Addis Ababa University

Addis Ababa Institute of Technology

School of Chemical and Bio-Engineering

Adsorption-Anaerobic Digestion coupling process for molasses vinasse Treating

By

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A Thesis submitted to Addis Ababa Institute of Technology, In Partial Fulfillment of the Requirements for the Degree of Master of Science in chemical Engineering (Process Engineering)

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This is to certify that the thesis prepared by Mohammed Seid, entitled: **Adsorption-Anaerobic Digestion coupling process for molasses vinasse Treating,** and submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in process Engineering complies with the regulation of University and meets the accepted standards with respect to originality and quality.

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DECLARATION

I, Mohammed Seid, hereby declare that the work on which this thesis is based on and entitled: **Adsorption-Anaerobic Digestion coupling process for molasses vinasse Treating**, is my original work not submitted for another degree in this or any other university, and all resources of material used for this thesis had been duly acknowledged/referred.

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ABSTRACT

The production of ethanol from biomass results in the co-current production of acidic material known as distillery spent wash or vinasse. It is generated at a rate of 10 to 15 times greater than the ethanol itself, and is characterized by a high dissolved organic matter content. Anaerobic digestion is the most effective methods for the treatment of such type of wastewater. In this work, a combined adsorption–anaerobic digestion treatment of distillery wastewater was studied in order to develop an effective procedure for increasing the anaerobic biodegradability of vinasse to reduce its environmental impact. The adsorption stage with banana peel as a pretreatment was evaluated for removal of phenolic compound. The removal of phenolic compound with this biosorbent was carried out using Box-Behnken experimental design taking 3 factors, adsorbent dose, contact time, and particle size. The maximum phenol removal recorded was 76.425% at the optimum condition (adsorbent dose of 20 g/L, contact time of 129.98 min, and particle size of 0.53 mm). Removals of 22% in chemical oxygen demand (COD) was obtained in this stage. Among the adsorption isotherm models analyzed, the Langmuir model fitted best to the experimental data with maximum adsorption capacity of 4.12 mg/g, and also the adsorption mechanism follows pseudo-second order model. The pretreated vinasse was undergone to an anaerobic digestion process in the second stage under mesophilic condition. After anaerobic digestion, a global removal of 84% in COD, and over 95% in phenols content were obtained. It was shown that, a combination of treatment method (i.e. banana peel biosorption and anaerobic digestion) is a promising option for simultaneous removal of phenol and COD from molasses vinasse under the stated conditions.

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ACRONYMS

AD……………………………Anaerobic digestion

ANOVA………………………Analysis of variance

ASTM………………………...American society for testing material

APHA………………………...American public health Association

BBD………………………… Box-Behnken Design

BDS…………………………..Barium Diphenyl amine Sulphonate

BET…………………………...Brunauer, Emmet, and Teller

BOD…………..………………Biochemical Oxygen Demand

COD…………….……………Chemical Oxygen Demand

CSTR…………….…………...Continuous Stirred Tank Reactor

DDG…………………………..Dried Distiller’s Grain

EPA…………………………...Environmental Protection Agency

FAS……………….………...…Ferrous Ammonium Sulphate

FTIR……………………..…... Fourier Transform Infrared Spectroscopy

HABR…………………………Hybrid Anaerobic Baffle Reactor

HRT…………………………...Hydraulic Retention Time

n.d……………………………..not determined

OLR…………………..……... Organic Loading Rate

RSM……………………….…. Response Surface Method

TS………………………….……. Total Solid

USAB…………………………Up-flow Anaerobic Sludge Blanket

VFA…………………………...Volatile Fatty Acid

VS…………………………...…Volatile Solid

1. Introduction

Many countries throughout the world are seriously looking for ways to reduce their petroleum imports because of recent spirals in petroleum prices. They are looking toward alternative sources of energy that can be produced locally. The recent interest in the usage of biofuels over fossil fuels has increased the demand for bioethanol. Globally, ethanol distillery industries are growing rapidly to satisfy the increasing demand for sustainable and renewable biofuel(Nure et al, 2017). It is expected that the global demand for ethanol will rise beyond 120,000 million liters in 2020. A big portion of bioethanol is produced from molasses substrate, which is a by-product of sugar processing from sugarcane and sugar beet(Arimi & Zhang, 2015).

The production of ethanol from biomass, whether from sugar crops (sugar beets, sugar cane, molasses, etc.), starch crops (corn, wheat, cassava, etc.), dairy products (whey) or cellulosic materials (crop residues, herbaceous energy crops bagasse, wood, or municipal solid waste), results in the co-current production of stillage or distillery spent wash or vinasse, which exhibits a considerable pollution potential(Wilkie et al., 2000). Stillage is a liquid residue produced in the distillation process. It is an acidic material which produced at a rate 10 to 15 times greater than the ethanol itself, and its disposal is a major environmental problem worldwide(Pramanik et al, 2012). This effluent presents a high dissolved organic matter content, as well as a considerable quantity of inorganic salts composed by chlorides, sulfates, phosphates, calcium, magnesium, and potassium. Vinasse is potentially toxic because of its bio-recalcitrant substance contents, such as phenolic compounds, and pigments like melanoidins, which can inhibit the activity of microorganisms present in water sources. It is not surprising that the utilization of the stillage raises serious problems, and that many attempts have been made all over the world to solve them. Therefore, an investigation is needed to establish which treatment methods are best suited to reach specific effluent quality goals.

Complete cleansing of wastewater pollutants will not be feasible with the adoption of a single treatment process. Combinations of chemical and biological treatments are often the only way to optimize the overall process(Sigge et al, 2007). There are a number of available methods for the exploitation and purification of vinasse, particularly biological methods (both aerobic and anaerobic). Aerobic biological wastewater treatment processes such as activated sludge have been dogged by operational problems when treating high organic load wastewaters such as distillery wastewater. In the last few years the search for sustainable treatment systems capable of minimizing energy consumption has encouraged the use of anaerobic biological wastewater treatment systems. Anaerobic digestion features some advantages that make it particularly suitable for processing this type of waste(Garcia-Garcia et al., 2011). It is widely known that, due to the high organic content of vinasse, its anaerobic processing to obtain methane is very interesting from an economical point of view. Energy from methane combustion could be an additional source of income for the distillery(Aquino & Pires, 2016).

