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COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY POSTGRADUATE PROGRAMM

Characterization and Application of Spent Kiselguhr as an Adsorbent for Removal of Volatile fatty acids and Nitrates from Habesha Brewery‘s wastewater

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As members of Examining Board of the Final M.Sc. thesis open defense, we certify that we have read and evaluated the thesis prepared by Haftu Mekonen entitled **"Characterization and application of spent Kiselguhr as an adsorbent for removal of volatile fatty acids and nitrates from Habesha Brewery's wastewater**and recommended that it can be accepted as fulfilling the thesis requirements for the Degree of Master of Science in Analytical Chemistry

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Declaration

I, the undersigned, declare that this thesis **Characterization and application of spent Kiselguhr as an adsorbent for removal of volatile fatty acids and nitrates from Habesha Brewery's wastewater** is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

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LIST OF ABBREVIATION

ANOVA	Analysis of variance
BOD	biochemical oxygen demand
BWW	beer waste water
CIP	cleaning in place
COD	chemical oxygen demand
CW	chemical waste water
DD	Donnan dialysis
ED	electro dialysis
FE	final effluent
FTIR	Fourier transforms infra rad
GC MS	gas chromatography mass spectroscopy
Hr	hour
IP	Input
MF	micro filtration
NF	nano filtration
PS	particle size
RO	reverse osmosis
TDIS	total dissolved inorganic solids
TDS	total dissolved solids
TS	total solids
TSS	total suspended solids
UASB	(Up flow Anaerobic Sludge Blanket)

UF	ultra filtration
VFA	volatile fatty acids

Abstract

Brewing process is accompanied by the release of a great variety of contaminant each of which can determine the usability of the water for certain applications and can cause problems with effluent discharge. The main constituents include; Nitrogen, H_2S, NH_3, and Phosphorous. Volatile fatty acids hydroxyl group compounds, nitrate compounds, the constituents of the effluent fluid are present in large quantities and require some pretreatment before discharging the effluent fluid into a sewage system. The spent kiselguhr is one of the beer wastes after filtration it discharges into the solid discharging unit as waste.

The spent kiselguhr was prepared for the adsorption process of waste water for different treatment tank, The particle size of the adsorbent was one factor for adsorption, 63, 80 micro m. and 1mm size was applied for investigation. The contact time for adsorption process was 48, 60 and 72hr was selected for different concentration of the waste water with different adsorbent particle size investigation. The sample was took from the tank there was different investigation from the three treatment plant tank, such physicochemical characteristics ,ammonium nitrates, phosphate compounds were characterized. The adsorption process was investigated with three replication experiment for each treatment tank sample collection.

There was no treatment in this tank. After two days or greater than this days the waste water send to upper aerobic sedimentation blanket tank for the aerobic digestion with the addition of aerobic bacteria for the breakdown of the starch and other composites. The adsorbent used to remove harmful wastes nitric acid and VAF which have a waste removing efficiency were 99.1% and 92.3% respectively. The final effluent tank was the treated waste with different measurement took for the environmental condition without factor affecting of the human being healthiness. The selection of good adsorbent was performed with laboratory result based on the PH, Chemical oxygen demand, biological oxygen demand, Acid value, nitrate compounds percentages, volatile fatty acid, and composition of the sample from each tank.

Key words: spent kiselguhr, volatile fatty acid, Conductivity, particle size, contact time.

INTRODUCTION

1.1. Background of the study

The industry is sustained by the extraction and processing of natural resources as raw materials. These same raw materials find their way into the environment in different forms as finished and waste products. Although the finished products are used for different activities, waste products become a burden to the environment. This means that although industrialization is considered as the cornerstone of the development strategies due to its significant contribution to the economic growth and hence human welfare, it may lead to serious environmental degradation.

Among the beverage sub-sector today, the beer brewing industry’s huge global business, consisting of several multinational companies and many thousands of smaller producers ranging from brewpubs to regional breweries. Beer is the fifth most consumed beverage in the world behind tea, carbonates, milk, and coffee and it continues to be a popular drink with an average consumption of 23liters/person per year(Chakraborty, Baran, & Aristov, 2014).Production of beer includes blending and fermentation of maize, barley malt and sorghum grits using yeast, which requires large volumes of water as the primary raw material. Traditionally, the amount of water needed to brew beer is several times the volume actually brewed. For instance, Among the beverage sub-sector today, the beer brewing industry’s huge global business, consisting of several multinational companies and many thousands of smaller producers ranging from brewpubs to regional breweries. Beer is the fifth most consumed beverage in the world behind tea, carbonates, milk, and coffee and it continues to be a popular drink with an average consumption of 23liters/person per year(Chakraborty, Baran, & Aristov, 2014).Production of beer includes blending and fermentation of maize, barley malt and sorghum grits using yeast, which requires large volumes of water as the primary raw material. Traditionally, the amount of water needed to brew beer is several times the volume actually brewed. For instance, the average water consumption of 6.0 hecto- liters is required to produce on hecto-liter of clear beer. Large volumes of water are being used by the industry for production of beer for two main purposes; as the main ingredient of the beer itself and as part of the brewing process for steam rising, cooling, and washing of floors, packaging, cleaning of the brew house during and after the end of each batch operation. The amount of wastewater that is being discharged from the industry after the production of beer also contributes to this large volume of water(Aristov, Glaznev, & Girnik, 2012).

The brewing process is accompanied by the release of a great variety of contaminant each of which can determine the usability of the water for certain applications and can cause problems with effluent discharge. The main constituents include; Nitrogen, H_2S, NH_3, and Phosphorous. The constituents of the effluent fluid are present in large quantities and require some pretreatment before discharging the effluent fluid into a sewage system(Li, Hou, Zhang, & Yuan, 2015).

The pollution of the aquatic environment with metals and an ion may be the either natural or anthropogenic origin. Several common treatment methods, including coagulation sedimentation, filtration, adsorption, chemical precipitation, ion exchange, classical solvent extraction, evaporation, and biological methods are used for the removal of inorganic contaminants from natural waters or wastewaters. Membrane processes such as reverse osmosis (RO), Nano filtration (NF), ultrafiltration (UF) and microfiltration(MF) in hybrid systems, Donnan dialysis (DD)and electro dialysis(ED) as well as in combination with extraction(liquid membranes)and bioreactors, are applied to remove inorganic micro pollutants from aquatic environment. However, these methods are not widely used, because economically not feasible, known re-generable produces toxic waste and inefficient for low-level contaminants. The need to find alternative inexpensive and effective methods for inorganic pollutants abetment from wastewaters becomes inevitable. The adsorption process is the best in comparison with other methods because of its ease of operation, uses low-cost adsorbents and effective towards the removal of organic and inorganic pollutants even at low concentration levels(Freni et al., 2013). Local clay is widely available, and it is effective towards the adsorption of inorganic and organic pollutants.

1.2. Statement of the Problem

Rapid urbanization and industrialization cause the generation of a high amount of wastewater containing toxic pollutants such as ammonia, hydrogen sulfide, nitrites, phosphate VFAs, etc. These pollutants have a high risk of the environment and human health.

Ammonia pollution will cause a chemical burn to the vegetation, absence of aquatic flora and fauna, shortness of breath, skin and eye irritation, a respiratory irritant, chemical burns to the respiratory tract, skin, and eyes, severe cough, chronic lung disease, and aquatic life is highly affected. Hydrogen sulfide causes in flammation of the moist membranes of the eye and respiratory tract, olfactory neuron loss, death, etc. Nitrogen and phosphorus pollution causes eutrophication of lakes and rivers. The effects of eutrophication of waters are undesirable because the aesthetic value of alake is lowered through excessive growth of aquatic weeds and algae and production of floating algal scum's which are a nuisance to those who used the water for recreational purposes. Other effects include undesirable odors and tastes, depletion of dissolved oxygen, destruction of aquatic life and impairment .Volatile fatty acids could be responsible for the unpleasant odor together with amines and sulfur compounds. Volatile fatty acids exist in environmental matrices in different concentrations from a few mg/l in surface water to thousands mg/L in landfill leachates. Recently, they can be analyzed by ion chromatography and(Chakraborty et al., 2014).To reduce these problems of health risk, different treatment options such as chemical precipitation, ionization, electrochemical treatment, membrane processes, and ion exchange have been employed. But those technologies are extremely expensive, inefficient to very low concentrations, further toxic wastes, and creating yet another disposal problem. But adsorption is the most efficient, low cost and easy operation and recovery of the material used.

1.3. Objectives of the Study

1.3.1. General Objective

The main objective of this study was to investigate the potential adsorption capacity of Kiselguhr for the removal of Volatile fatty acids and Nitrate from Habesha brewery waste water.

3.1.2. SpecificObjectives

To study functional group of spent kiselguhr using FTIR.

To investigate the adsorption capacity of adsorbent towards Volatile fatty acids and Nitrate effluent from the beer industry with wastewater.

To investigate the effects of different parameters such as pH, particle size,the dosage of adsorbent, initial concentration of adsorbate and contact time on adsorption efficiency and removal capacity of Kiselguhr.

1.4. Significance of the Study

The major motive for the removal of Volatile fatty acids and Nitrate pollutants of brewery wastewateristomakefreethesurroundingenvironmentandtoreducetheireffectonhumanhealth due to direct exposure. The final outcome of the study will benefit the surrounding society, the brewery and other industrial sectors due to the use of a cheap, effective and easily operable technique to treat the contaminated waste before discharge.

LITERATUREREVIEW

1.5. Description of Brewing Process

The brewing process uses malted barley and/or cereals, malt grains and sugar (corn syrups, adjuncts), hops, water, and yeast to produce beer. Most brewers in the world use malted barley as their principal raw material. Depending on the location of the brewery and incoming water quality, water is usually pretreated with reverse osmosis, carbon filtration or another type of filtering system (Freni et al., 2013).

The brewing process which involves malting of grain, milling, mashing, wort cooling, fermentation, packaging, and pasteurization consume resources such as water, energy, grist materials, adjuncts and auxiliary materials such as Kiselguhr, bottles, cans, crown corks, glue, enzymes, antioxidants, foam stabilizers, colloidal stabilizers caustic soda and detergents for cleaning bottles and equipment(Fulfillment & For, 2012).

Brewing is based on the standard of four processes of wort production, fermentation and maturation, beer processing and bottling. It is important to know the total consumption and discharge of organic load and wastewater for environmental reasons. The main water using areas of a typical brewery are brewhouse, cellars, packaging and general water use. Water use attributed to these areas includes all water used in the product, vessel washing, general washing and cleaning in place (CIP); which is of considerable importance both in terms of water intake and effluent produced(Anagement, 2014).

Fermentation processes or a combination of these processes are assuming importance in this realm particularly in waste water of beer production process. Among these processes, fermentation is considered as a viable method due to its relative efficiency over other biological processes, operation at ambient temperature and pressure and feasibility in using different types of substrates including wastewater. More recently, utilizing wastewater as primary fermentative substrate in production is gaining importance due to the fact that it has dual benefits of in beer production as well as wastewater treatment. Fermentative conversion of substrate to waste water is generally manifested by diverse group of bacteria through a series of complex biochemical reactions similar to anaerobic conversion(Trela& Płaza, 2018).

Anaerobic conversion requires physiologically distinct groups of microorganisms where hydrocarbons are converted from complex to simple molecules. Fermentative/ hydrolytic microorganisms (hydrolysis) hydrolyze complex organic polymers to monomers, which ferment the monomers.

having chemical oxygen demand (COD) of 3.2 g/l was used. Chemical wastewater (CW) used was an aggregate from bulk drugs, chemical intermediates, dye and dye intermediates, pharmaceuticals, pesticides and various chemical process units and was characteristically, complex in nature due to its composite nature, low-biodegradability (BOD5/ CODw0.3) and high sulphate concentration (1.75 g/l) [pH – 7.6, total alkalinity – 1.20 g/l, total dissolved inorganic solids (TDIS) – 25.45 g/l, COD – 6.24 g/l, biochemical oxygen demand (BOD5) – 1.14 g/l, total nitrogen – 0.129 g/l and total phosphorus – 0.361 g/l]. Combined domestic sewage (DW) (pH – 7.06 COD – 0.43 g/l; BOD5 – 0.28 g/l) was also used as substrate. Brewery is one of the traditional industries with an important economic value in the agro-food sector. In brewery industry, approximately 3-10 l of wastewater is generated for each liter of beer produced(Caliskan, Giray, Gundogdu, & Azbar, 2014).

Beer production steps include both chemical and biochemical reactions such as mashing, boiling, fermentation, maturation and also separation processes (wort separation, wort clarification and rough beer clarification, filtration, CIP (Clean In Place), packaging, etc.) respectively (Atasoy, Owusu-agyeman, Plaza, & Cetecioglu, 2018)For every 1,000 tons of beer produced, 137 to 173 tons of solid waste may be created in the form of spent grain, trub from wort production, waste yeast. During these processes different types of wastewater is released based on the production process. Therefore, pollution parameters such as pH, temperature, suspended solids, organic materials etc. of brewery effluent and temperature vary depending on the source. Nitrogen and phosphorous levels mainly depend on the handling of raw material and the amount of spent yeast present in the effluent. Elevated phosphorous levels can also be the result of phosphorous containing chemicals used in the CIP unit. Brewery effluent include sugar, soluble starch, volatile fatty acid, ethanol(Smith & Smith, 2015), high content of suspended solids, e.g. spent maize, malt, and yeast, etc. which also contribute to the organic pollution which is amenable for biodegradation (BOD - Biochemical Oxygen Demand/COD - Chemical Oxygen Demand ratio of 0.6-0.7.

The brewery process results in the generation of wide variety of solid wastes including spent grains, trub, spent yeast, and diatomaceous earth slurry from filtration. Some of these residues have a commercial value as byproducts for livestock feed, even though the nutritional value of spent grain is less than that of the same amount of dried barley. Amongst slurry type wastes, trub consists of heavy fats, wort, inactive yeast and hop particles and unstable colloidal proteins coagulated during the wort boiling. Surplus yeast which has a high content of organic matter is a residue produced during natural sedimentation at the end of the fermentation and conditioning. Most of the spent yeast is sold as a feeding material for livestock. Another solid waste during the brewery process is diatomaceous earth slurry from the filtration of beer which is composed of large amount of Suspended Solid (SS) and high BOD/COD ratio(Yang et al., 2015). Due to the high organic loadings of the brewery industry, the demand for environmental investments are high, on the other hand, the organic material available in brewery wastes has also very high potential for bioenergy production allowing an environmentally friendly disposal solution.

The conversion of brewery wastewater into bioenergy is reported at real scale and the bioenergy potential of other solid organic waste streams such as malt wastes and grid wastes were examined using BMP (Biochemical Methane Potential) protocol. To the best of our knowledge, there is only one literature report in regard to full scale performance of a UASB (Up flow Anaerobic Sludge Blanket) reactor. In our study, we report the performance of a novel bioreactor configuration, namely EGSB reactor and furthermore; we also report additional data on the extra bioenergy potential of the brewery wastes (malt waste and grid waste) which doubles the bioenergy potential of the brewery waste streams.Suspended or dissolved solids in influent and effluent were also analyzed.

In this study, a TSS value in the influent was 900 mg l-1. SS values in the influent were found to be slightly higher than the literature values; on the other hand, finals discharge had low SS values around 200 mg l-1. In order to minimize the COD contribution of residual SS in the final discharge, employs a final sedimentation tank before discharging into publicly owned sewer.The average COD value of influent of the anaerobic biodegradation system is 6000 mg l-1. The average COD value was observed to be significantly dependent on the beer production process. But, the existing anaerobic bioreactor which had a HRT of 1-2 days was able to accommodate these variations resulting in a final discharge COD values between 200-500 mg l-1 COD before the final discharge point.COD removal and methane yields are affected by organic loading rates (OLR).10 kg COD m-3day-1. The anaerobic digestion of brewery wastewater where an UASB bioreactor configuration was employed with a low COD removal efficiency of 57% COD removal efficiency (Münch, 1998).

