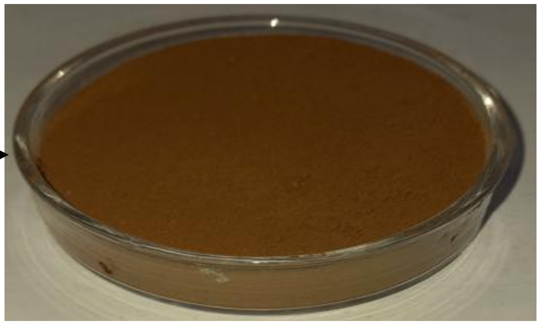
2nd Size reduction

Raw Bottom ash

2nd size reduction

Raw white clay

2nd size reduction



Raw red clay

2nd size reduction

Mixing of raw samples

Molding of the mix

Air drying of the green bricks in the laboratory

Firing of green bricks

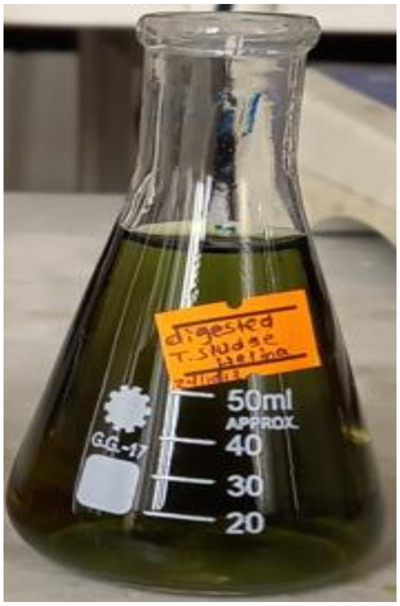
Fired control and TS-BA amended clay bricks

Water absorption test

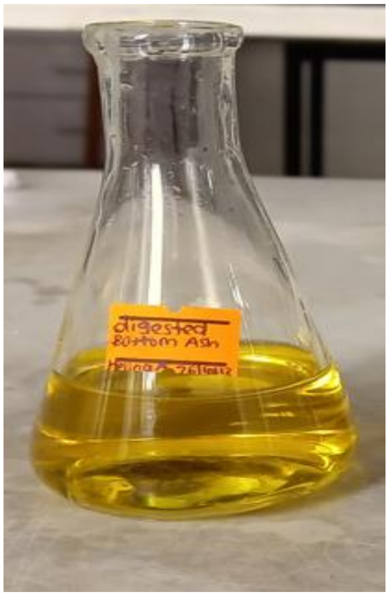
Capping of the bricks with gypsum

Compression test

Digestion process of tannery sludge and bottom ash



Digested tannery sludge



Digested bottom ash