The technology of production of biogas is very important as it may combine the treatment of various organic wastes with the generation of energy carriers, methane. Anaerobic digestion (AD) is a method of organic waste treatment wherein wastes are decomposed in a controlled, oxygen-free environment for the purpose of pollution reduction and the generation of biogas, a renewable natural gas comprised primarily of methane and carbon dioxide. Anaerobic digestion technology is quite versatile technology, in that it can be applied in many different situations and is capable of handling many different forms and amounts of organic waste. Anaerobic digestion not only serves to improve sanitation, but also soils through the application of the treated liquid effluent (a viable replacement for chemically engineered fertilizers), and the production of renewable energy in the form of clean-burning biogas(Gamble et al., 2015). Moreover, low production of stabilized excess sludge, low nutrient requirement, no energy input required for operation, production of methane as a potential energy source and therefore cost saving, etc. are advantages confirming the choice of anaerobic digestion for distillery wastewater treatment(Lorraine X. M., 2006). However, research indicates that the presence of certain recalcitrant and inhibitory substances in the vinasse severely hinders the anaerobic process in terms of its kinetics, COD removal and methane production. These substances are mainly phenolic compounds. In addition, heavy metals, melanoidins, glycerol, antibiotics and other organic xenobiotic pollutants are also present(Aquino & Pires, 2016). Thus, Pre-treatment of Phenol is required before bio-degradation of the desired organic compound. Most of the time, a physicochemical step can be applied as a pre-treatment process.

Polyphenol concentrations in some distillery wastewaters vary considerably and can range from 29 - 474 mg/l(Lorraine X. M., 2006). Polyphenols are responsible for strong inhibitory effects on microbial activity; therefore, they must be removed during wastewater treatment as they pose environment and public health risks. Phenol is an aromatic compound that is commonly found in the industrial wastewater from the manufacturing of synthetic chemicals, pesticides, coal conversion, pulp-paper, oil-refining, distilleries, etc. As a toxic and potentially carcinogenic chemical, the release of phenol into the environment is of great concern(Fang et al, 2006).

The most common methods used for removal of phenol from industrial effluents include stripping, solvent extraction, oxidation, ion exchange, biodegradation and adsorption methods(Hegazy, 2014). Out of all these treatment methods, adsorption process is recognized as the most efficient, promising and widely used fundamental approach in wastewater treatment processes, mainly hinging on its simplicity, economically viable, technically feasible and socially acceptable(Hegazy, 2014; and Bello et al, 2013).

Adsorption is a process in which a substance (adsorbate), in gas or liquid phase, accumulates on a solid surface (adsorbent). It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). Adsorption processes using activated carbons are widely used to remove color and other pollutants from wastewaters but the high cost of activated carbon makes its use limited. Recently scientists are giving considerable attention on the use of biological-based materials and their by-products as the biosorbent for the removal of pollutants from different wastewaters because of presence of carboxyl, hydroxyl and amino groups over their surfaces. These groups are responsible for the biosorption process. Biological-based materials such as agricultural-based biomasses are cheap and easily obtainable in considerably substantial quantities(Bhatti et al, 2015).

Many sorbents based on low cost agricultural by-products can be used for phenolic compound sorption from wastewater. The banana peels are the most popular adsorbent because of its availability and simple processing and satisfactory results. Banana peels can remove wide variety of contaminants from waste water like oil spills, biological waste, carcinogenic elements, heavy metals and various dyes in water from textile and other sources(Khan et al, 2017).

The aim of this study was to research the performance of the coupling between the adsorption and the anaerobic biodegradation of vinasse to reduce its environmental impact, in which the effect of banana peels biosorption on Distillery Wastewater to remove phenolic compound was investigated firstly by monitoring contact time, dosage and particle size and, secondly, by investigating the effect of biosorption on the biodegradability of the wastewater.

1.1. Statement of Problem

Distillery industries are one of the largest consumer of water which ends up into the waste stream. Effective handling and disposal of the generated effluent is a major concern. In many developing countries, most of distillery industries discharge their wastewater without adequate treatment, due to the lack of know-how and financial support and also due to a lack of incentives to produce bioenergy from them. This wastes may be utilized in the production of energy through anaerobic digestion. Vinasse anaerobic treatment has been highly used in major ethanol producing countries such as Brazil and India where ethanol is produced from sugar cane molasses. But, currently in Ethiopia only one distillery, Balezaf alcohol and liquor factory, is engaged in anaerobic digestion of waste water with biogas being produced and the other are used some of their wastewater for the production of bio-compost by combining it with filter cake from the clarifying unit. They discharge their surplus wastewater without treating to near around water stream. Effort should be made towards providing wastewater treatment option for these industries to allow environmentally friendly disposal of their waste water.

There are many proposals for physico-chemical and biological treatments for vinasse. Biological treatments are known to be effective methods for the treatment of different types of highly contaminated industrial wastewaters. These treatments can be classified into aerobic and anaerobic systems. Anaerobic systems provide a cheaper alternative which produce biogases such as hydrogen or methane; the latter can be used as fuel to generate the energy required for the industrial plant itself. The process produces little sludge, which facilitates its disposal.

On the other hand, vinasse is chemically very complex; it contains a host of phenolic compounds, some of which resist biodegradation, at concentrations high enough to delay anaerobic digestion. Phenolic content in vinasse bothers the methanogenic bacteria in the digester. Therefore, pretreatment to remove phenol must be done to get maximum degradation of COD. Thus, an effective pretreating method prior to anaerobic digestion is necessary.

Many pretreatment techniques such as ozonation, chemical oxidation, aerobic fermentation with fungi cell, electro-dissolution of iron and hetero-coagulation with $Ca(OH)_2$, etc. have been used prior to anaerobic digestion to reduce the inhibitory effect of the process by different authors. In this work, a combined adsorption–anaerobic digestion treatment of distillery waste was studied in order to develop an effective procedure for increasing the anaerobic biodegradability of vinasse to reduce its environmental impact.

1.2. Objectives

1.2.1. General Objectives

The main objective of this work is to evaluate the removal efficiency of banana peel as low cost adsorbent for adsorption of phenolic compounds from ethanol distillery and to investigate the performance of the coupling between adsorption and biodegradation of vinasse.

1.2.2. Specific Objectives

- To prepare and characterize biosorbent from locally available material.
- To determine the biosorption potential of banana peel, through optimization of different operating parameters such as particle size, sorbent dosage and contact time for adsorption process using Box-Behnken Design.
- To characterize properties of adsorption effluents.
- To evaluate the performance of anaerobic digestion with pretreated vinasse at optimum parameter.
- To characterize the anaerobic digestion effluents.
- To determine the efficiency of combined technique, adsorption with banana peel followed by anaerobic digestion, for removal of both phenolic compounds and organic compounds.