1.6. Source of Volatile fatty acids and Nitrate Pollutants in Wastewater

Beer is about 95% water in composition; however, the amount of water used to produce container of beer is far greater than the amount of water contained in the beer that is actually packaged and shipped out. Most craft brewers receive their water from municipal suppliers, while a few use well water alternative source(Yeom& Kim, 2017).In addition to the water used in production, wastewater generation and disposal present another improvement opportunity for brewers. Most breweries discharge 70%of their incoming water as effluent. Effluent is defined as waste water that is generated and flows to these were system. In most cases, brewery effluent disposal costs are much higher than water supply costs. In many communities, breweries may be the largest consumer of water and the largest source of organic effluent that must be treated by the municipal treatment plant.

When combining that cost with treatment (physical and chemical) and effluent disposal costs, brewers are presented with a reflection of the true or full cost of water. Establishing this concept of the full cost of water is an important factor in cost/ benefits analyses and will be discussed later in this document (Zhang, Zhang, & Zhang, 2008).

Water awareness and conservation practices provide an effective mechanism for brewers to reach out to communities. brewhouse, cellars, packaging, and utilities. In addition, ancillary operations such as food service and restrooms contribute to water usage(Scortichini, Chiara, Silvi, & Fiorini, 2020).Whereas the legislation imposed more stringent cost for waste disposal by the authorities. Water consumption in a brewery is not only an economic parameter but also a tool to determine its process performance in comparison with other breweries.

The food and beverage industries including brewing are water consumed in the production process, the consumption of water rangingfrom4to11hlwater/hl beer. In the production of beer the average water consumption of around5-6hL/Hl beer is correlated to beer production for industrial breweries. According to Perry and De Villiers water consumption is divided into 2/3 of it and is used in the process and 1/3 is used in the cleaning operations and the effluent loadisverysimilartothewaterload.Of this water is used to brew beer and most of it is exposed as effluent. Diatomaceous earth has various important mechanisms for filtration in the production process brewing as reported(Mohammed et al., 2018).

2.3 Adsorption Process

Adsorptionistheprocessbywhichasolidadsorbentcanattractacomponentinwatertoitssurface and form an attachment via a physical or chemical bond, thus removing the component from the fluid phase. The advantages of the adsorption process are simplicity in operation, inexpensive compared to other separation methods and no sludge formation. The adsorption process is generally classified as either; physic sorption (physical adsorption), or chemisorptions (chemical adsorption)(Sun & Chakraborty, 2015)

Physisorption (physical adsorption)Adsorption in which the forces in volvedareintermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapors, and which do not involve a significant change in the electronic orbital patterns of thes pecies involved. Physical adsorption is generally a multi-layer process, not limited by the available solid surface area, reversible, more rapid, occurs on almost all solid surfaces. Chemisorption(chemical adsorption) Chemisorption (or chemical adsorption) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. Chemisorption limited to the formation of a monomolecular adsorbed layer has some activation energy, much slower than physical adsorption, may not be reversible(Chakraborty et al., 2014).

2.4Effect of the initial concentration of Adsorbate

The adsorption capacity of the adsorbent increased with an increasing initial concentration of the adsorbate which can be attributed to an increase in electrostatic interactions involving sites of progressively lower affinity for the adsorb ate up to the point of saturation. Conversely, the percentage removal of the adsorbate decreases markedly with an increase in the initial concentration of the adsorbate.

This phenomenon might be due to the rapid saturation of all adsorb atebindingactivesitesoftheadsorbentatacertainconcentrationoftheadsorbate(Sapienza et al., 2016).The adsorption process is highly dependent on the initial concentration of adsorb ate because, at lower concentration, the ratio of the initial concentration of adsorb a teto the available surface are a slow (concentration /surface area) and subsequently the fraction adsorption of adsorb ate increases. However, at higher concentrations, the availability of active sites for adsorption becomes less and hence the percentage removal of adsorb ate decreases(Mohammed et al., 2018).

2.4.1. Effect of particle size

The particle size has an important role to play in the amount of the adsorbate adsorbed. With a decrease in the particle size, the amount of the adsorbate adsorbed also increases. The pore structure of the adsorbents affects the adsorption of the adsorbate in two ways: the size exclusion limits the adsorption of the adsorbate of a given size and shape (sieve effect), and the adsorption capacity may increase with the increase in the specific pore volume. Theincreaseintheadsorptioncapacity ismoresignificant fortheincreaseinthesurfacearea, through decreaseintheparticle size(Aristov et al., 2012).

2.4.2 Effect of Adsorbent Dose

Removal efficiencies of adsorption increase with an increase in adsorbent dose and reach a saturation level at higher doses for all adsorbents that can be related to an increase in contact surface area of adsorbent particles. Adsorbent doses beyond the steady-state do not improve adsorption due to the availability of excess adsorption sites than that of sorbets, assuming that the number of adsorption sites per unit mass of adsorbents remains constant. At a lower dosage of adsorbents, there are insufficient active sites that the adsorbate can easily occupy. However, at a higher dosage, active adsorption sites are sufficiently available for the adsorbate to occupy(Kuang et al., 2020).

2.5. Kiselguhr as an Adsorbent

Kiselguhris among the cheapest, abundant, environmentally friendly, ion exchangeable andnon- toxic adsorbents that can be used to substitute the expensive commercial activated carbon in tackling environmental pollution problems.Focusing on the selection and /or production of low- cost adsorbents with good metal- binding capacities, which could be utilized as an alternative to the most widely used adsorbent in wastewater treatment- activated carbon. Natural materials of both organic and inorganic nature (such as chitosan, zeolites, clay and clay materials, etc) and certain waste products from industrial operation (such as fly ash, coal, oxides, and silicates)are classified as low- cost adsorbents because they are economical and locally available(Freni et al., 2013).Diatomite (DE) is fine grand, low-density biogenic sediment, which consists essentially of diatoms.

It is the fossilized remnants of diatoms, tiny planktonic algae residing in all the earth water.

The death of large numbers of diatoms in an area leads to sedimentation of the minerals present in the cell walls leading to large deposits in their high purity, oftengreaterthan85%silica. As a result, diatomite is both non-toxic and odorless, present naturally in large quantities and at high purities and it is available at low cost. Diatomite is of particular interest due to its unique properties such as high porosity, high permeability, small particle size, high surface area, low thermal conductivity, and chemical inertness. These properties of diatomite led to its early use for water purification, in which it was used to remove particulate matter from water for applications.

The kiselguhror diatomaceous earth($SiO_2 \cdot nH_2O$) are composed essentially of more or less well- crystallized silica, as well as a small quantity of alumina, iron oxide, and traces of other oxides. It is a natural material formed from the remains of diatoms and has many important industrial applications due to its unique properties, i.e. Micronized and sub micronized porous structure, high permeability, small particle size, low thermal conductivity and density, and high specific surface insulating materials and recently, the use of kiselguhr as possible additive for improvement of hydrogen storage properties of MgH_2 has also been reported.

The aim of this study was to characterize the Kiselguhr and sand to their use together in various industrial applications such as filtration, insulation, and sensor. Characteristics of Kiselguhr in different countries are shown in the. The main limitations of Kiselguhrare, reduction in the flow ability of grain, reduction of the bulk density of grain, ineffective in some situations, discomfort due to airborne dust and health concerns due to crystalline silica. (their distribution , properties, 1943).

An important index of beer stability is the visual appearance of the product. With the exception of a few well-known examples, such as Weiss beer, consumers associate a starbright product as a mark of freshness. While a beer is likely to deteriorate in terms of flavor before the appearance of haze, most consumers will probably notice the latter first. (O`Rourke, 2002).

The purpose of filtration is to preserve the beer so that no visible changes occur in the long run and the beer keeps its original appearance. Generally, the filtration steps fulfill two roles, to remove suspended materials from the beer and to unhinge potential turbidity formers (Lindemann, 2009). Filtration is an important process step whereby hazeactive substances (proteins, tannins, yeasts, etc.) are removed and thus biological and colloidal stability can be achieved (Fontana a Buiatti, 2009; Clemens, 2010). Filtration of beer can not to reduce its foaming, to deliver oxygen into beer, metal ions which catalyzing oxidative reaction during storage also the other compounds, which would be negative, affect chemical composition and organoleptic properties of beer (Basařová et al., 2010).

Yeast, bacteria and colloids are almost completely removed from beer depending on the selected filtration plate. Filtration plates consist of cellulose fibers from different types of wood, kieselguhr, perlite, synthetic fibers and resins that increase stability of filters. Large surfaces serve optimum adsorption of turbidity substances (Bamforth, 2003; Briggs et al., 2004). Filtrations can be classified as surface and depth filtration depending on the place of solid separation. In surface filtration, the particles to by separate are retained on the surface of the active media but in depth filtration, the separation process takes place inside of the filter material. This process is called a cake filtration. An important representative of cake filtration is kieselguhr filtration (Lindemann, 2009).

Kieselguhr is diatomaceous earth, which is mined from Miocene period deposits in Europe and North and South America. It consists of skeletons of marine algae containing silicon dioxide. Kieselguhr powders for use in brewing are prepared by drying and milling on size of particles 5 – 20 μm (Briggs et al., 2004; Basařová et al., 2010). The conventional dead-end filtration with filter-aids (kieselguhr) has been the standard industrial practice for more than 100 years and will be increasingly scrutinized from economic, environmental and technical standpoints in the coming century (Hrycyk, 1997; Knirsch et al., 1999). Kieselguhr

2.5.1. Structure and composition of Kiselguhr

Commonname: SilicondioxideKiselguhrSynonym:Kiselguhr,Diatomaceous earth Molecular formula Silicon dioxide Kiselguhr is composed of a mixture of inorganic oxide structural characteristics Silicon dioxide Kiselguhr is composed of a mixture of inorganic oxides. SiO_2Silicon dioxide Kiselguhr contains SiO_2in an amorphous form. Molecules build up tetrahedral room-net structures (SiO_4), which are connected through siloxane-bridges (Si-O-Si). Particle size distribution: L50D > 7μm; Specific surface area: 30 - 45 m²/g Content in silicon dioxide Kiselguhr Minimum content of silicon dioxide in silicon dioxide Kieselguhr:70%.Initially, the name of the active substance in the review program was Silicium dioxide (Silicium dioxide Kiselguhr), however, silicium is the French word for silicon. The name was changed to the English version. There is no modification of the active substance definition(Caliskan et al., 2014).Silicon dioxide Kiselguhr is composed of the skeletal remains of diatoms, a microscopic formof alga. The diatom shells and fragments can range in size from 1-1000µm, however, the average size is between 50-100µm depending on species and growth conditions. Depending on species the shape of the shells can also vary but are frequently boat-shaped or wheel like in appearance(Zhang et al., 2008).

2.6. Physicochemical Properties of Kiselguhr

The active substance silicon dioxide Kiselguhr is a white powder. Its melting point is above 1400°C; its boiling point is above. 2200˚C. The tap density is 0.32 g/mL. Silicon dioxide particle is not soluble in water or organic solvents. However, it forms stable suspensions. Partition coefficient - n-octanol/water is not relevant for silicon dioxide.Silicon dioxide Kiselguhr is neither flammable nor auto-flammable nor degradable. Silicon dioxide Kiselguhr has no oxidizing or explosive properties and shows no reactivity towards its container material (polyethylene high density (PE/HD) foil as an inner package surrounded by a card box as an outer package)(Zhang et al., 2008).

2.7. Consistencies of Adsorption Models of Beer waste water with Adsorbent

Silica-gel (SiO_2) is widely used in many industries due to its strong hydrophobicity towards water. There are many types of silica-gel such as A. Silica-gel is commonly employed in adsorption cooling systems and dehumidification applications. The ad- sorption isotherm of silica-gel/water is measured by either the gravimetric or volumetric methodology, while the isothermal or non- isothermal approach was proposed to extract the surface diffusivity. Although there are many publications in the adsorption characteristics, there are inconsistencies among the different experimental measurements of the surface diffusivity. During the adsorption, the surface diffusivity, then the instantaneous uptake is estimated. The values of the activation energy and pre-exponential factor are modified to keep this difference is less than 0.001 kg/kg. Adsorption rates of the two types of silica-gel are measured at different operating pressures (1.0–20.0kPa) and adsorbent temperatures (10–70 °C). Multiple samples of silica-gel with different particles sizes are tested. Effective particle size of the sample still provides reasonable results of the surface diffusivity. It is worth to mention that this approach is valid as long as the time response of the load cell and thermocouple is comparable because both the instantaneous temperature measurements and load cell response are used to calculate the surface diffusivity. Also, the thickness of the sample should be less than 5 mm, which is comparable to the thickness of adsorbent layer in real ad- sorption bed, to be able to achieve uniform temperature distribution within the tested sample. As a result, this proposed approach is applicable in measuring the surface diffusivity in nano porous adsorbents under operating conditions like those in the real adsorption cooling systems.

Materials and Methods

3.1. Apparatus and Equipment

Different sized beakers, Erlenmeyer flasks, funnels, volumetric flasks, block digester, fume hood, centrifuge, hydrometer, shaker, droppers, glass pipettes, spatula, measuring cylinders, steeliness knife, vinyl gloves, steel less steel auger, stirrer, polyethylene bags, analytical balance, conical flasks and oven were used.FTIR were be used.

3.1.1 Cleaning of Glassware and Sample Containers

All sample containers and glass were washed using detergent and soaked in 2M Nitric acid for 2hr to leach out adsorbed. Finally, tap water was used to rinse the materials,

3.1.2Chemicals, Reagents and Standard Solutions

Analyticalgradereagentslike0.1N NaOH for removing of different compounds from spent kiselguhr, 0.1NHCl,89%phenol,1MNa_2CO_3,0.5M citrate and 2M NaCl, 30% H_2O_2, ammonium met vanadate, trisodiumcitrate, nitric and DPD, oxalate photometer reagent,ethanol (95%) and distilled H2O were used.

3 1.3 Sample Collection and Preparation

Water samples from 100 m above the point of discharge (sample point), at the point of effluent discharge100 m (samplepoint1IP),200m (samplepoint2, UASB Up flow Anaerobic Sludge Blanket after effluent 300m (sample point 3FE), from the point of effluent took respectively. Water sample 100 m above the point of the effluent was analyzed to compare it with the brewery effluent and water samples down the stream in order to check whether the pollution is from the brewery or from any other source. All the samples to be analyzed for removal of VFA and NO3 and for the characterization of Kiselguhr. The results of brewery effluent water and the samples taken down the stream were compared to the waste water sample taken from the Habesha waste water treatment plant above the point of the effluent of Habesha brewery and t hewater quality standard for irrigation water set by

3.2 Preparation of Kiselguhr

The spent Kiselguhr was collected from the Habesha brewery, 4 km away from Debrebrhan. The spent kiselguhr dispersed in distilled water for 24hrs to remove impurities. After this, the spent kiselguhr was centrifuged for 30min at 3000 rpm.

The washed spent Kiselguhr was once more dispersed in distilled water and heated to $80^{o}C$in the presence of 1M Na_2CO_3, 0.5M citrate, and 2M NaCl. Carbonates were removed bytreatingwith1MHClandchloridesremovedbywashing withdistilledwater.Organic compounds were completely removed by 30% H_2O_2 at $70^{o}C$ (Danila S. Paragas 2004)

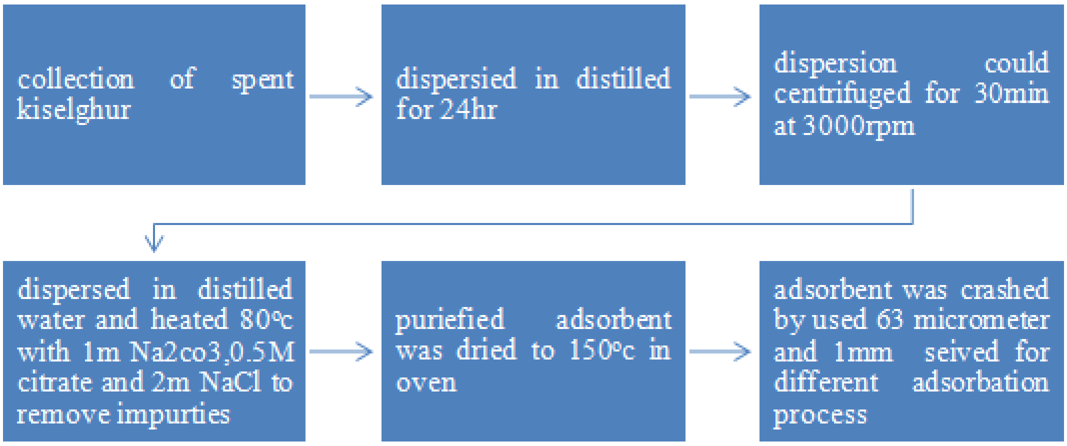


Figure 3. 1 Preparation procedure of the adsorbent [Hemant W. Khandareet2016].