1.3. Significance of the Study

Pollution control is one of the major issues that have given enormous attention today. Disposed untreated industrial wastes directly into natural ecosystem causes a serious environmental problem. Governmental and industrial sectors have been preparing and implementing environmental policies aimed at reducing the negative impacts on nature. In order to assure their sustainability, Industries have to utilize their available resource efficiently as well as focus on the reduction of effluent streams. Distilleries are among the industries having high polluting effect to the environment due to large organic load associated with their discharges. Disposing of this waste to water stream or releasing it to the environment contributes to pollution of the environment and violates the environmental regulation. So, an appropriate handling and disposal of these waste is highly recommended in ethanol plants now and in the future. One way of handling these wastes is to treat it as much as possible. If not, it has to convert it into a value added product like bio compost or biogas.

The purpose of this work is to investigate the efficiency of banana peel as a biosorbent for removal of phenolic compounds from distillery wastewater in order to increase the biodegradability of the residue. Moreover, it provides an appropriate alternative technology for treating distillery wastes.

2. Literature Review

2.1. Introduction

Environmental pollution due to development in modern industrial practice is one of the most significant problems of this century. Various pollutants produced in industries directly or indirectly are accumulating in our environment. These pollutants cause severe degradation in pedosphere, hydrosphere, atmosphere and thus causing a potential menace to the health and welfare of mankind.

Improper disposal methods and inadequate treatment of toxic constituents from different industries have led to the widespread contamination of surface and ground waters and have made the water resources unfit for usage. Hence there is an urgent need for waste water treatment. Environmental pollution by distillery industry has recently been the subject of much research. Distilleries are the major agro-based industries that have crucial effect on water body pollution and ecological concern.

Distilleries can be categorized among the most polluting industries generating large volume of wastewater, known as spent wash or vinasse. Distilleries generate wastewater at various stages in the manufacturing process as distillation, condenser cooling, fermenter cooling, fermentation and washing stages. The larger amount of the effluent is produced at distillation and condenser cooling stages(Murugesan et al, 2017).

2.2. Production of Ethyl Alcohol in Ethiopia

Ethiopia has high labor force, land potential and suitable climate for the development of bio-fuels. Bio-fuel can help the country to reduce imported fuel demand and meet the national consumption. The country has huge potential with respect to production of alcohol for beverage as well as bio fuel. Even, the country has the potential to supply to the international market at large scale and thereby strengthen its international finance and technical cooperation (kiros B., 2016). Production of ethyl alcohol as a beverage or drinking liquors in Ethiopia was started in the house hold level and practiced for long time in the high land parts of the country. This liquor is manufactured on fermenting maize, barley and other cereals(Mirkena, 2014). Ethanol production in Ethiopia is linked with sugar factories. Thus, the total identified irrigable land for sugarcane plantation in the country is about 700, 000 hectares, estimated at a potential to produce one billion liters of ethanol. At present, the main supply line in the domestic market is dominated by two sugar factories (Fincha and Metahara) with the combination of their annual production capacity at around 19.8 million liters (kiros B., 2016). Besides, there are small scale industries like Mollamaru, Balezaf and National Alcohol and liquor Factories that produces fermented liquor. In the near future, Wonji-Shoa and the other new factories under construction together are also expected to start producing ethanol and raise the total annual quantity significantly.

The alcohol industry uses molasses to produce ethanol, normally with the aid of fermentation yeasts. Once obtained, the alcohol must be removed from the fermentation broth, which is usually done by distillation. This operation leaves a residue known as vinasse, consisting of water and non-volatile components from the fermentation broth. Taking into account that alcoholic fermentation is usually facilitated by a low sugar concentration (12-20%), the amount of vinasse produced can be up to 10 times larger than that of ethanol(Garcia Garcia et al., 2011).

Disposing of this waste to water stream or releasing it to the environment contributes to serious pollution of the environment and violates the environmental regulation. If the Vinasse problem is not properly handled today and into the future, it could considerably compromise the supply of a clean burning Ethanol fuel and create one of the biggest and most damaging problems to our environment and to our way of life. So, an appropriate handling and disposal of these waste is highly recommended in ethanol plants now and in the future.

2.3. Characteristics of molasses Vinasse

Vinasse is classified as a class II residue, not inert but not dangerous. The chemical composition of sugarcane ethanol vinasse is variable and depends on the wine raw materials. The wine characteristics depend also on the method of preparation, alcoholic fermentation system, types of yeast, distillation and separation (Ahmed et al, 2013). Many researchers have studied the characteristics, in terms of its organic strength and nutrient content of vinasse generated from several types of ethanol-producing feed stocks.

Information available in the literature suggests that the major organic components of sugar cane vinasse are glycerol, lactic acid, ethanol, acetic acid, oxalate, malate and other alcoholic compounds, carbohydrates and a high content of phenols(Parnaudeau et al., 2008). Table 2.1 presents the characterization of vinasse from sugarcane juice and sugar cane molasses feed stocks.

Table 2.1 Characterizations of sugarcane molasses and sugar cane juice (Espana-Gamboa et al., 2011).

	Cane juice	Cane molasses
BOD, g/dm^3	16.7	39.5
COD, g/dm^3	30.4	84.9-95
Total N, mg/dm^3	102-628	153-1230
Total p, mg/dm^3	71-130	1-190
K, mg/dm^3	1733-1952	4893-11,000
Total S, mg/dm^3	1356	1500-3480
pH	4.04-4.6	4.46-4.8
Cu, mg/dm^3	4	0.27-1.71
Cd, mg/dm^3	n.a.	0.04-1.36
Pb, mg/dm^3	n.a	0.02-0.48
Fe, mg/dm^3	16	12.8-157.5
Phenol, mg/dm^3	n.a.	34

2.4. Environmental impact of vinasse

While the production and the characteristics of vinasse are highly variable and dependent on the raw material used and various aspects of the ethanol production process, thus the environmental impacts of vinasse are variable. Recalcitrant nature of vinasse is due to presence of the brown polymers, melanoidins, which are formed by Maillard amino carbonyl reaction. These compounds have antioxidant properties, which render them toxic to many microorganisms such as those typically present in wastewater treatment processes(Mohana et al., 2009). The defiance of melanoidins to degradation is apparent from the fact that these compounds escape various stages of wastewater treatment plants and finally enters into the environment.