After preparing the adsorbent, where is the batch or continues adsorption process (procedure).To calculate the percentage removal of nitrate and volatile fatty acids using the prepared adsorbent from Habesha brewery wastewater. This is the objective of the study.

3.2.1 Properties of Adsorbent

3.2.1.1 Moisture content

The moisture content of the was calculated using. The formula below was used to calculate the percentage of moisture content in each of the spent kiselguhr samples

$$\text{Moisture content percent (MC \%)} = \frac{Loss\ in\ weight\ on\ drying(g)}{Initial\ sampleweight(g)} x\ \mathbf{100}\ldots$$

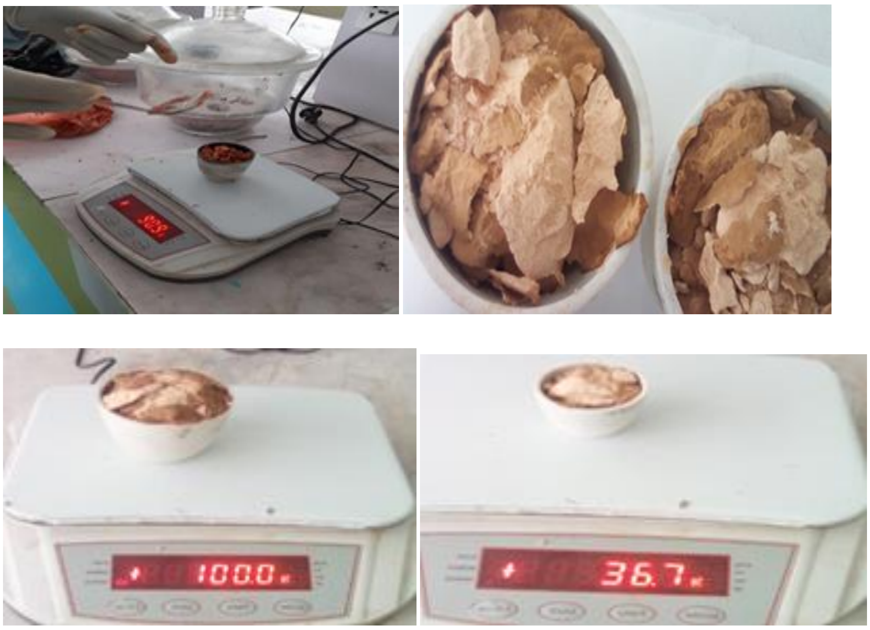


Figure 3. 2 the moisture content of sample prepared kiselguhr and preparation of adsorbent and the instrument.

3.2.1.2 Ash content

The furnace was heated until it reaches to a temperature of 550°C. The spent kiselguhr sample was heated at 550°C for 1 hour 30 minutes in a furnace. The weight of the spent kiselguhr sample before heating and after heating was used to determine the amount of ash content present in the sample. In this test, the amount of residual substance is equal to the ash present in the sample. The percentage of ash in the sample was calculated using the formula:

Ash % = (D÷B)*100---eqn (3.2)

Where, D amount of adsorbent after heating, B the amount of adsorbent before heating.

The figure below indicates the color of the kiselguhr before the oven and the balance in fig A and B. After moisture content removal and ash content at 550degree centigrade in fig D and the moisture content at 105 in the fig C degree centigrade. the comparison was performed for the adsorbent properties of kiselguhr for good adsorption process with different particle size and time difference.

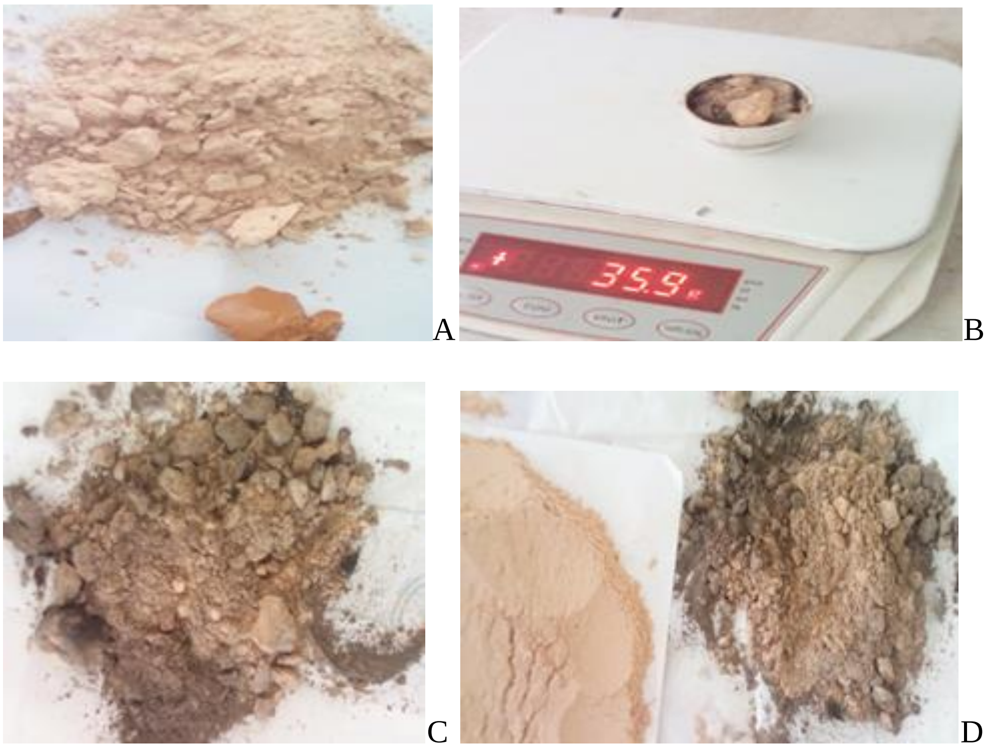


Figure 3. 3 Preparation of ash content

3.2.1.3 Adsorption process with Habesha brewery waste water effluent

The milled adsorbent was sieved by different mesh size, these adsorbent was mixed into the prepared different waste water with stirrer for 5min.

Figure 3. 4 adsorption process

3.2.3 Characterization of adsorbed solution after addition of adsorbent

3.2.3.1. Acid value

After done all things I checked the acidity of the solution of waste water .Take 250gm or 250ml of mixed solution in accurately weighed by using 60^{O}c temp, in 250 ml mixture of equal volume of alcohol but the alcohol concentration 97% and solvent hexane, the flask was connected to reflux condenser and slowly heated, until sample was dissolved completely, to this three drop of phenolphthalein added and titrated with 0.1N NaOH, until the color changed pink color appears after shaking for 30 seconds Belibasakis NG and Tsirgogianni D (1996)

Acid value = V*N*56.1/W……………………….eqn.3.3

Where V volume of expressed in milliliter of 0.1N solution of ethanoic, NaOH. N, concentration of the NaOH. W, weight of the solution

3.2.3.2 Total solids

The amount of solids in the solution after filtration and evaporation was measured to be known for determination in which amount of the solid waste exist in the liquid waste.

TS= TSS+TDS, where the TS total solids, TSS, total suspended solids, TDS total dissolved solids.

3.2.3.3 pH value

The pH value of the sample solution was measured before applying of the adsorbent and the mixed process of the adsorbent sample for collection or knowing of the best adsorption process in the waste treatment tank of all IP, UASB, and FE tank of treatment waste water the expected result was from neutralization tank must be good PH value.

3.2.3.4 BOD value

The biochemical oxygen demand from the result was good from different sample solution the expected range from beer waste treatment methods the BOD content was measured with different time duration with different adsorbent size with the addition of different sample waste or level of waste water. The result was good from the UASB tank from the other treatment tank level, due to the aerobic digestion system in this tank.

3.2.3.4 COD value

The COD also the same with biochemical oxygen demand mechanism the procedure also similar the expected result was good from the UASB tank as similar condition.

3.2.3.5 Nitrate Content

The nitrate compounds also reflected with the GC-MS device and the amines compounds also expected result. The size of the adsorbent also one factor to performed the laboratory work with concentration of the waste water, from the smallest particle size 63 micro meter size of adsorbent. The waste collected sample treatment tank also one factor from the UASB tank sample the nitrate compounds also highly investigated.

3.2.3.6 Concentration of the waste water with adsorbent ratio

The concentration of the waste sample also one factor affecting the adsorption process the concentration with adsorbent ratio was determined with PH, acid value, TSS, TDS, amount of adsorbent particle size also measured with balance with its size determination factors.

3.2.3.7 Expected result from the lab work

The adsorption process of beer waste from different sedimentation tank or treatment tank were the amount of nitrate compounds, volatile compounds were highly investigated or analyzed. Such compounds were expected from the result such as acetic acid Propanoic acid, methyl compounds, and propyl compounds nitrile amines. The GC-MS analyzed were involved with highly effect on the size, time and waste level tank or treatment sample tank.

Figure 3. 5 The final result sample after extra experiment investigation

3.2.3.8 Experimental set up for filtration process

The experiment was performed for separation of TSS by such filtration mechanisms

Figure 3. 6 filtration process of waste for TS separation system.

Result and Discussion

4.1 Proximate Analysis of the spent kiselguhr

The spent kiselguhr was collected from habeshaBrewery Company, the spent kiselguhr was not any advantageous after filtration. But the spent could use for different process such as to treat soil efficiency, ceramic production as adhesive, to treat wastes. The samples was collected after filtration in last run then the amount is measured. The spent was dried by sun light and oven at 105^{o}c for 48 hrs.The moisture content of the spent kiselguhr was become:

Moisture content = (the sample weight in kg/total weight of sample in kg)*100%---------eqn 4.1

= (100gm/174.6gm)*100%=57.4% the remaining amount 42.53% was the moisture content.

The ash content from the spent was (35/40)*100=87.5 weight was free from ash content the remaining amount 12.5%was the ash. The amount of the carbon content of spent kiselguhr wasn't not major factor for investigation and value asses of adsorbent. The ash of the sample of the adsorbent were so good for measuring the value because of the composition of the adsorbent was light substances the compounds of the adsorbent was silica gel or diatomite substances, the diatomite substances is found in the ocean for the long time duration.(Kumari, Kumar, Reddy, & Jha, 2014).

4.2 Physicochemical Characteristics of Adsorbent

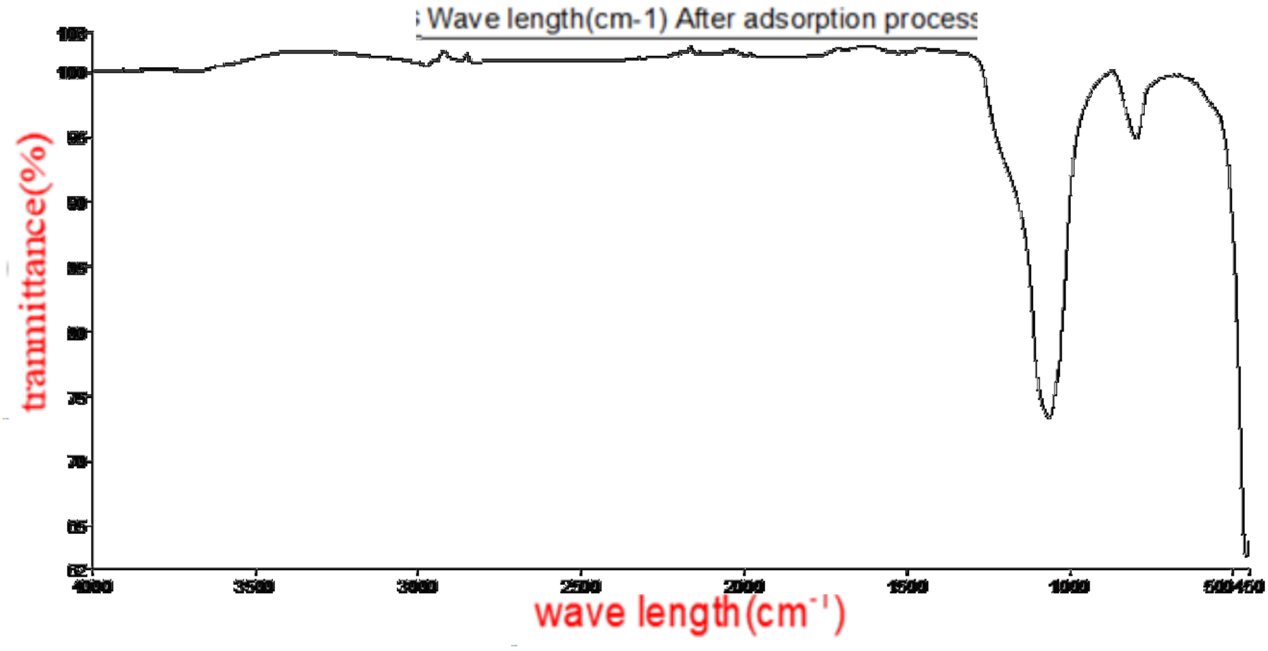
The odor of the spent was not good due to the coexistence of surplus yeast and some haze materials, the color of the spent was to be nearest red before removed moisture content, but after removed moisture content the color was to become nearest to white powder. The density of the spent kiselguhr 0.29g/ml.the adsorbent was light substances in because of the composition of the adsorbent was silica gel content is highly light substances. The other substances in the adsorbent also in small content silicon die oxide, and also contains water loving substances to make the bonding with adsorption process with waste water to ionize the composition of the substances.