Disposal of vinasse into the environment is hazardous and has high pollution potential. High COD, total nitrogen and total phosphate content of the effluent may result in eutrophication of natural water bodies(Kumar et al., 1997). Direct disposal of vinasse into the aquatic environments tend to increase the organic content of water and consequently causes the proliferation of bacteria that depleted the dissolved oxygen and water quality (Mohana et al., 2009). The highly colored components of the vinasse reduce sunlight penetration in rivers, lakes or lagoons which in turn decrease both photosynthetic activity and dissolved oxygen concentration affecting aquatic life(Kumar et al., 1997).

The effects of the application of this residue on the soil depend on various factors, such as the quantity applied in the soil, soil type and chemical composition, relief, crop type, and the economic conditions involved in the process. By promoting changes in the physical properties of the soil, vinasse can increase the infiltration capacity of the soil, contaminating the groundwater, reducing it, and increasing drainage with possible contamination of surface waters(Christofoletti et al., 2013).

2.5. Vinasse treating technology

The world is now producing a huge amount of ethanol (ethyl alcohol) through the fermentation of agricultural materials or molasses from sugar industry followed by separation of the formed ethanol by distillation process. The distillation process produces highly polluting residue called vinasse or stillage. Vinasse, a residual substance left after sugarcane alcohol distillation, represents a major environmental problem for the ethanol industry. It is characterized by its dark brown color, high temperature, low pH, and high percentage of dissolved organic and inorganic matter. It also contains nearly 2% of the dark brown recalcitrant pigment called melanoidins which imparts dark brown color to the effluent(Kaushik, 2015). Different ways of utilization treatment and final disposal of vinasse have been developed to avoid its negative impacts on the environments. Research has demonstrated that vinasse disposal in river basins alone isn’t a convenient disposal solution. Due to its high BOD, this material can cause damage to aquatic life, especially when dumped in large volumes in rivers, streams, and landfills (Ahmed et al, 2013).

Various physical, chemical, and alternate treatment methods have been adopted for the removal of color from this wastewater. But these methods only change the form of contaminants rather than degrading them completely(Kaushik, 2015). A number of treatment methods such as reverse osmosis, trickling filter, industrial recycling, incineration, coagulation, evaporation, oxidation/reduction, activated sludge, aerobic and anaerobic treatment, etc. are utilized for vinasse treatment(Kuusisto, 2013). However, most of the existing technologies are often ineffective, uneconomical or very technically complicated and some methods have disadvantages of high reagent usage, high energy requirements and toxic secondary sludge production. The high bio-recalcitrance and toxicity of phenolic contaminants in the wastewater cause difficulties in biological treatment. While the chemical methods are quite disadvantageous in terms of their high operation cost and consumption of chemical agents as well as variations in color removal efficiency and high volume of solid waste produced(Ordoño and Rollon, 2012). A physicochemical step can be applied as pretreatment process when high concentration organic or toxic compounds are present. The combination of chemical and biological treatment is often the way to optimize the overall process of treating wastewaters(Ordoño and Rollon, 2012).

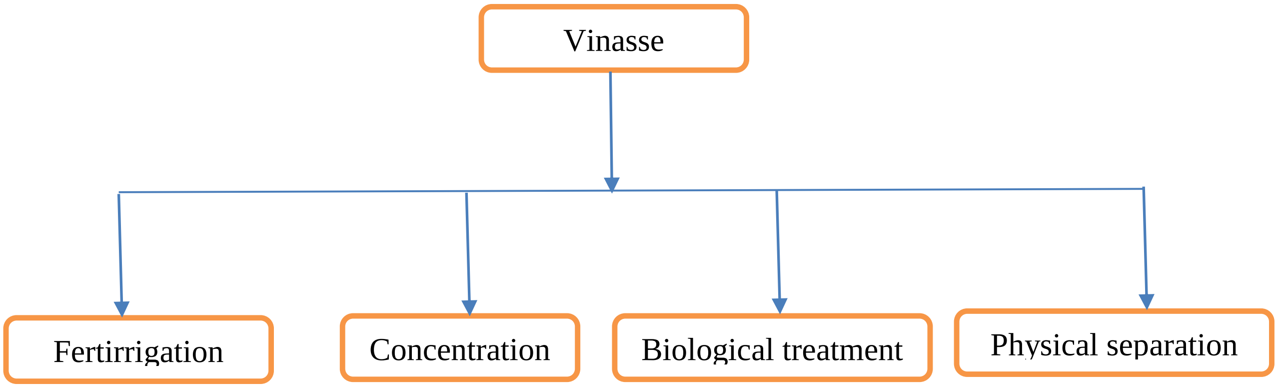


Fig 2.1: vinasse treatment methods

2.5.1. Fertirrigation

Among the alternatives for the use of vinasse developed around the world, fertirrigation is the most commonly used. However, according to the literature, the direct application of vinasse in the soil can cause salinization, leaching of metals present in the soil to groundwater, changes in soil quality due to unbalance of nutrients, mainly manganese(Christofoletti et al., 2013). The presence of high concentrations of phenolic compounds, salinity, phosphates, nitrates and ammonia in a vinasse can cause a toxic effect to groundwater and other fresh water bodies and eutrophication.

In Brazil, most of the vinasse that results from ethanol production is being used as fertilizer due to its high potassium content. The problem occurs when some soils don't respond positively to the application of this acid material. Sometimes part of the organic matter content in vinasse was likely used as an electron donor for heterotrophic denitrification in soil which causes dinitrogen monoxide (N_2O) emissions, an intermediary product of denitrification. In this case, the environmental impact would be more harmful because the global warming potential of N_2O is 296 times higher than that of carbon dioxide (CO_2)(Moraes et al., 2014).

2.5.2. Evaporation

Another possibility is to concentrate the vinasse, either by evaporation or through reverse osmosis. With evaporation, stillage is concentrated to a syrup in multi-effect evaporators with the co-production of evaporator condensate which is lower in organics (COD<10 g/l) and devoid inorganic salts. While evaporation serves to concentrate stillage components into smaller volume, the significant energy required to evaporate the stillage (equivalent to 10% of the energy content of ethanol) can negatively impact the energy balance of ethanol plant(Wilkie et al., 2000). The product obtained in this process is used in the production of livestock feed and to improve the quality of vinasse as fertilizer. It can also be burned in special boilers generating energy or decreasing the water use in the facility, and the condensate removed by evaporation can be treated and reused by the factory(Christofoletti et al., 2013)

2.5.3. Biological treatment

Biological methods produce relatively little amount of product after treatment by resolving a large amount of organism elements into carbon dioxide to be stabilized, i.e aerobic, or by removing organic matters contained in wastewater with the generation of methane gas, i.e anaerobic. In the biological treatment methods, pollutants in wastewater can be resolved, detoxified, and separated by using mainly microorganisms. Due to the relatively low cost and the variations of work progress, the biological methods have been most widely used all over the world. A number of fungi, bacteria, yeast, and algae have been reported to have effluent treatment capabilities by the process of absorption, adsorption, and enzymatic degradation techniques. Toxicity studies of the biologically treated wastewaters also suggested that the process is efficient enough to reduce the toxicity of the spent wash by around 80%. Hence, compared to the common and expensive physical or chemical ways for decolorization, an efficient bioremediation system has been found successful through biosorption and enzymatic ways of decolorization (Kaushik, 2015).

Aerobic biological wastewater treatment processes such as activated sludge have been dogged by operational problems when treating high organic load wastewaters such as distillery wastewater. In the last few years the search for sustainable treatment systems capable of minimizing energy consumption has encouraged the use of anaerobic biological wastewater treatment systems. Anaerobic digestion features some advantages that make it particularly suitable for processing this type of waste(Garcia-Garcia et al., 2011). Anaerobic digestion of waste can contribute positively to environmental management since it combines both waste removal and stabilization with net fuel (biogas) production. The anaerobic biodigestion treatment increase the fertilization potential of vinasse (phosphorus, potassium and nitrogen content), dramatic reducing the BOD, making safer the use of treated vinasse for field fertirrigation. The process also yields methane, a very convenient and eco-friendly fuel gas(Salomon et, 2015).

Iqbal syaichurrozi (2016), stated that biogas technology is the best choice to treat vinasse. COD content in vinasse will be converted into biogas. Some authors have studied the vinasse treatment through biogas technology. It is more effective to degrade organic materials than aerobic treatment.

Moraes et al., (2014), investigated that anaerobic digestion of vinasse followed by fertirrigation of biodigeted vinasse. They concluded that vinasse anaerobic digestion could potentially provide significant energy advantages that could even stimulate second-generation ethanol production. They also explain that fertirrigation with bio-digested vinasse could reduce environmental impacts due to the decrease of global warming potential impacts and pollutant loads, which were comparable (in terms of organic matter) to the populations of some cities for a single sugarcane processing plant. From a global economic perspective, sugarcane plants could also have higher profits with vinasse biodigestion and biogas use than with traditional fertirrigation.

Wilkie et al. (2000), advocated the advantages of the anaerobic digestion because of its effective reduction of the organic load and because it produces biogas. He concluded that the thermophilic anaerobic digestion of the vinasse could be achieved in smaller reactors than conventional aerobic treatment, because of higher loading rates.

2.5.4. Physical/mechanical separation

This option is widely used in the United States for the corn-based vinasse. The separated solids are dried and sold as animal feed, known as dried distillers' grains (DDG). However, this process is not feasible for sugar crops and cellulosic crops due to the high water content in the vinasse generated by these crops. Other types of treatment technologies may be applied, following the physical separation, such as evaporation and/or membrane separation, anaerobic digestion, and single cell protein production(Kuusisto, 2013).

2.5.5. Anaerobic digestion coupled with other treatment

Even though anaerobic digestion of vinasse is one of the promising vinasse treatment methods, the presence of Phenolic compounds causes inhibitory effects on anaerobic digestion processes and has an adverse environmental impact. An alternative for treating vinasse from distilleries by using an effective pretreating method prior to anaerobic digestion is necessary.

Phenols can exert negative effects on different biological processes. Because of this increased awareness and concern about environmental pollution, stringent national and international legislation has been set up, generating more efforts of research work in this area, especially in finding better and more efficient techniques to treat wastewater bearing these organic pollutants. Conventional methods for the removal of phenolic compounds from Wastewater can be divided into three main categories: biological, chemical and physical treatment. Among them, physical adsorption method is generally considered to be the best, effective, low cost and most frequently used method for the removal of phenolic compounds. Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications.

Paz Pino L. et al. (2014) studied that a novel treatment for vinasse using pretreatment stage of electro-dissolution of iron and hetero-coagulation with $Ca(OH)_2$. They were found that a promising result by using iron electro-dissolution and hetero-coagulation as a pretreatment of anaerobic digestion to remove phenolic compounds and to enhance the degradation of distillery vinasse. During the pretreatment they obtained that a decreasing of phenol content of 92%, the chemical oxygen demand decreased 52%, and the volatile fatty acids content increased 18%. Afterwards, the pretreated vinasse was subjected to anaerobic digestion and was reached a global diminution close to 93% in BOD5; 83% in COD and up to 99% in phenol content.

S. Aquino and E. C. Pires, (2015), assessed that the effects of prior ozone oxidative on the biodegradability of sugar cane vinasse, aiming at increasing the methane yield by anaerobic digestion of this effluent. Ozone dosage and vinasse pH are the two optimized parameter in these work. They have obtained an average of 13.6% increment in methane yield of pretreated vinasse. However, they concluded that ozonation of raw vinasse to increase the methane production in a subsequent anaerobic process is economically unfeasible, since the amount of electricity consumed in a full-scale ozonation plant would be almost 6 times higher than the energy recovered from the combustion of the additional methane produced.

Lekshmi S.R. (2013), studied the performance of Hybrid Anaerobic Baffle Reactor (HABR) for the treatment of distillery wastewater and explored the use of anaerobic digestion as complete solution to treat BOD and COD in the same reactor in conjunction with suitable oxidation technique, in which he obtained an overall COD removal efficiency of 92% at the end of the whole cycle of process.

2.6. Removing of phenol from wastewater by low cost and locally available material

Developing green and sustainable technology for the effluent treatment is very important research area in this era of industrial and social development. Many researchers have carried out the research in this field. One of the important pollutants from this point of view is phenol(Kulkarni, 2013). Phenols are among the most common water pollutants, and considered as major toxic pollutant, even at a concentration of as low as 0.1 ppm. The US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to 1 mg/l(Hegazy et al, 2014). Anaerobic digestion can be affected by the presence of these compounds, which are highly refractory and prejudicial to methanogenic reactions. The inhibitory effects of phenol are problematic for the anaerobic treatment of wastewater(Hernandez & Edyvean, 2004).