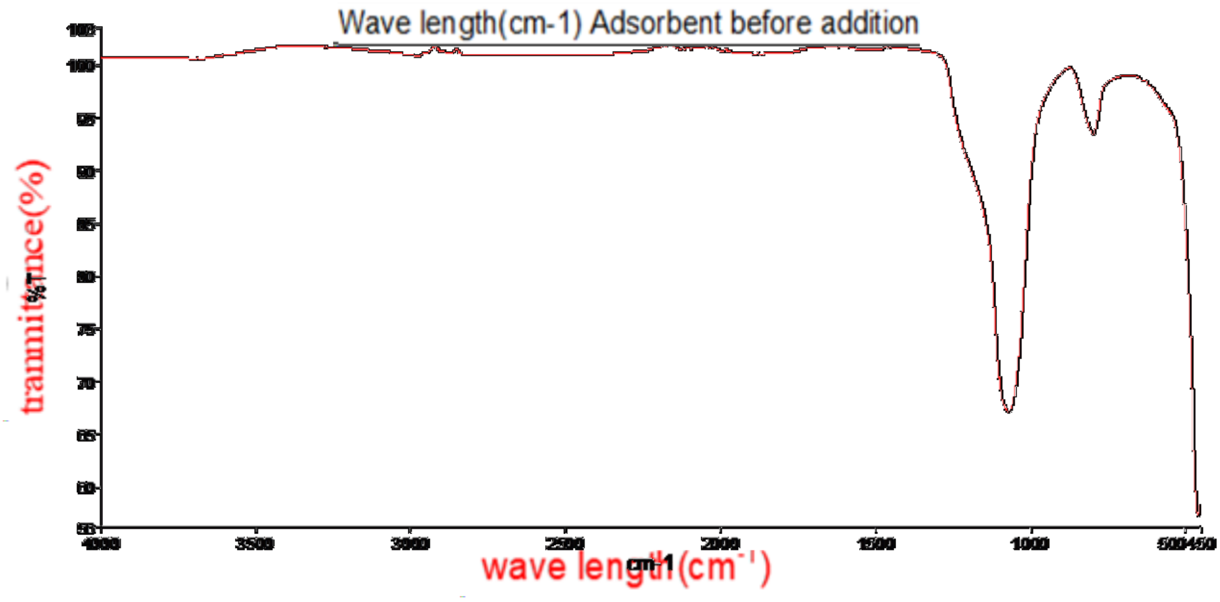
4.3 FTIR spectroscopy analysis of adsorbent

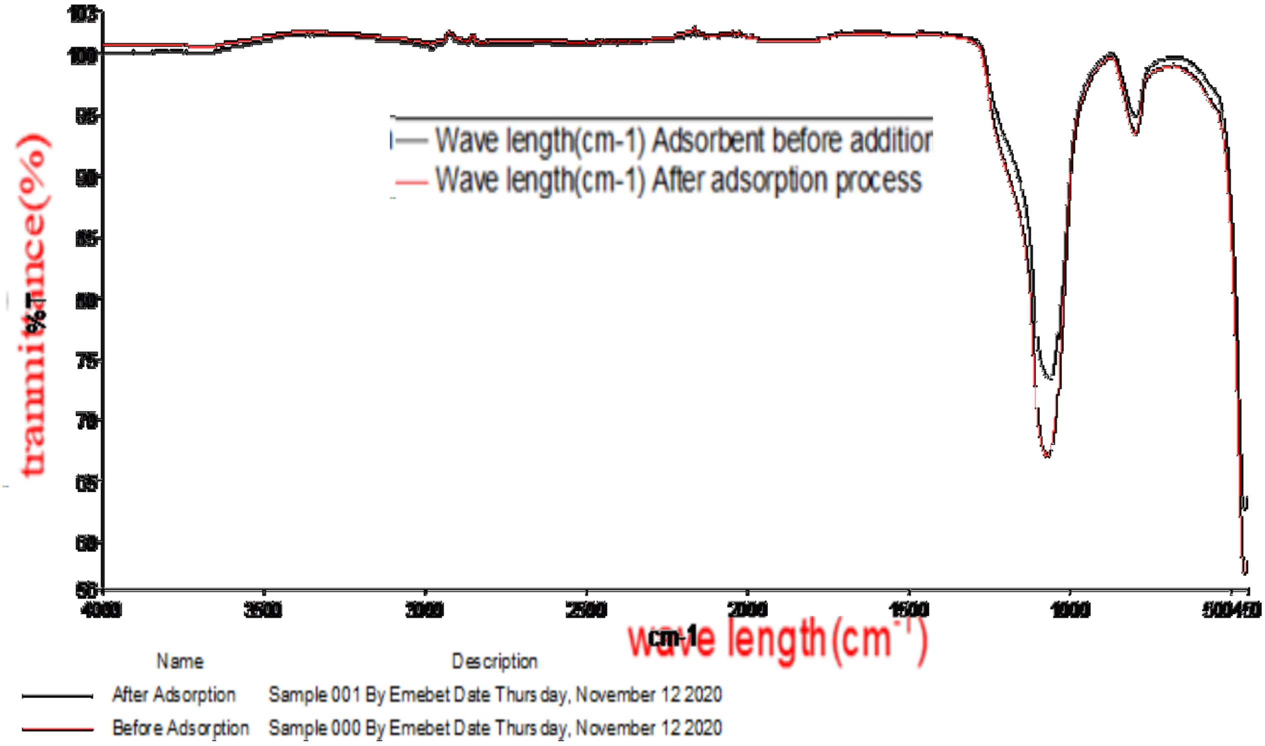
The adsorbent samples were investigated with mass by mass 53%*w*/*w* two standard-added (addition) samples were prepared: the first one is zero-added sample (add.0) is the adsorbent sample, add.1 has an added concentration of diatomite or pure kiselguhr at 5%*w*/*w*, at 10%*w*/*w*, and at 15%*w*/*w*. All added samples (and a pure adsorbent sample) were analyzed by FTIR. In the spectra of adsorbent the contribution of silica, biogenic, is dominant. In the fingerprint region (600-1500 cm1), strong signal was found at about 1500 cm-1 (informing aromatic ring). Vinyl related compound was also found at about 1000 cm-1.

Silicon-oxy compounds Organic siloxane or silicone (Si-O-Si) 1095–1075/1055–1020 Organic siloxane or silicone (Si-O-C} {1110–1080. For hydroxyl compound, it should be followed by the presence of spectra at frequencies of 1600–1300, 1200–1000 and 800–600 cm1.

Such spectra exhibit has its own characteristic vibrational bands. The two main bands at 1050 and 471 cm $^{-1}$ are attributed to triply degenerated stretching and bending modes, respectively, of the [SiO4] tetrahedron. The band at 500 cm $^{-1}$ corresponds to an inter-tetrahedral Si–O–Si bending vibration mode, and the band near 750 cm^{-1} to a Si–OH vibration mode. Previous studies have shown that the absorbance centered around 1640 cm $^{-1}$ and between 3000 and 3750 cm $^{-1}$ can be attributed to hydroxyl vibrations because hydroxyl ions are major constituents of clay minerals, opal, and organic compounds present in the samples.







Name	Description
After Adsorption	Sample 001 By Emebet Date Thursday, November 12 2020
Before Adsorption	Sample 000 By Emebet Date Thursday, November 12 2020

4.4. Physicochemical Characteristics of Waste water sample Analysis

The sample was analysis with the three replication experiment by design expert this replication used for avoiding of error. The waste water samples were characterized by considering the following factor affecting variability's.

Table 4. 1 the waste water sample code

Samples	Code	Sample point level (m) code
Influent put	IP	100
UASB	UASB	200
Final effluent	FE	300

Table 4. 2 the physico chemical charctersitics of waste water

Rno	FactorA lev l(m	Factor B:time(hr	COD (mg)	BOD (MgL	Conductivity Micro Simon/cm
1	300	60	1114.	980	2820
2	300	72	1100	977	2814
3	100	72	2375	2410	2997
4	200	72	1404	1460	2032
5	200	60	1400	1478	2027
6	200	60	1396	1487	2027.5
7	200	60	1390	1482	2029
8	200	60	1394	1480	2022
9	300	48	1085	977	2807
10	100	48	2370	2475	2900
11	200	60	1389	1455	2021.9
12	100	60	2365	2460	2906

4.5. Characteristics of waste solution after Adsorption process

The ration of the adsorbent with waste water from different level was similar 1:5 the time was vary to get accurate solution from the experiment, the following design expert was given for experiment result summarization.(From appendix c)

Table 4.3results of the solution after mixing process of adsorbent

Run no	Waste level(m)	Time(hr)	Adsorbent particle size(μm)	COD (mg/L)	VFA	PH	BOD (Mg/L)	PO^-_4 mg/l	NO^-_3 mg/l	NH^+_4 mg/l	Conductivity
1	200.00	60.00	80	180.4	87	7.9	170	10.9	2.19	0.295	2010
2	200.00	60.00	100	190.1	98	7.6	172	10.1	2.1	0.3	2007
3	200.00	60.00	80	181.5	91	7.8	175	10.7	2.2	0.21	2002
4	200.00	72.00	80	180.3	86	7.5	169	10.8	2.4	0.22	2005
5	200.00	72.00	100	185	93	7.7	10.06	10.7	2.32	0.2	2004
6	300.00	60.00	100	32	63	7.5	12.04	8.00	1.95	1	2810
7	300.00	48.00	63	27	67	7.3	11.20	8.04	1.83	1.3	2800
8	300.00	72.00	80	30.5	71	7.4	10.18	8	1.87	1.2	2805
9	100.00	72.00	100	216	206.	9.5	302.5	11.6	3.47	1.53	2990
10	100.00	60.00	80	215.5	203	9.3	301.4	11	3.3	1.5	2985
11	300.00	48.00	100	40.75	74	7.6	10.10	7.79	1.9	1.1	2809
12	100.00	48.00	100	220.5	208	9.4	302.0	11.3	3.49	1.6	2996
13	100.00	72.00	63	217	198	9.1	301.2	10.5	3.1	1.3	2982

14	300.00	48.00	80	63	62	7.2	10.09	8.4	1.8	1.5	2809
15	200.00	60.00	80	181.9	81	7.8	170.6	10.3	2.4	1.1	2010
16	200.00	60.00	80	181.5	83	7.7	171.7	10.5	2.3	1.0	2011
17	300.00	60.00	80	26.2	61	7.3	10.07	8.2	1.9	1.1	2800
18	200.00	48.00	100	186.8	85	7.8	181.2	10.8	2.5	1.5	2014
19	200.00	48.00	63	181	83	7.4	180.5	10	2	1.3	2012
20	300.00	60.00	63	31	65	7.5	12.00	7.9	1.7	0.9	2809
21	100.00	72.00	80	215.2	201	9.3	306.1	11.5	3.4	1.4	2980
22	200.00	60.00	63	180	84	7.3	170.1	10.4	2.2	1.2	2009
23	100.00	48.00	80	217	197	9.5	301.7	11.3	3.5	1.5	2983
24	100.00	60.00	63	213	192	9.1	305	11.2	3.1	1.3	2987
25	300.00	72.00	63	25.7	59	7.1	10.05	8	1.7	1	2807
26	300.00	72.00	100	34.6	72	7.4	11.10	8.4	1.9	0.89	2806
27	200.00	72.00	63	179.8	79	7.6	170.4	9	2.4	0.27	2008
28	100.00	48.00	63	215.5	205	9.4	301.9	11	3.3	1.4	2993
29	200.00	60.00	80	185.3	87	7.7	171.5	8.3	2.3	0.3	2011
30	100.00	60.00	100	218	201	9.5	302.7	11.5	3.6	1.6	2995
31	200.00	48.00	80	187	89	7.6	181.3	8.5	2.6	0.25	2008
32	200.00	60.00	80	184.6	83	7.5	180.9	8.2	2.4	0.23	2010

the clarity of the solution was good with the adsorbent particle size of 63 micro meter and time duration of 72 hr of with sample took from the level of 300. But this was with similar the determination of the concentration.the TDS was 18 gm/l from the 200ml of the solution after adsorbing process.the TDS was gm from 200ml of the optimum adsorbtion process. The amount of the adsorbent was the same around40gm for different concentration waste sample. The result summerized below in the table.The sample was taken from the sample point 200m level(UASB tank) and the optimum time duration 60hr.the adsorbent to waste concentration was 1:5,1:6,1:7,1:8(Baran, El-sharkawy, Thorpe, & Critoph, 2011).

Table 4. 4 deterimination of the effect of concentration for adsorption process

No	Amount of adsorbent in gm	Waste water concentration	BOD mg/l	COD mg/l	TDS
1	40	200ML	172	175	135.5
2	40	240ML	184	180	140
3	40	280ML	192	183	142
4	40	320ML	195	189	143

The total dissolved substances was highly increase in which the amount of concentration increase so the amount of adsorbent ratio was so good for 1:5 from UASB tank.

4.6 The Statically analysis of COD waste Adsorption process

ANOVA for Response Surface Quadratic Model

Table 4. 5 Analysis of variance table [Partial sum of squares].

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	72545.26	9	8060.58	1.71	0.1470not significant
A	3154.83	1	3154.83	0.67	0.4224
B	16674.42	1	16674.42	3.53	0.0735
C	165.01	1	165.01	0.035	0.8534
A^2	23493.44	1	23493.44	4.98	0.0362
B^2	18754.76	1	18754.76	3.97	0.0588
C^2	5821.68	1	5821.68	1.23	0.2788
AB	7910.47	1	7910.47	1.68	0.2089

AC	2685.02	1	2685.02	0.57	0.4587
BC	696.16	1	696.16	0.15	0.7046
Residual	1.039E+005	22	4720.54		
Lack of Fit	87478.28	17	5145.78	1.57	0.3250not significant
Pure Error	16373.57	5	3274.71		
Core Total	1.764E+005	31			

The "Model F-value" of 1.71 implies the model is not significant relative to the noise. There is 14.70 % chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case $A^2$are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The "Lack of Fit F-value" of 1.57 implies the Lack of Fit is not significant relative to the pure error. There is a 32.50% chance that a "Lack of Fit F-value" this large could occur due to noise.

Table 4. 6 lack of fit

Std. Dev.	Mean	C.V	PRESS	R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision
68.71	150.74	45.58	2.308E+005	0.4113	0.1704	-0.3085	4.982

A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 4.982 indicates an adequate signal. This model can be used to navigate the design space.

Table 4. 7 Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean	F	Prob > F

			Square	Value	
Mean	7.271E+005	1	7.271E+005		Suggested
Linear	19994.26	3	6664.75	1.19	0.3303
2FI	11291.65	3	3763.88	0.65	0.5913
Quadratic	41259.35	3	13753.12	2.91	0.0571Suggested
Cubic	33497.57	7	4785.37	1.02	0.4563Aliased
Residual	70354.29	15	4690.29		
Total	9.035E+005	32	28234.67		

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

Table 4. 8 Lack of Fit Tests

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Linear	1.400E+005	23	6088.23	1.86	0.2545
2FI	1.287E+005	20	6436.88	1.97	0.2337
Quadratic	87478.28	17	5145.78	1.57	0.3250 Suggested
Cubic	53980.71	10	5398.07	1.65	0.3027Aliased
Pure Error	16373.57	5	3274.71		

Lack of Fit Tests Want the selected model to have insignificant lack-of-fit.

Table 4. 9 Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS
Linear	74.74	0.1133	0.0183	-0.1605	2.047E+005

2FI	76.19	0.1774	-0.0201	-0.3406	2.365E+005
Quadratic	68.71	0.4113	0.1704	-0.3085	2.308E+005Suggested
Cubic	68.49	0.6012	0.1757	-1.2617	3.990E+005Aliased

Model Summary Statistics Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

Std. Dev	Mean	C.V	PRESS	R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision
68.71	150.74	45.58	2.308E+005	0.4113	0.1704	-0.3085	4.982

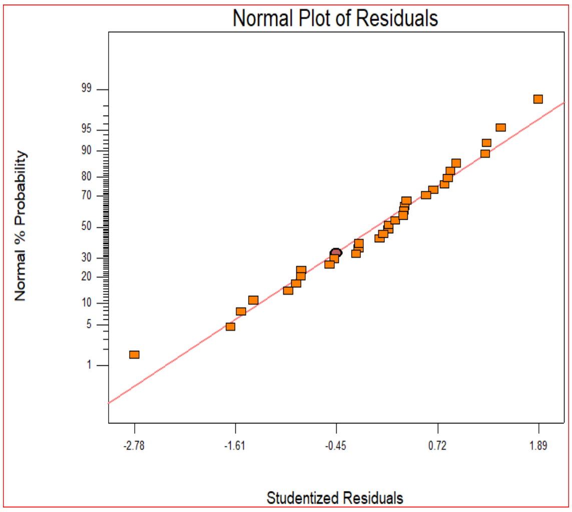
A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 4.982 indicates an adequate signal. This model can be used to navigate the design space.