The main sources of phenol which are released into the aquatic environment are the wastewater from major chemical and pharmaceutical industries such as petrochemical industries, petroleum refineries, coal gasification operations, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills, steel industries and domestic wastewaters, agricultural runoff and chemical spills, dye industries and pharmaceutical industries(Kulkarni, 2013; Hegazy et al, 2014; and Girish and Murty, 2012).

Phenol is a highly corrosive and nerve poisoning agent(Kulkarni, 2013). The ingestion of such chemical in the human body causes protein degeneration, tissue erosion and paralysis of the central nervous system and also damages the kidney, liver and pancreas(Hegazy, 2014). Phenol causes harmful side effects such as sour mouth, diarrhea, impaired vision, excretion of dark urine. It is also toxic for aquatic life. The toxic levels usually range between the concentrations of 10-24 mg/L for human and the toxicity level for fish between 9-25 mg/l (Kulkarni, 2013). A toxicity threshold of 64 mg phenol/liter was found for bacteria, protozoa and fungi (World Health Organization, Geneva 1994).

The most common methods used for removal of phenol from industrial effluents include stripping, solvent extraction, oxidation, ion exchange, biodegradation and adsorption methods. Out of all these treatment methods, adsorption process is recognized as the most efficient, promising and widely used fundamental approach in wastewater treatment processes, mainly hinging on its simplicity, economically viable, technically feasible and socially acceptable(Hegazy, 2014).

Adsorption on activated carbon is currently being used and is most effective in treating high strength and low volume of phenolic wastewaters. But the disadvantage associated with it is its high cost due to the use of non-renewable and relatively expensive starting material such as coal, which is a major economic consideration. This has prompted a growing research interest in the production of activated carbons from locally available materials especially for application concerning wastewater treatment. Several agricultural byproducts have been found to be suitable precursors for production of activated carbon. Because the biomass obtained from these materials are cheaper, renewable and abundantly available and have high carbon and low ash contents(Girish & Murty, 2012).

A comparative overview of some low cost biosorbent based and their removal performances are reported in the following Table.

Table 2.2: Comparison of adsorption capacities of adsorbents for phenol and its derivatives removal from waste water(Girish & Murty, 2012).

Adsorbent	Solute	Adsorption capacity (mg/g)
Coconut shell	Phenol	205.8
Coconut shell	Phenol	206

Coconut shell	4- Chlorophenol	267
Coconut shell	4- Nitrophenol	251
Coconut husk	2,4,6-trichlorophenol	191.73
Coir pith	Phenol	48.31
Coir pith	p- nitrophenol	3.66
Almond shell	Phenol	70.4
Hazelnut shell	Phenol	100
Walnut shell	Phenol	145
Apricot stone	Phenol	126
Almond shell	Pentachlorophenol	9.6
Date stones	Phenol	90.4
Date pit	Refinery waste water	16.64
Date pit	Synthetic waste water	12.6
Black stone cherries	Phenol	133.33
Plum kernels	Phenol	257.4
Nutshells of *Sterculia alata*	Phenol	2.8
Corn cob	Phenol (KOH/char:2)	232
Corn cob	Phenol (KOH/char:6)	340
Corn cob	CP (KOH/char:6)	485
Pomegranate peel	2,4-dichlorophenol	65.7
Palm seed coat	Phenol	18.3
Rubber seed coat	Phenolic solution	56
Palm pith carbon	2,4- dichlorophenol	19.16
Oil palm empty fruit bunch	2,4,6-trichlorophenol	500
Oil palm empty fruit bunch	Phenol	4.868
Oil palm empty fruit bunch	Phenol (KOH 30 %)	90.09
Oil palm empty fruit bunch	(KOH 50 %)	91.74
Oil palm empty fruit bunch	(KOH 70 %)	89.29
Hemidesmus indicus roots	Phenol	16.1

Beet pulp	Phenol	89.5
Pine wood	Phenol (activation 2.7 hours)	232.6
Pine wood	(activation 4 hours)	240.6
Pine wood	(activation 4 hours)	415.2
Pine bark	Pentachlorophenol	8.6
Pinus pinaster bark	0.4 min	0.15
Saw dust (KOH)	Phenol	149.25
Saw dust ($ZnCl_2$)	Phenol	2.82
Tamarindus indica wood	Phenol	80
Rice husk	Phenol	4.5
Rice husk char	Phenol	14.382
Rice husk char	Chlorophenol	0.15322
Olive pomace	Phenol (kinetic studies)	2.59
Olive pomace	Phenol (kinetic studies)	11.4
Olive cake	Phenol	20.68
Barley straw	Phenol	0.067
Barley straw ash	Phenol	0.0314
Shorea robusta leaf	Phenol	0.216
Hazelnut Bagasse carbon	Phenol (25 ^{0}C)	97.36
Hazelnut Bagasse carbon	35 ^{0}C	91.32
Hazelnut Bagasse carbon	45 ^{0}C	99.27
Jute fibre	Phenol	181

2.7. Adsorption

The adsorption involves a surface adhesion phenomenon. In adsorption process if some biological material is used as an adsorbent then the process is known as bio-sorption. This process involves solid and liquid phase interaction. Due to this interaction of sorbent and sorbate exchange the ions remove unwanted dissolved species. Solid and liquid phase distribution in sorption process is very important for determining the effectiveness of the process and degree of sorbent affinity plays a key role in this aspect

Industrial applications of adsorbents became common practice following the widespread use of charcoal for decolourizing liquids and, in particular, its use in gas masks during the 1914-18 World War for the protection of military personnel from poisonous gases.

Over the last few decade adsorption has gained paramount importance in industry and environmental protection. Adsorption processes are widely applied for separation and purification because of the high reliability, energy efficiency, design flexibility, technological maturity and the ability to regenerate the exhausted adsorbent. Adsorption works on the principle of adhesion. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The process can take place in any of the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. The adsorbing phase is the ‘adsorbent’, and the material concentrated or adsorbed at the surface of adsorbing phase is the ‘adsorbate’(Kandasamy et al., n.d.). The removal capacity by this method may be up to 99.9%. Due to these facts, adsorption has been used for the removal of a variety of organic pollutants from various contaminated water sources (Ali et al., 2012).

Adsorption is a process in which a substance (adsorbate), in gas or liquid phase, accumulates on a solid surface (adsorbent). It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages(Bello et al, 2013):

a. Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
b. Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore–filled liquid and migrate along the solid surface of the pore.
c. Solute molecules adsorption on the active sites on the interior surfaces of the pores.
d. Once the molecule adsorbed, it may migrate on the pore surface through surface diffusion.

2.7.1. Commercial adsorbent

2.7.1.1. Activated Carbons

Activated carbon is the most popular and widely used adsorbent in waste water treatment. Charcoal has been recognized as the oldest adsorbent known in waste water treatment. It is used for the removal of bad tastes and odours from water in 1970(Bello et al., 2013).

Carbonaceous materials have long been known to provide adsorptive properties. The earliest applications may date back centuries with the discovery that charred materials could be used to remove tastes, colours and odours from water. Now activated carbons are used widely in industrial applications which include decolourizing sugar solutions, personnel protection, solvent recovery, volatile organic compound control, hydrogen purification, and water treatment(Thomas and Crittenden, 1998). Activated carbon is produced by a process consisting of pyrolysis of raw material followed by activation with oxidizing gases. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2,000 m^2/g(Grassi et al, 2012).

Though commercially available, activated carbon is usually derived from natural materials such as biomass, lignite or coal, but almost any carbonaceous materials may be used as precursor for the preparation of carbon adsorbents(Višekruna et al., 2011). The most common raw materials are wood, wood charcoal, peat, lignite and lignite coke, hard coal and coke, bituminous coal, petrol coke as well as residual materials, such as coconut shells, sawdust, or plastic residuals(Eckhard Worch, 2012).

Based on its size and shape, activated carbon is classified into four types: powder, granular, fibrous and clothe. Activated carbon has been popular choice as an adsorbent (the best adsorbent) for the removal of toxic substances from wastewater but its high cost poses an economical problem.

2.7.1.2. Clays

Natural clay minerals are well known from the earliest day of civilization. Because of their low cost, high surface area, high porosity, and abundance in most continents, clays are good candidates as adsorbents. There are many kinds of clay: smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite, sepiolite, bentonite, kaolinite, diatomite, and

Fuller’s earth (attapulgite and montmorillonite varieties). The adsorption capacities depend on negative charge on the surface, which gives clay the capability to adsorb positively charged species(Grassi et al., 2012).

2.7.1.3. Minerals

Another class of adsorbents includes natural minerals. Among these zeolite and goethite had been investigated in the adsorption of pharmaceuticals. Zeolite is typically used for the removal of dyes and heavy metals. Like clay, minerals adsorption capacity is linked to negative charge on the structure(Grassi et al., 2012).

Zeolites are porous crystalline aluminosilicates which comprise assemblies of SiO_4 and AlO_4 tetrahedral joined together through the sharing of oxygen atoms. More than 150 synthetic zeolite types are known. Cavities (or cages) are contained within the framework of a zeolite and are connected by regular channels (pores) which are of molecular dimensions and into which adsorbate molecules can penetrate. In crystal form, zeolites are distinct from other adsorbents in that, for each type, there is no distribution of pore size because the crystal lattice into which the adsorbate molecules can or cannot enter is precisely uniform. The internal porosity is high and thus the majority of adsorption takes place internally. For this reason, zeolites are capable of separating effectively on the basis of size and they have been assigned the popular description of molecular sieves. The processes of adsorption and desorption of molecules in zeolites are based on differences in molecular size, shape and other properties such as polarity(Thomas & Crittenden, 1998).

2.7.2. Low Cost Adsorbents

Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world and has been successfully utilized for the removal of diverse types of pollutants including metal ions. However, the high capital and regeneration cost of the activated carbon limits its large-scale applications for the removal of metals and other aquatic pollutants, which have encouraged researchers to look for low-cost alternative adsorbents utilizing agro-industrial wastes. The utilization of agro-wastes as adsorbents is currently receiving wide attention because of their abundant availability and low-cost owing to relatively high fixed carbon content and presence of porous structure(Bhatnagar et al,, 2010). Generally, biosorption processes can significantly reduce capital costs, operational costs and total treatment costs compared with the conventional systems(Abdolali et al., 2014).

2.7.2.1. Agricultural Waste

The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing a variety of functional groups. In particular, agricultural materials containing cellulose show a potential sorption capacity for various pollutants. If these wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent, if developed, can reduce the treatment of wastewaters at a reasonable cost(Bhatnagar et al., 2010). Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness.

The agricultural waste materials have been used in their natural form or after some physical or chemical modification. Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), and dyes for the purpose of removing soluble organic compounds, color and metal from the aqueous solutions have been performed(Grassi et al., 2012).

2.7.2.2. Industrial Waste

Widespread industrial activities generate huge amount of solid waste materials as by-products. Industrial wastes such as sludge, fly ash, and red mud are classified as low-cost materials, locally available and can be used as adsorbents for removal of pollutant from aqueous solution. Fly ash is a waste material originating in combustion processes. Although it may contain some hazardous substances, such as heavy metals, it has been showing good adsorption qualities for phenolic compounds. The maximum phenol adsorption capacity has been found to be 27.9 mg/g for fly ash and 108.0 mg/g for granular activated carbon at initial phenol concentration of 100 mg/L(Grassi et al., 2012).

2.8. Banana peel

Bio-sorbents are certain types of biomass used to bind and concentrate pollutants from even much diluted aqueous solution. A biosorption process offers a number of advantages compared to conventional methods currently used. These include low operational costs and minimizing the volume of chemical and/or biological waste sludge as well as a high degree of efficiency in decontamination of much diluted effluents. Banana peel, a discarded agricultural waste, will be used to produce bio-adsorbent through easy and environmental friendly processes. This natural bio-sorbent will be evaluated for adsorptive removal of phenolic compound from distilleries wastewater(Ibrahim et al, 2013). The peel is characterized by a heterogeneous, rough and porous surface with crater like pores that helps to its possible use as an adsorbent(Pandharipande and Deshpande, 2013). At present, these peels are not being used for any other purposes and are mostly dumped as solid waste at large expense. It is thus significant and even essential to find applications for these peels as they can contribute to real environmental problems(Mohammad et al, 2015).

Table 2.3 Chemical and physical properties of banana peel (Achak et al, 2009).