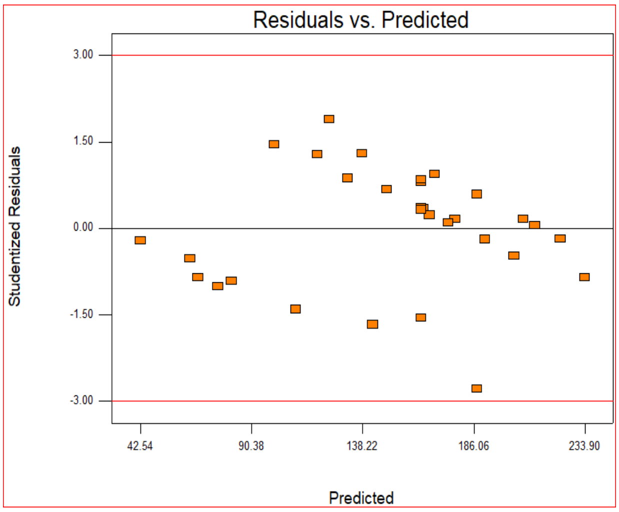
Factor	Coefficient Estimate	DF	Standard Error	95% CI low	95%CI High	VIF
I	163.35	1	23.09	115.47	211.23	
A	13.24	1	16.19	-20.35	46.82	1
B	-30.44	1	16.19	-64.02	3.15	1
C particl	3.03	1	16.19	-30.56	36.61	1
A^2	57.31	1	25.69	4.03	110.58	1
B^2	-51.20	1	25.69	-104.48	2.07	1
C^2	-28.53	1	25.69	-81.80	24.75	1
AB	25.67	1	19.83	-15.46	66.81	1

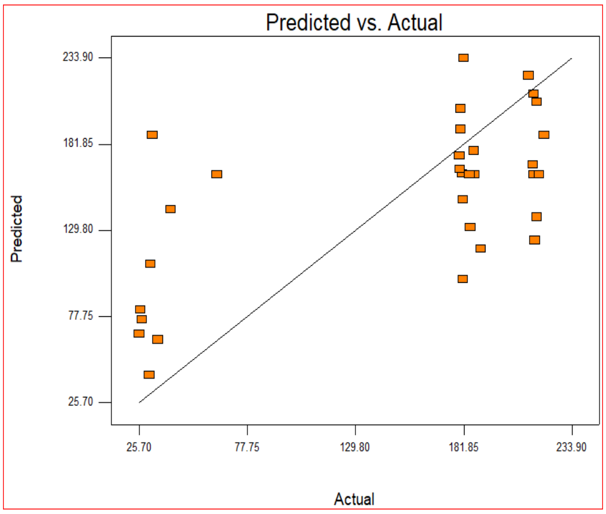
AC	14.96	1	19.83	-26.17	56.09	1
BC	7.62	1	19.83	-33.52	48.75	1

The confidence interval from the above table with low and high value for each level factor with quadratci and linear formulation model.the negative value of the coefficent estimate and the low level confidence interival was highly detrimenat factor for each level of factor for waste level,time duration,particle size,and it’s square of each factors for the adsorpation prcoess fit model.

From the figures the COD with the other diteriminats factor affecting were highly dependent with the value,the predictied value from the graph were scatterd over theinitial line of the piont this indicates that predicted value highly error occurred.







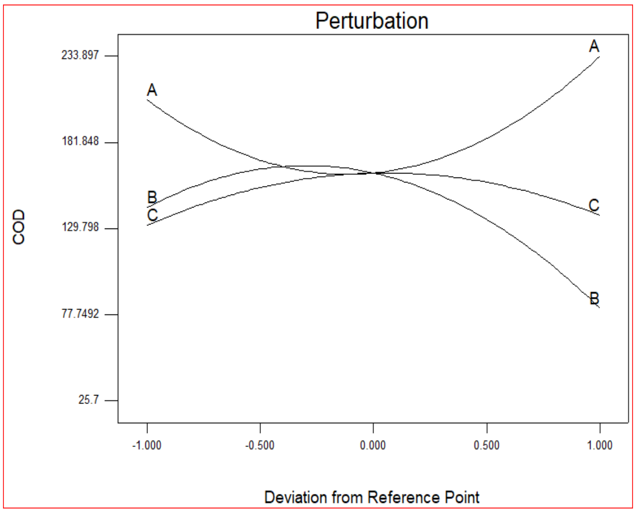
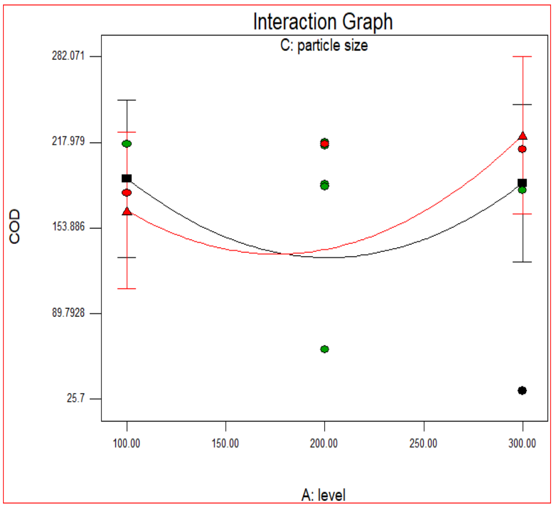


Figure 4. 1 Indivisual factor affecting on the COD of the wasteand actual vs predicted value graph

The actual value from the graph were little difference with predicted value small amount of error were displaed, the one factor effect from the graph for the COD were highly affect on the adsorption process espescially the sample point took or the sample level was mian effect,such as from the graph the 100m or IP,200UASB,and 300FE.big difference for sample collection and result after adsorption process.this effect indicates that factors for measuring of the COD.

4.6.1 Effect of the interaction variables

the three graph indicates that the COD depend on the factor afacting on the particle size.time and sample point this means that the time increase and also the particle size of the adsorbent decrease the sample point so good that from UASB from un ariobic sedimentation tank.



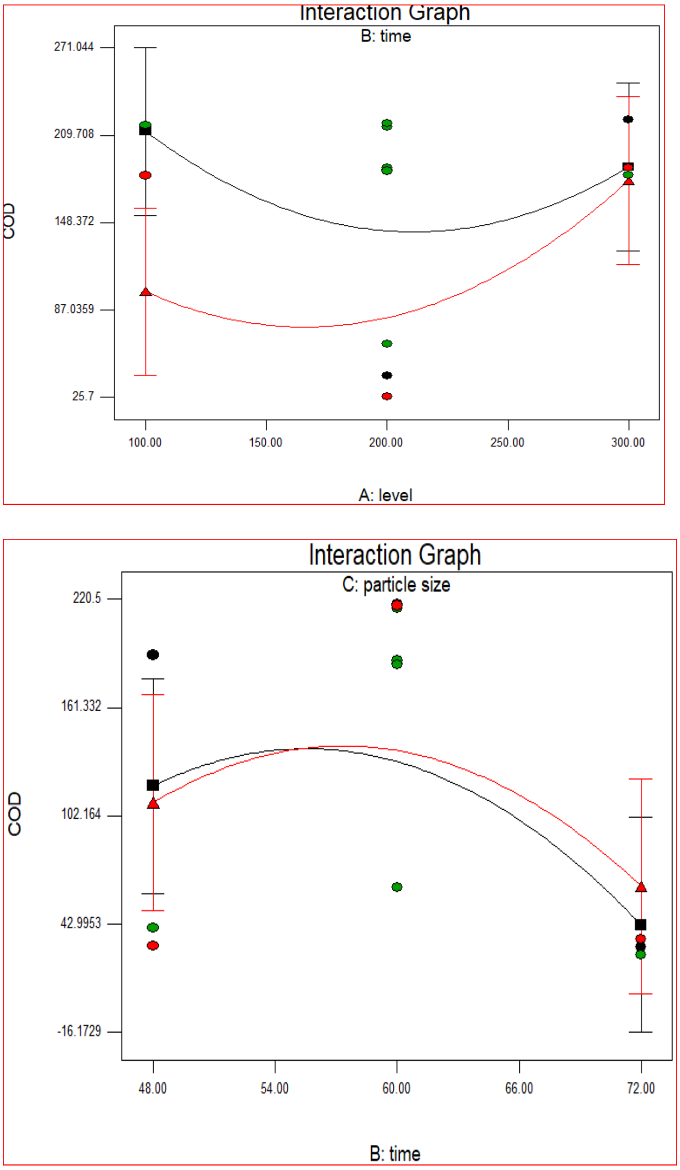


Figure 4. 2 the interaction graph of prticle size of adsorbent,time and sample point on the COD.

The interaction graph was one of the detrimenant factor for the effect on the BOD ,COD, and conductivity.the time and the particle size and sample took level was the detrimenant factor from the above intraction curve both sample level from,200m was the optimum range for the COD measurment and the time duration with 62Hr.atthe particle size,63micro.m. was the optimum condition for COD measurment.

The counter graph of COD and the effect of the variables the three variables were affected the adsorption process and some constraint.from the above graph on the interaction variables time,particle size and sample collected level were main factors when the time increase with the interaction from the first graph COD also highly increased.the other graph also simlar with time factors, but the particle size decreased the with increasing time the COD were good anlysis measured.

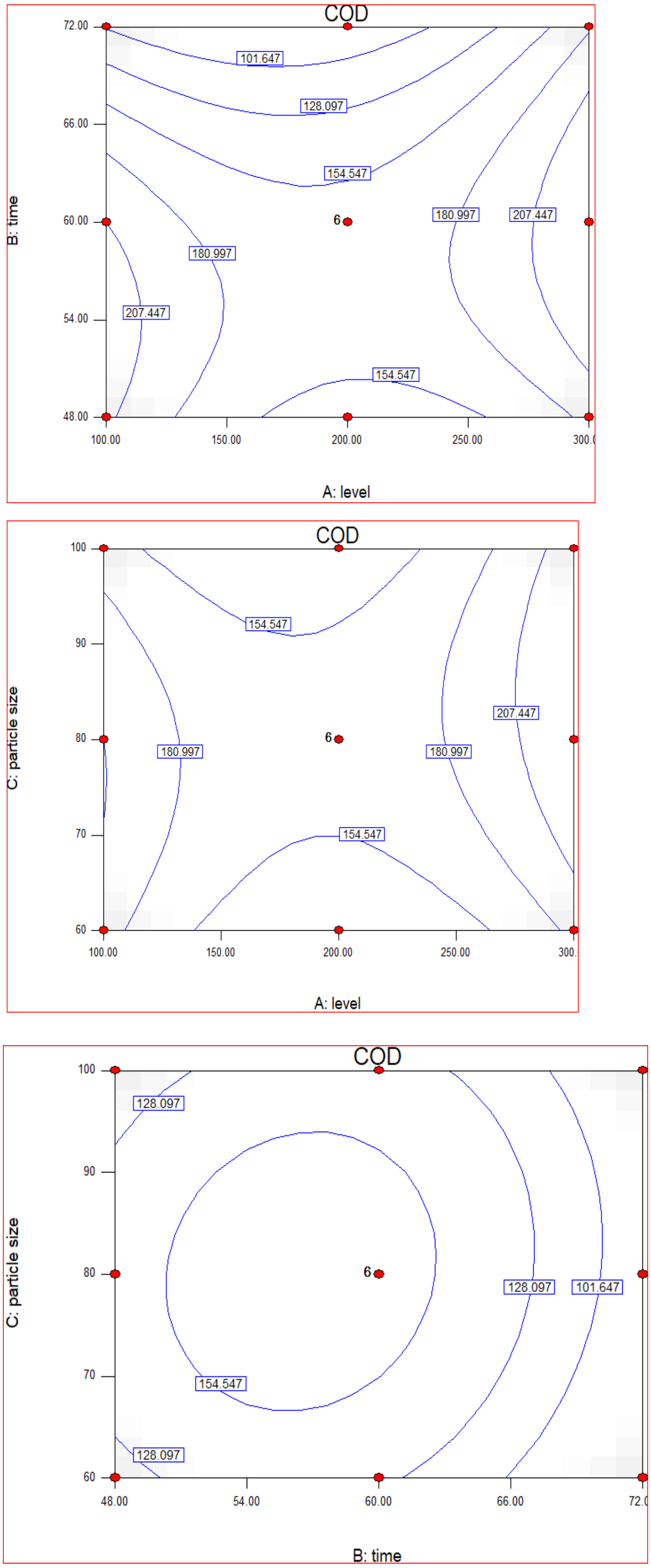


Figure 4. 3 Contour graph of COD and standard error of the COD

The counter graph indictes that the optimum measured variables were performed with the factor affecting process.time,particle size,and the waste water concentration was highly affect on the graph displed,the maximum amount of the COD from the time of the 60 hr was 180g/ml,the value was the optimum point in the counter graph.when ever the standard error of the COD with thethree factors highly increased.

The graph indicated that the factors and the response of the given sample were good separation involved in the graph the adsorption with the Size time and waste sample collected level was mainly factors for the adsorption process the level point from 200m, time 60hr, and the particle size 63micro m. were the optimum condition of the preferable result for the waste water separation process.

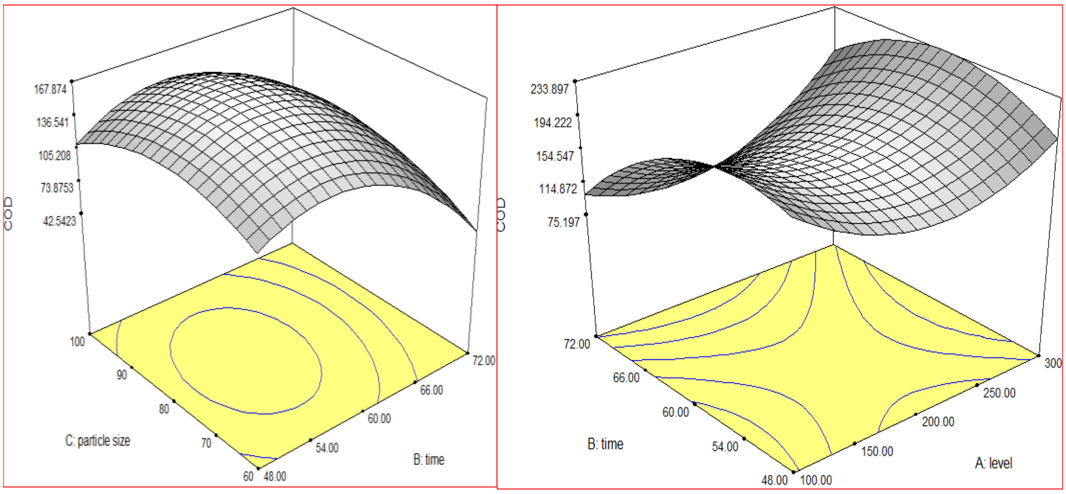


Figure 4. 4 the 3D surface graph interaction of the factor affecting variables

Table 4. 10 BOD ANOVA Analysis of variance table [Partial sum of squares]

Source	Sum of squares	DF	Mean square	F value	Prob> F
Model	1.616E+005	9	17959.75	1.60	0.1777not significant
A	10740.41	1	10740.41	0.95	0.3392
B	31308.36	1	31308.36	2.78	0.1095
C	10511.05	1	10511.05	0.93	0.3443
A2	65276.31	1	65276.31	5.80	0.0248
B2	21555.47	1	21555.47	1.92	0.1802
C2	22691.85	1	22691.85	2.02	0.1696

AB	9072.25	1	9072.25	0.81	0.3789
AC	6603.99	1	6603.99	0.59	0.4518
BC	1081.67	1	1081.67	0.096	0.7594
Residual	*2.475E+005*	22	*11251.77*		
Lack of Fit	1081.67	17	11144.67	0.96	0.5749not significant
Pure Error	2.475E+005	5	11615.91		
Cor Total	1.895E+005	31			

The "Model F-value" of 1.60 implies the model is not significant relative to the noise. There is a 17.77 % chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case $A^2$are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F-value" of 0.96 implies the Lack of Fit is not significant relative to the pure error. There is a 57.49% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4. 11 Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Mean	8.114E+005	1	8.114E+005		Suggested
Linear	52559.82	3	17519.94	1.38	0.2706
2FI	16757.91	3	5585.97	0.41	0.7466
Quadratic	92320.07	3	30773.36	2.73	0.0680Suggested
Cubic	98632.34	7	14090.33	1.42	0.2684Aliased

Residual	1.489E+005	15	9927.11		
Total	1.221E+006	32	38143.26		

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

Table 4. 12 Lack of Fit Tests

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Linear	2.985E+005	23	12979.89	1.12	0.4991
2FI	2.818E+005	20	14088.98	1.21	0.4531
Quadratic	1.895E+005	17	11144.67	0.96	0.5749Suggested
Cubic	90827.10	10	9082.71	0.78	0.6547Aliased
Pure Error	58079.53	5	11615.91	1.12	

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

Table 4. 13 Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS
Linear	112.86	0.1285	0.0351	-0.1229	4.595E+005
2FI	116.59	0.1694	-0.0299	-0.3369	5.470E+005
Quadratic	106.07	0.3950	0.1475	-0.2837	5.252E+005Suggested
Cubic	99.63	0.6361	0.2479	-0.8925	7.744E+005Aliased

Table 4. 14 Model Summary Statistics

Std. Dev	Mean	C.V.	PRESS	R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision
106.07	159.24	66.61	5.252E+005	0.3950	0.1475	-0.2837	4.849

A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 4.849 indicates an adequate signal. This model can be used to navigate the design space

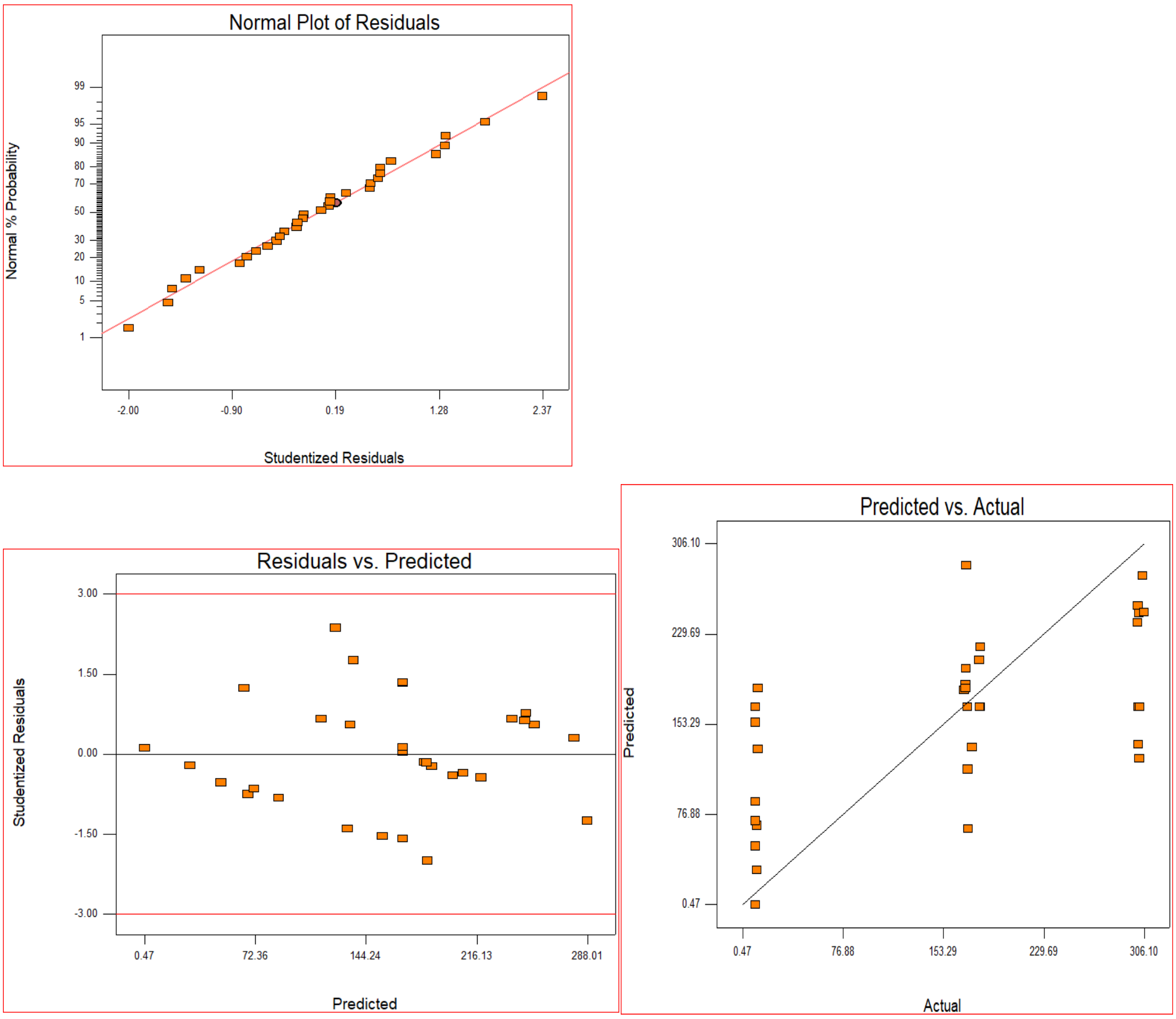


Figure 4. 5 the interaction probability and standard error BOD graph

The standard error for the BOD measured value was no more grater from the experiment result within the three factor effect from the graph the size, time and sample point was given maximum result.

4.5.2Interaction effect of variables for BOD analysis

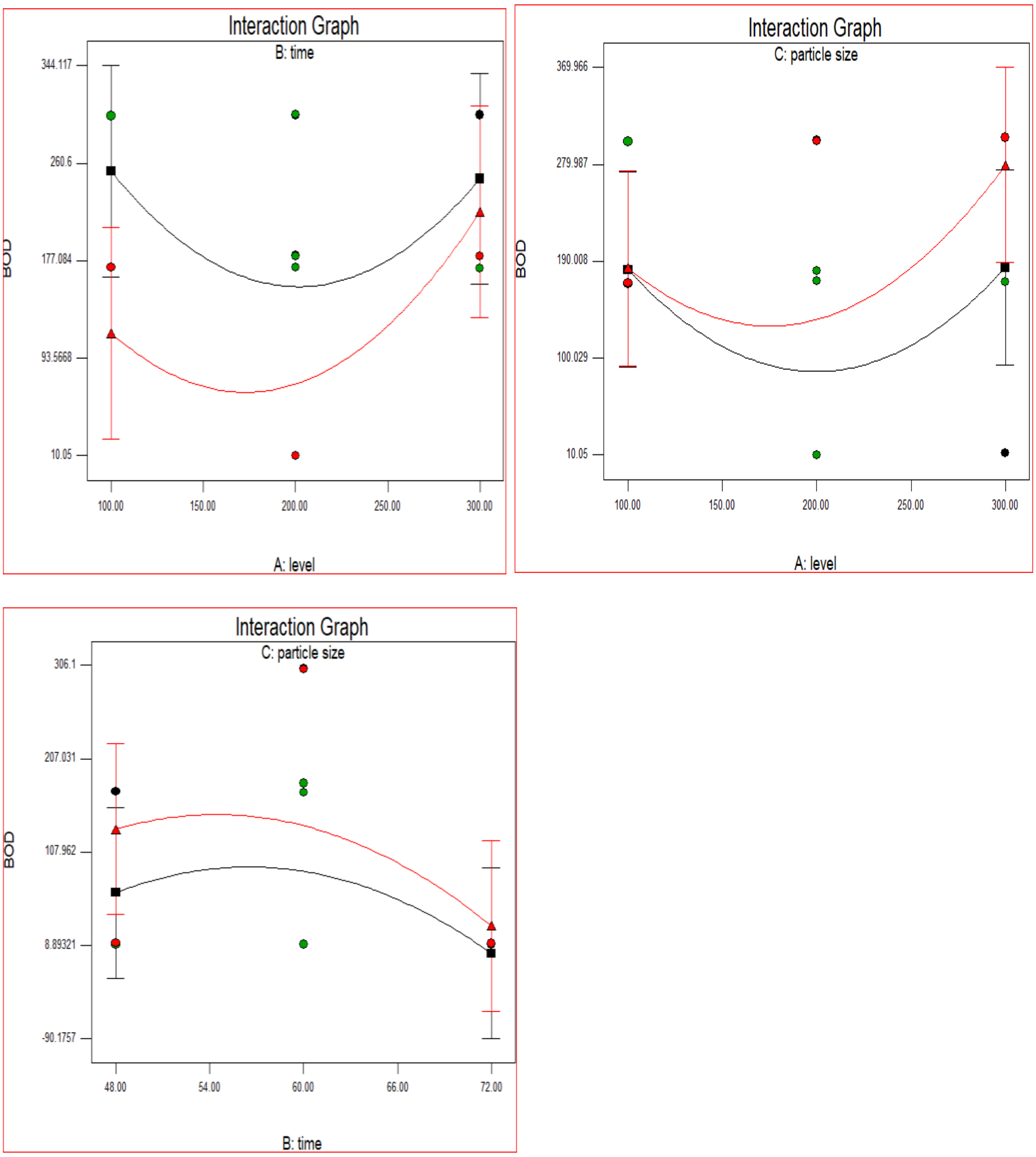
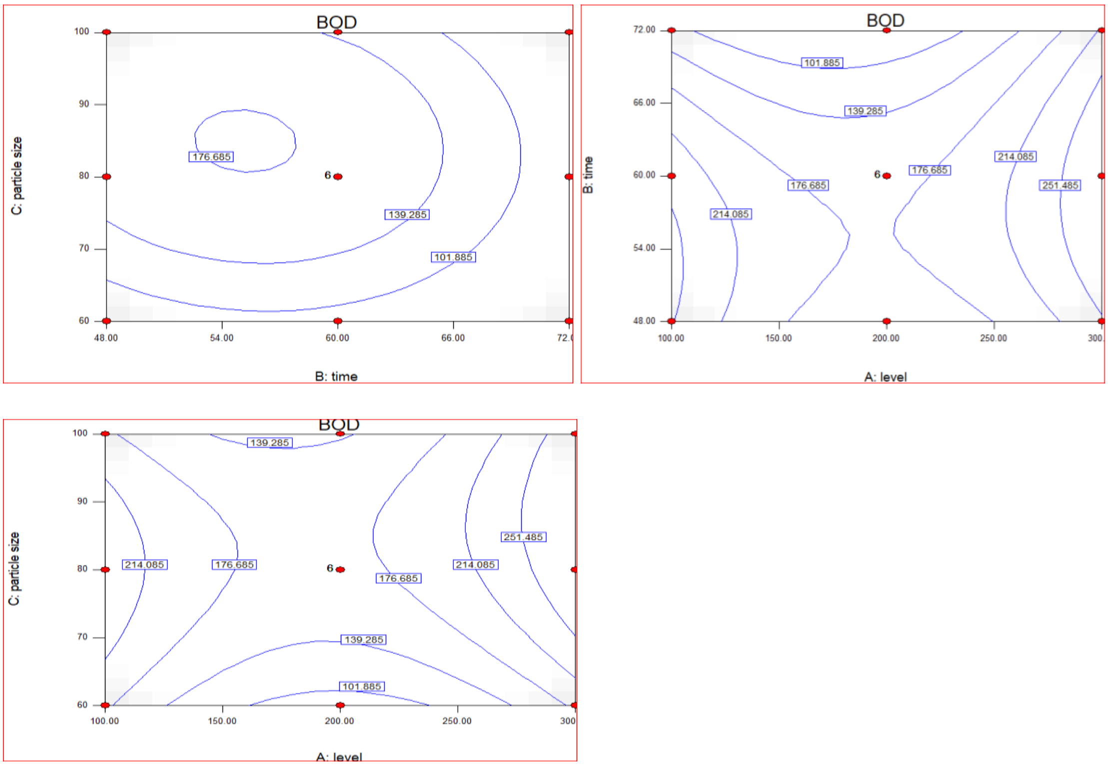


Figure 4. 6 The interaction of the time, particle size, and sample point.

Both the interaction effect on the BOD measurement were time and sample collection level or the mainly the level for the all measurement analysis was given similar performance investigation from the above 200m,and the time 60hr.was good adsorption process result to conducted the BOD with in the interaction process variables.

On the 3 D graph for BOD measured data were with time, particle size so good investigation from the other response the maximum BOD were recorded the time with 60hr was so good for all investigation in the UASB due to the cause of the availability of the bacteria for the digestion process of the waste water and liquids waste from the beer waste after the input of all waste type, there is aerobic digestion system in this blanket tank and the other some spent also ionized or degraded and changed into some nitrile compounds and volatile fatty acids, so the graph also indicated this kind of effect on the adsorption process of the waste water for purification or removal of the organic and inorganic substances with the adsorbent.



the 3D graph th BOD interaction with level sample,particle size,and time interction the amount washighly affected by the particle size,the particle size mainle affected the BOD and the other adsorption process.

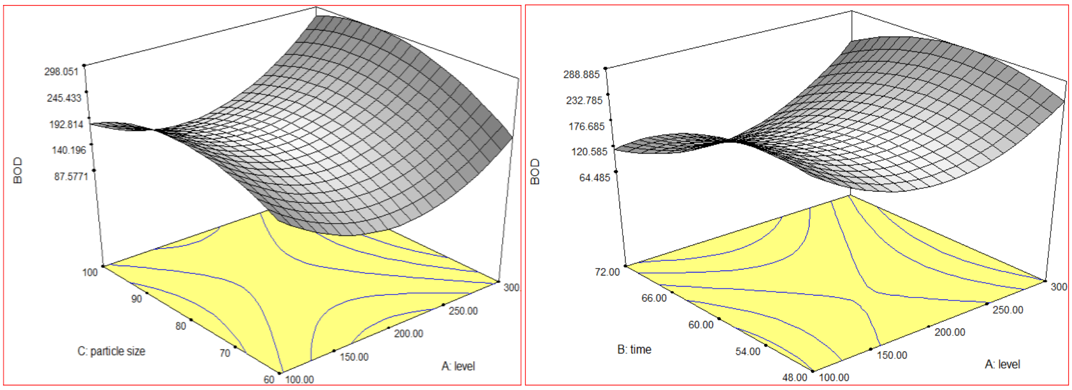


Figure 4. 7 counter and 3D surface interaction graph on the BOD factors

4.6.3 Conductivity ANOVA methods analysis

Table 4. 15 ANOVA for Selected Factorial Model of conductivity

Source	Sum ofSuares	DF	Mean Square	F Value	Prob > F
Model	6.364E+006	9	7.071E+005	52629.81	<0.0001sig
A	1.487E+005	1	1.487E+005	11067.71	< 0.0001
B	76.06	1	76.06	5.66	0.0264
C	32.00	1	32.00	2.38	0.1370
A^2	5.640E+006	1	5.640E+006	4.198E+005	< 0.0001
B^2	11.61	1	11.61	0.86	0.3626
C^2	74.44	1	74.44	5.54	0.0279
AB	33.33	1	33.33	2.48	0.1295
AC	8.33	1	8.33	0.62	0.4393
BC	10.08	1	10.08	0.75	0.3957
Residual	295.57	22	13.43		
Lack of Fit	235.57	17	13.86	1.15	0.4763 Not significant
Pure Error	60.00	5	12.00		
Cor Total	6.364E+006	31			

The Model F-value of 52629.81 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, A^2, $C^2$are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The "Lack of Fit F-value" of 1.15 implies the Lack of Fit is not significant relative to the pure error. There is a 47.63% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4. 16 Sequential Model Sum of Squares

Source	Sum of Square	DF	Mean Square	F Value	Prob > F
Mean	2.013E+008	1	2.013E+008		
Linear	1.488E+005	3	49600.76	0.22	0.8793
2FI	51.75	3	17.25	6.939E-005	1.0000
Quadratic	6.215E+006	3	2.072E+006	1.542E+005	< 0.0001 Suggested
Cubic	105.07	7	15.01	1.18	0.3692 Aliased
Residual	190.50	15	12.70		
Total	2.077E+008	32	6.491E+006		

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

Table 4. 17 Lack of Fit Tests

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Linear	6.215E+006	23	2.702E+005	22518.64	< 0.0001
2FI	6.215E+006	20	3.108E+005	25896.22	< 0.0001
Quadratic	235.57	17	13.86	1.15	0.4763 Suggested
Cubic	130.50	10	13.05	1.09	0.4934 Aliased
Pure Error	60.00	5	12.00		

Lack of Fit Tests: Want the selected model to have insignificant lack-of-fit.

Table 4. 18 Model Summary Statistics.

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS
Linear	471.14	0.0234	-0.0813	-0.2631	8.038E+006
2FI	498.60	0.0234	-0.2110	-0.6992	1.081E+007
Quadratic	3.67	1.0000	0.9999	0.9999	679.58 Suggested
Cubic	3.56	1.0000	0.9999	0.9999	937.85 Aliased

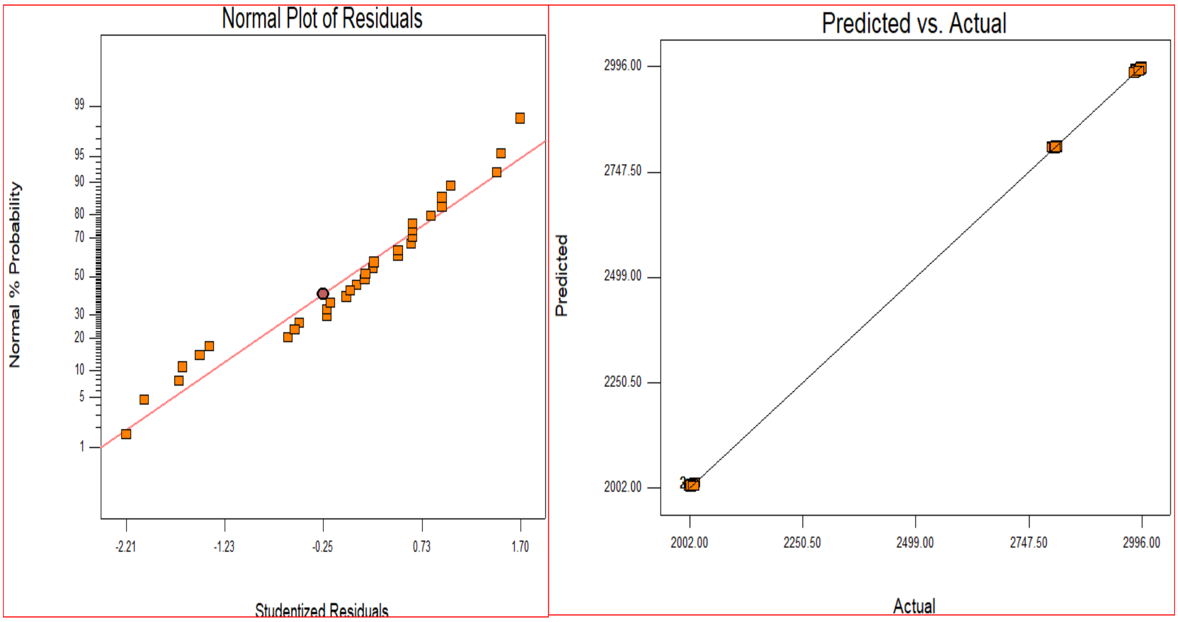


Figure 4. 8 the normal probability and interaction graph with level and time for the conductivity

The probability curve of the data were efficient the first factors were above 95%.were affected the process of the adsorption the first factor were time. From the interaction graph time and level with the conductivity analysis was turning point of the 200or from the UASB and the time around 60hr with interaction the adsorption.

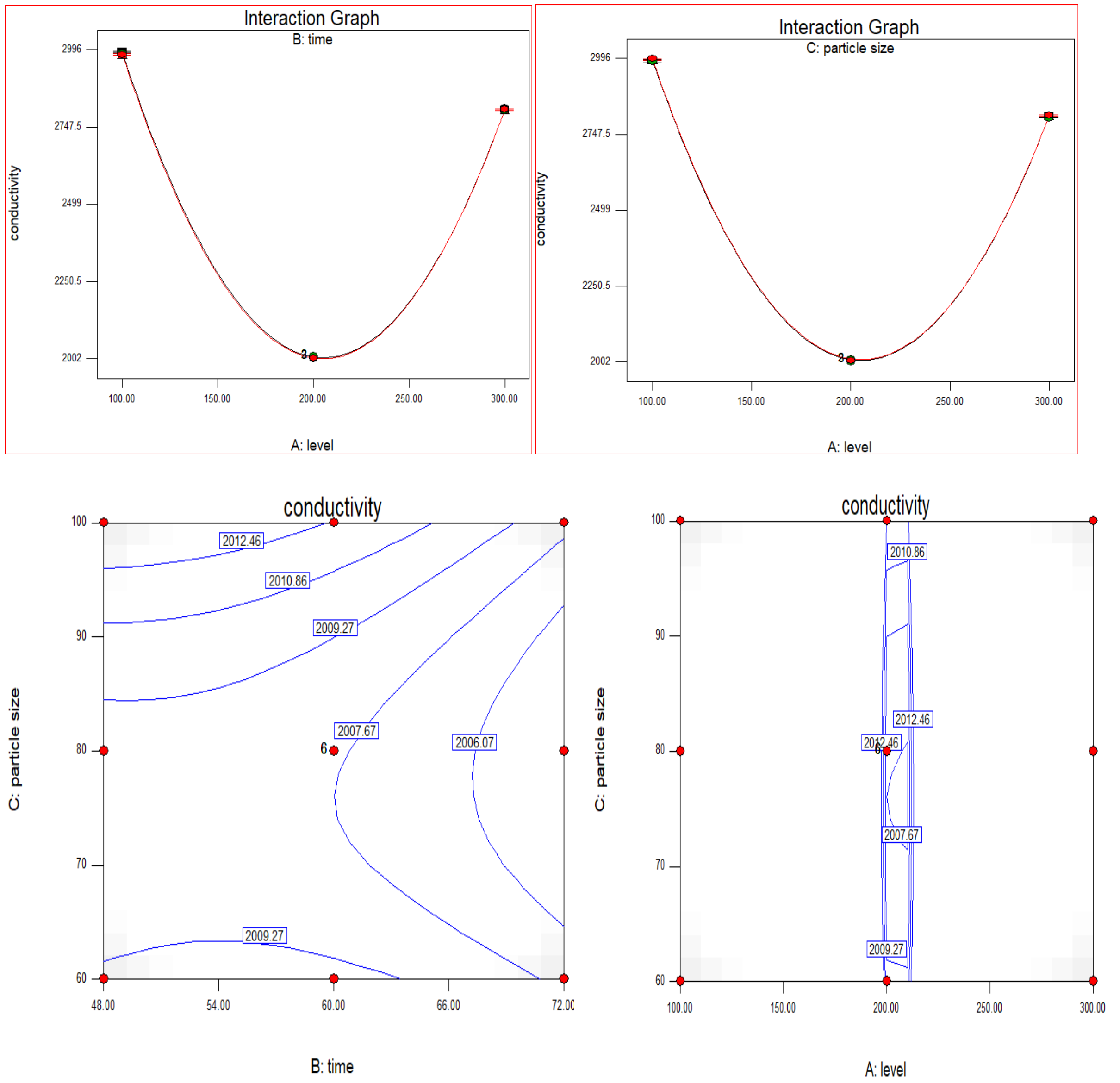


Figure 4. 9 The counter curve of the interaction variables on the response of conductivity

On the counter graph the conductivity measured data were given the information about the time, particle size and sample point level were with optimum condition the conductivity also optimum, for the adsorption process also conductivity measured data also in good manner.

On the three D graph all process variables factors for adsopition was displed with numerically data investigated the time was optimum for other process variables such condition with three D graph given real information the maxium adsortion was performed with time 60hr, particle size 63micro m. and level or sample point from200 or UASB. In sample collection the UASB were given some information the digestion and other PH,acid value and conductivity,nitrates and some volatile fatty acids were highly observed due to the reason of the availbel of micro organism and the ionazation procsss with adsorpent.

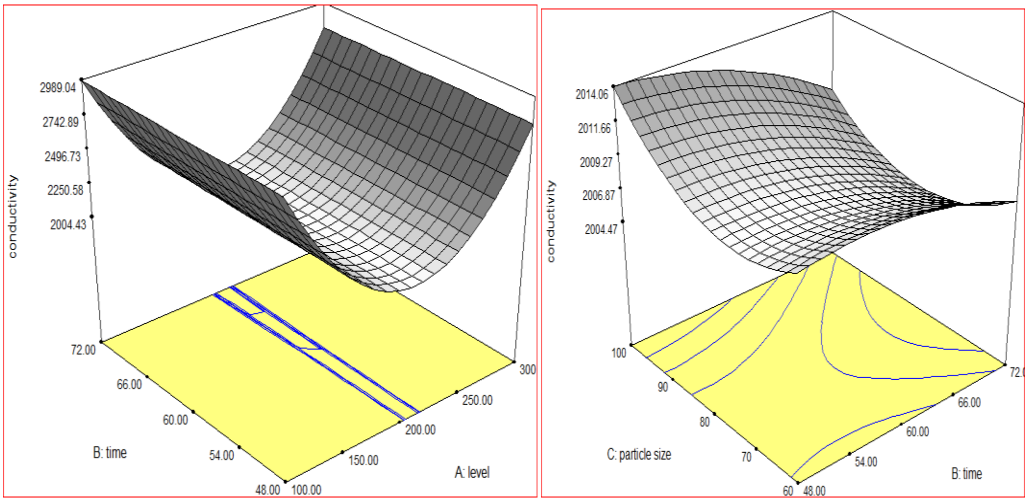


Figure 4. 10 the three D curve of the conductivity analysis.

4.6.4 model adequecy check for adsorbestion process

COD =+163.35+13.24* A -30.44* B +3.03* C +57.31* A^2 -51.20* B^2 -28.53* C^2 +25.67* A * B +14.96* A * C +7.62* B * C

COD =-701.55806 -4.04195* level +33.31384* time +8.16214* particle size +5.73065E-003 * level2-0.35557 * time2 -0.071317 * particle size2 +0.021396 * level * time +7.47917E-003 * level * particle size+0.031736 * time * particle size.

BOD =+168.06 +24.43 * A -41.71 * B +24.16* C +95.52* A2 -54.89 * B2 -56.32 * C2 +27.50 * A * B +23.46 * A * C-9.49* B * C

BOD = -1387.50876 -5.88981* level +40.84994 * time +23.76400 * particle size +9.55230E-003 * level2 -0.38119 * time2 -0.14080* particle size2 +0.022913* level * time +0.011730 * level * particle size -0.039559* time * particle size

conductivity =+2007.81 -90.89 * A -2.06 * B+1.33 * C +887.89 * A2 -1.27 * B2 +3.23 * C2

+1.67 * A * B -0.83 * A * C -0.92 * B * C.

4.6.5Optimuazaton of the Adsorbtion Process Variables

Table 4. 19 the optimaztion of the adsorption process

Factor	Name	Level	Low Level	High Level
A	Level	200.00	100.00	300.00
B	Time	60.00	48.00	72.00
C	particle size	80.00	63	100.00

	Prediction	SE Mean	95% CI low	95% CI high	SE Pred	95% PI low	95% PI high
COD	163.352	23.09	115.47	211.23	72.48	13.04	313.67
BOD	168.062	35.64	94.15	241.98	111.90	-64.01	400.13
Conductivity	2007.81	1.23	2005.25	2010.36	3.87	1999.79	2015.83

Number	level*	time*	particle size*	Desirability
1	269.08	56.22	70.664	1.000Selected
2	164.66	70.57	76.304	1.000
3	201.34	68.13	62.556	1.000
4	279.60	68.32	68.368	1.000
5	163.22	58.80	62.508	1.000
6	209.18	60.93	80.64	1.000
7	173.70	48.09	75.448	1.000
8	154.80	55.32	69.16	1.000
9	221.88	69.63	82.008	1.000
10	111.62	62.03	64.528	1.000

from the above optimuazed data the optimum model was the sample collection from the 200m or the uasb tank with the time duration of the adsorpiton 60hr and the particle size 63 so the three cod bod and the conductivity analysis was performed with the model. the integration of three factor affected process level 269.08,time56.22,particle size 70.664,and desirability was selected.so the adsoprtion prcoess was performed and the gc –ms and the ftir result were depending on the value of this optimum model process.

4.6.6 PH Value

The adsorption process with the addition of prepared adsorbent was tested by PH, the solution was taken from different waste after adsorbed condition level from 100,200,300m. The addition of adsorbent was involved after 48hr,60hr, and 72hr. PH measurement was taken from this different sample point from optimum point after adsorption process. The sample point PH value was, from100, 200,300was 11.25 7.9, 6.7.

4.6.7 Acid Value

The value was titrated with 0.1N NaOH with in the same sample amount after adsorption process was performed, 250 ml solution was taken from different level with different sample level with different time interval duration .the result were below in the table, the indication of experiment to know whether the acidity were available was color changed from colorless solution into rose pink color.

Table 4. 20 the interaction of the PH and acid value

Level (m)	Time	PH	0.1N NaOH	Acid value
100	48	10	200ml	5.2
100	60	10.4	250ml	5.7
100	72	9.49	250ml	5.7
200	48	8.5	245	5.5
200	60	7.9	258	5.8
200	72	8.2	256	5.6
300	48	6.7	287	6.3
300	60	6.7	303	6.8
300	72	6.8	298	6.7

This indicates the value of PH and acid value was to become decreased when the level of beer waste water be increment. It indicates that the clarity of waste become with the addition of the adsorbent was good

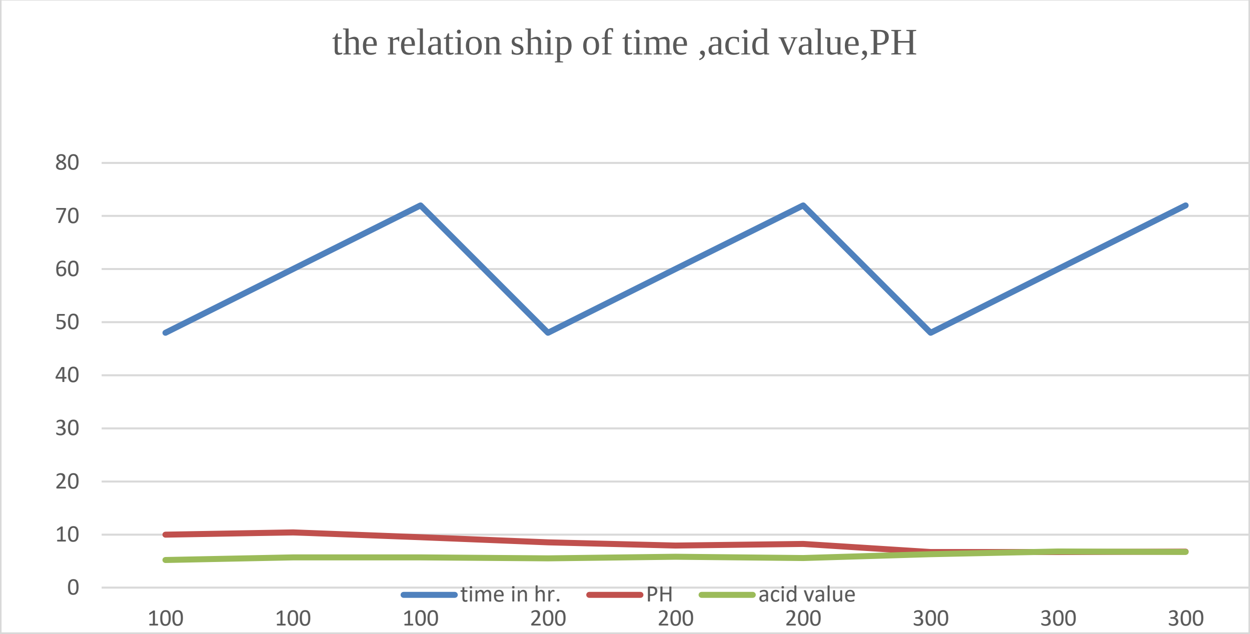


Figure 4. 11 the interaction curve of the contact time, PH and acid value

5. Conclusion

The effluents from habesha brewery industry contain extremely high levels of SS, COD, and BOD5, nitrateand phosphate and volatile fatty acids. These values are mostly characterized by the company limits prescribed by the Ethiopian environmental authority. However, their rich organic materials open the way fortheir biological treatment. As such, the purification performance of input discharge in the treatment tank, UASB sewerage tank, for thetreatment of waste effluents showed good removal efficiency of $PO4^{-3}$, SS, COD, BOD5 and nitrate volatile fatty acids. However, thetreatment is more efficient with the addition of the adsorbent than with other mechanismAcombination of both aerobic digestion system could make the treatment but from the research more effective with a view to enhance the value of this effluent in the treatment plant especially in UASB treatment process. Waste management in breweries remains a critical and practical problem. Brewing industries exhibit a wide range ofproduction capacities, which induces a strong difference in waste management. All breweries try to keep disposal coststringent. Spent grains, Kiselguhr sludge, yeast surplus and waste labels represent the most important wastes. The most common disposal alternative is to sell these wastes as feed for livestock. However, other technical alternative such as biofuel production via anaerobic biological approach appear to be promising due to the sustainability advantages of the final products (bio-methane and potential fertilizer).All malt waste anaerobic biodegradation options used in this study has a good and high biogas production. In terms of improvinganaerobic biological degradation of raw organic matter available, malt waste provided the best results low whilst the legislation concerning waste disposal is becoming more and more effective. The adsorbent substances was also good for the improvement of the waste water from Beer Company in the reduction or minimization of the waste ingredient by the ionization process. For the time of the 48, 60, 72 hr. with level of waste treatment tank of the three level such level IP (100m), UASB(200m), FE(300m),with the spent kiselguhr production of the adsorbent. The spent kiselguhr was one criteria for the purification of the waste water. The adsorbent was prepared with best particle size of the adsorbent. The production of the adsorbent from waste spent kiselguhr also had the best practical procedure with the lab of the habesha brewery share company. Generally from the result of the adsorption process of the waste water was performed with expected result of reduction of the ingredient. The optimum adsorbent particle size also investigated with the proportion concentration of the waste from the different treatment tank.

The time, conductivity, BOD, COD, PH, particle size the level of the waste sample took also factors. For the involved of the waste clarifying adsorbed process.

6. Recommendations

The adsorption process of beer waste in the world was performed with the additive of the chemicals in the treatment process for neutralization process, in our country there are a lot of industries, company's, commercial sectors,hospitals, governmental organization, municipalities, etc. the main waste is from different areas without treatment plant or waste disposal settlement place. This is the general problem in our country. Now a days the waste simply through into the river, or other water body surfaces areas was adopted. From the understanding of this the waste treatment methodology will develop for the reduction.

The industries by them self-have not good treatment technology's, due to the awareness of the human healthiness and or other additional cost varieties. The treatment of the waste is not only for company or other responsiveness coherence simply every society's duty in order to get good environmental healthiness or friend ship weather condition for our healthy. The main output from this research was the spent kiselguhr from Beer Company changed for the adsorbent of the waste of beer, it is cost free, chemical free, environmental friend ship and easily accessed waste deduction by the adsorption process.

Finally from my understanding view from I got the result the following points will more advantageous for all the societies or companies that apply for the out effluent waste.

The beer company for the future will be the spent kiselguhr is one of the best treatment additives for the different tanks with the help of the size and the time contact. The other company will also can use this adsorbent easily by taking the spent kiselguhr from the beer companies. The performances of the adsorbent were good adsorbed additives especially in the beer factories in the UASB treatment tanks highly remove some volatile fatty acids, nitrates, phosphates, COD and BOD, with its concentration of waste it's also optimize the bacteria aerobic digestion efficiencies. For the universities this adsorbent also can use for their treatment plant for the reduction of some ionized substances and also for Oder removal in toilet place.

For all the societies there must be aware of how to reduce or minimize wastes for removing of air, liquid and environmental pollution.From this research the other researcher will be used as reference point for further investigation of process with production of the adsorbent.

This adsorbent will be used for enterprise sector by packing the powder of the adsorbent for the waste and odor minimization process for homemade liquid waste treatment process.

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8. Appendices

Appendix A: ANOVA case statistics of the COD, BOD and conductivity

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 225.462 indicates an adequate signal. This model can be used to navigate the design space.

Table 8. 1 Diagnostics Case Statistics of BOD

Standard ord	Actual value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier T	Run Order
1	170.00	186.95	-16.95	0.497	-0.225	0.005	-0.220	28
2	172.00	64.90	107.10	0.340	1.242	0.079	1.259	19
3	175.00	133.89	41.11	0.497	0.547	0.030	0.538	7
4	169.00	182.13	-13.13	0.340	-0.152	0.001	-0.149	24
5	10.06	87.58	-77.52	0.211	-0.823	0.018	-0.817	22
6	12.04	184.07	-172.03	0.340	-1.996	0.205	-2.155	20
7	11.20	67.53	-56.33	0.497	-0.749	0.056	-0.741	13
8	10.18	0.47	9.71	0.340	0.113	0.001	0.110	27
9	302.50	124.46	178.04	0.497	2.367	0.554	2.679	25
10	301.40	253.47	47.93	0.340	0.556	0.016	0.547	23
11	10.10	154.88	-144.78	0.211	-1.537	0.063	-1.589	31
12	302.00	247.33	54.67	0.340	0.634	0.021	0.625	14
13	301.20	239.16	62.04	0.211	0.659	0.012	0.650	10
14	10.09	168.06	-157.97	0.113	-1.581	0.032	-1.641	3
15	170.60	288.01	-117.41	0.211	-1.247	0.042	-1.263	17

16	171.70	115.06	56.64	0.340	0.657	0.022	0.648	21
17	10.07	71.46	-61.39	0.211	-0.652	0.011	-0.643	4
18	181.20	218.91	-37.71	0.340	-0.437	0.010	-0.429	8
19	180.50	207.35	-26.85	0.497	-0.357	0.013	-0.350	12
20	12.00	132.21	-120.21	0.340	-1.395	0.100	-1.427	18
21	306.10	248.13	57.97	0.497	0.771	0.059	0.763	11
22	170.10	183.54	-13.44	0.340	-0.156	0.001	-0.152	30
23	301.70	135.91	165.79	0.211	1.760	0.083	1.855	2
24	305.00	279.32	25.68	0.340	0.298	0.005	0.292	6
25	10.05	49.96	-39.91	0.497	-0.531	0.028	-0.522	9
26	11.10	29.82	-18.72	0.340	-0.217	0.002	-0.212	5
27	170.40	200.72	-30.32	0.497	-0.403	0.016	-0.395	26
28	301.90	168.06	133.84	0.113	1.340	0.023	1.366	32
29	171.50	168.06	3.44	0.113	0.034	0.000	0.034	15
30	302.70	168.06	134.64	0.113	1.348	0.023	1.375	1
31	181.30	168.06	13.24	0.113	0.132	0.000	0.130	29
32	180.90	168.06	12.84	0.113	-0.225	0.000	0.126	16

Table 8. 2 COD ANOVA analysis

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1209.53	1	11.15	1186.41	1232.65	
A-level	-493.56	1	7.82	-509.77	477.34	1

B-time	-1.11	1	7.82	-17.33	15.11	1
C-particle size	-8.78	1	7.82	-24.99	7.44	1
A^2	319.30	1	12.40	293.57	345.02	1
B^2	-17.37	1	12.40	-43.09	8.35	1
C^2	11.63	1	12.40	-14.09	37.3	1
AB	-0.42	1	9.58	-20.28	19.4	1
AC	-18.92	1	9.58	-38.78	0.94	1
BC	1.83	1	9.58	-18.03	21.6	1

Table 8. 3 Conductivity

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	2007.81	1	1.23	2005.25	2010.36	1
A-level	-90.89	1	0.86	-92.68	-89.10	1
B-time	-2.06	1	0.86	-3.85	-0.26	1
C-particle size	1.33	1	0.86	-0.46	3.13	1
A^2	887.89	1	1.37	885.05	890.73	1
B^2	-1.27	1	1.37	-4.12	1.57	1
C^2	3.23	1	1.37	0.38	6.07	1
AB	1.67	1	1.06	-0.53	3.86	1
AC	-0.83	1	1.06	-3.03	1.36	1
BC	-0.92	1	1.06	-3.11	1.28	1

Optimization model of the adsorption process

Factor	Name	Level	Low Level	High Level
A	Level	200.00	100.00	300.00
B	Time	60.00	48.00	72.00
C	particle size	80.00	63	100.00

	Prediction	SE Mean	95% CI low	95% CI high	SE Pred	95% PI low	95% PI high
COD	163.352	23.09	115.47	211.23	72.48	13.04	313.67
BOD	168.062	35.64	94.15	241.98	111.90	-64.01	400.13
Conductivity	2007.81	1.23	2005.25	2010.36	3.87	1999.79	2015.83

Number	level*	time*	particle size*	Desirability
1	269.08	56.22	70.664	1.000Selected
2	164.66	70.57	76.304	1.000
3	201.34	68.13	62.556	1.000
4	279.60	68.32	68.368	1.000
5	163.22	58.80	62.508	1.000
6	209.18	60.93	80.64	1.000
7	173.70	48.09	75.448	1.000
8	154.80	55.32	69.16	1.000

9	221.88	69.63	82.008	1.000
10	111.62	62.03	64.528	1.000

Appendix B: Infrared Spectroscopy Correlation Table

Simplified Infrared Correlation Chart			
	Type of Vibration	Frequency (cm^{-1})	Intensity
C-H	Alkanes (stretch)	3000-2850 1450 and 1375	s
	-CH3 (bend)	1465 3100-3000	m
	-CH2- (bend)	1000-650 3150-3050	m
	Alkenes (stretch)	900-690	m
	(out-of-plane bend)		s
	Aromatics (stretch)		s
	(out-of-plane bend)		s
	Alkyne (stretch)	~3300	s
	Aldehyde	2900-2800 2800-2700	w
			w
C-C	Alkane not interpretatively useful		
C=C	Alkene	1680-1600	M
	Aromatic	1600 and 1475	-m

C≡C	Alkyne	2250-2100	-m
C=O	Aldehyde	1740-1720	- s
	Ketone	1725-1705	s
	Carboxylic Acid	1725-1700	s
	Ester	1750-1730	s
	Amide	1670-1640	s
	Anhydride	1810 and 1760	s
	Acid Chloride	1800	s
C-O	Alcohols, Ethers, Esters, Carboxylic Acids, Anhydrides	1300-1000	s
O-H	Alcohols, Phenols		
	Free	3650-3600	m
	H-bonded	3500-3200	m
	Carboxylic Acids	3400-2400	m
N-H	Primary and Secondary Amines and Amides		
	(stretch)	3500-3100	m
	(bend)	1640-1550	M
C-N	Amines	1350-1000	m-
C=N	Imines and Oximes	1690-1640	-w
C≡N	Nitriles	2260-2240	ˉm
X=C=Y	Allenes, Ketenes, Isocyanates, Isothiocyanates	2270-1950	M
N=O	Nitro (R-NO2)	1550 and 1350	ˉ s

S-H	Mercaptans	2550	w
S=O	Sulfoxides	1050	s
	Sulfones, Sulfonyl Chlorides, Sulfates, Sulfonamides	1375-1300 and 1200-1140	S

Formulas and procedures

Moisture content = (the sample weight in kg/total weight of sample in kg)*100%

Ash %=(D/B)*100

Acid value = V*N*56.1/W……………………….eqn.3.3

Where V volume of expressed in milliliter of 0.1N solution of ethanoic, NaOH. N, concentration of the NaOH. W, weight of the solution.

Total solids

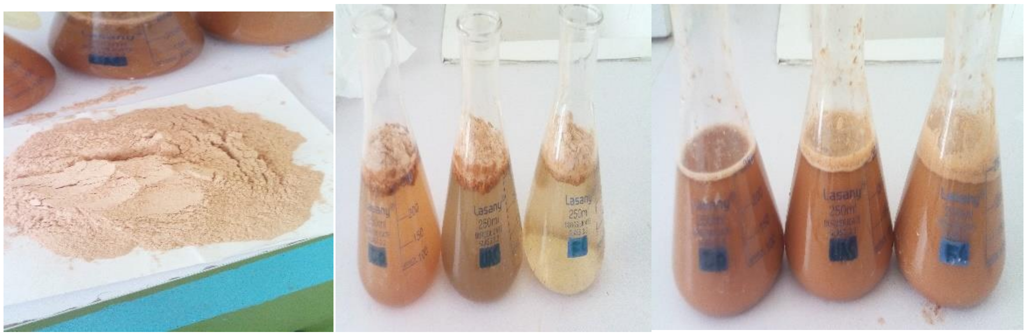
TS= TSS+TDS, where the TS total solids, TSS, total suspended solids, TDS total dissolved solids.

Appendix C: labartory result and final output

Picture 1.The raw sample of the waste water and spent kiselghur with the measuring of the moisture content

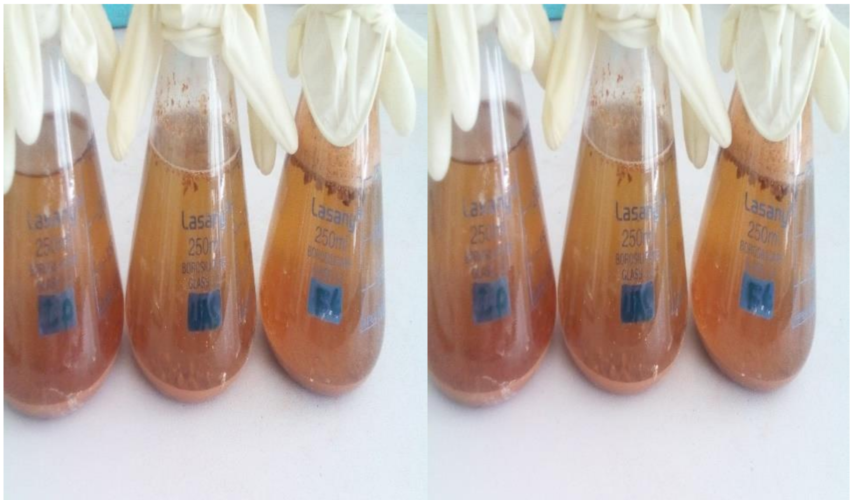
Picture 2 Measuring of the moisture content of the spent kiselghur after perpartion of the adsorbent

Picture 3 Perpartion of the adsorbent for crashing by different size



Picture 4 The adsorbent and the waste water with out stirring simply manully mixed solution

Picture 5 After using the sitrrer the sample solution



Picture 6 The sample solution after 48, 60 and 72 hr time interval duration

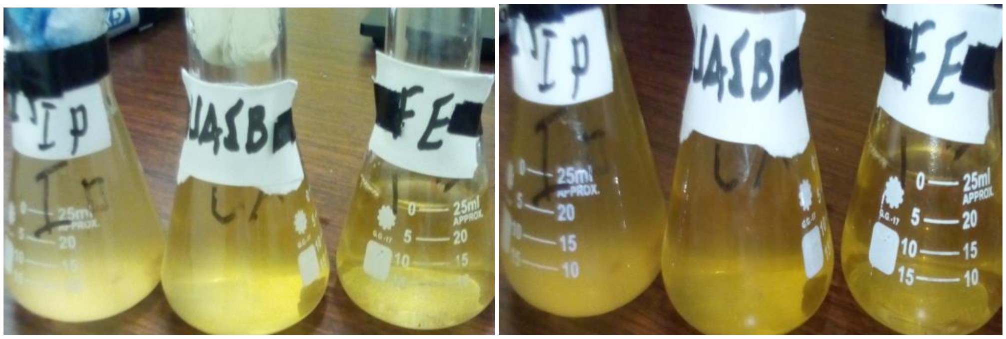
Picture 7 The final experiment sample after extra reaptation process with 60hr, and 72hr.time investigation and particle size of 63 micro meter.

The UASB PH result at atm. temprature with 63 p.size,48,60,72,hr respectively with order

The IP PH result of maximum or from purified final result at atm. temperature with P.size.63,48,60,72hr

Picture 8 The FE of the PH result at atmospheric temprature with p.size 63 micro.m.and at 60,72hr

Picture 9 Total dissolved solids measuring process



Picture 10 The final result of purified waste water from different tank

Picture 11 The final experiment of the phosphate, nitrate, COD, BOD in the habesha berewry factory

Appendix D : Measuring device and insturments

OVEN

Muffle furnace for ash content measurement

FTIR Analysis of sample measurement