Parameters	Data
Moisture content, (%)	13.55
Volatile matter, (%)	86.44
Ash content, (%)	3.85
C content, (%)	31.79
O content, (%)	42.87
K content, (%)	14.86
Na content, (%)	1.33
Si content, (%)	1.48
Al content, (%)	1.05
Cl content, (%)	3.22

Different types of fruit peels have been investigated so far for wastewater treatment, which included banana pith, orange peel, wheat straw, sawdust, powdered waste sludge, wheat shells, wheat bran and hen feathers(Achak et al., 2009). The purpose of this work is to investigate the efficiency of banana peel as a biosorbent for removal of phenolic compounds from distillery wastewater.

2.9. Banana Production in Ethiopia

Banana is the major staple food in developing countries. The fact that it produces fruit throughout the year adds to its importance as a food security crop in Africa. It is a primary food and cash crop for over 30 million people in East Africa. Uganda is Africa's largest producer while Rwanda and Burundi are the second and third largest producers in East Africa, respectively(Yoseph et al., 2014).

Banana has been cultivated for several years in Ethiopia as a garden plant. In Ethiopia, major banana producing regions are Southern, Oromia and Amhara regions. As in some other tropical and sub-tropical regions, bananas are produced by: small plantations in home gardens owned by small farmers - especially in the South-Western and Western provinces, medium-sized plantations of not more than 10 hectare supplying local consumers, and relatively large plantations above 20 hectares developed to supply export markets. Especially in the south and southwestern parts of the country, it is of great socioeconomic importance contributing significantly to the overall wellbeing of the rural communities including food security, income generation and job creation (Woldu et al., 2015). Banana in Ethiopia covers about 59.64% (53,956.16 hectares) of the total fruit area, about 68.00% (478,251.04 tones) of the total fruits produced, and about 38.30%(2,574,035) of the total fruit producing farmers. On the other hand, about 68.72% (37,076.85 hectares) hectares of land covered by banana, about 77.53% (370,784.17 tones) of the banana produced and 22.38% (1,504,207) of the banana producers in Ethiopia are found in the Southern Nations Nationalities and Peoples' National Regional State- SNNPRS. Gamo-Gofa, Bench-Maji and Sheka zones are among the major banana producing zones of the SNNPRS, of which Gamo-Gofa zone alone covers over 70% of the total banana marketed across the major market outlets in Ethiopia(Mamuye, 2016).

2.10. Adsorption Mechanisms

The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages.

1. Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
2. Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore–filled liquid and migrate along the solid surface of the pore.
3. Solute molecules adsorption on the active sites on the interior surfaces of the pores.
4. Once the molecule adsorbed, it may migrate on the pore surface trough surface diffusion.

There are two types of adsorption; physical and chemical adsorptions.

Physical Adsorption

Physical adsorption is achieved by Van der Waals forces, dipole interactions, and hydrogen binding. There is no electron exchange between adsorbent and adsorbate. Because there is no activation energy required for physical adsorption, the time needed to reach equilibrium is very short. Physical adsorption is a non–specific and a reversible process.

Chemical Adsorption

Chemical adsorption results from the chemical link between adsorbent and adsorbate molecule, therefore it is specific as well as irreversible and chemical as well as electronic properties of adsorbent are changed. Binding between adsorbent and adsorbate by covalent bond is called weak chemical adsorption, and that by ionic bonds is called strong chemical adsorption.

2.11. Adsorption Isotherms

Adsorption is generally described through isotherms, that are amount of adsorbate on the adsorbent as a function of pressure (for gases) or concentration (for liquids), at a constant temperature. It is an adsorption isotherm which relates concentration of solute on the surface of the adsorbent to the concentration of the solute in the liquid with which it is in contact. This model assumes that adsorption takes place on heterogeneous surface(Samal, 2014).

In a solid–liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (2.1):

$$qt = \frac{(Co-Ct)}{m}V \qquad (2.1)$$

Where q_t (mg/g) is the amount of adsorbate per mass unit of adsorbent at time t, C_0 and C_t (mg/L) are the concentration of adsorbate at initial and at time t, respectively, V is the volume of the solution (L), and m is the mass of adsorbent (g).

Taking into account that adsorption process can be more complex, several adsorption isotherms were proposed. Among these the most used models to describe the process in water and wastewater applications were developed by (i) Langmuir, (ii) Brunauer, Emmet, and Teller (BET), and (iii) Freundlich(Grassi et al., n.d.).

The Langmuir adsorption model is valid for single-layer adsorption, whereas the BET model represents isotherms reflecting apparent multilayer adsorption. So, when the limit of adsorption is a monolayer, the BET isotherms reduce to the Langmuir equation. Both equations are limited by the assumption of uniform energies of adsorption on the surface.

The Langmuir isotherm is described by the Eq.(2.2)

$$\frac{qe}{qm} = \frac{bCe}{1+bCe} \qquad (2.2)$$

Where, q_e (mg/g) is the amount of adsorbate per mass unit of adsorbent at equilibrium, C_e is the liquid-phase concentration of the adsorbate at equilibrium (mg/L), q_m is the maximum adsorption capacity (mg/g) and b is the Langmuir constant related to the energy of adsorption (L/mg).

With the additional assumption that layers beyond the first have equal energies of adsorption, the BET equation takes the following simplified form:

$$q \downarrow \mathrm{e}/q \downarrow \mathrm{m} = (\mathrm{BC} \downarrow \mathrm{e})/((\mathrm{C} \downarrow \mathrm{s} - \mathrm{C})[1 + (\mathrm{B} - 1](\mathrm{C} \downarrow \mathrm{e}/(\mathrm{C} \downarrow \mathrm{s}))) \qquad (2.3)$$

In which C_s is the saturation concentration of the solute, B is a constant which takes into account the energy of interaction with the surface, and all other symbols have the same significance as in Eq. (2.2).

The data related to adsorption from the liquid phase are fitted better by Freundlich isotherm equation. It is a special case for heterogeneous surface energies. Freundlich isotherm is described by the Eq. (2.4):

$$qe = KfCe^{1/n} \tag{2.4}$$

Where, K_F (mg/g) $(L/mg)^{1/n}$ is the Freundlich capacity factor and 1/n is the Freundlich intensity parameter. The constants in the Freundlich isotherm can be determined by plotting log q_e versus log C_e.

2.12. Factors Affecting Adsorption

The factors affecting the adsorption process are: (i) surface area, (ii) nature and initial concentration of adsorbate, (iii) solution pH, (iv) temperature, (v) interfering substances, and (vi) nature and dose of adsorbent(Grassi et al., n.d.).

Since adsorption is a surface phenomenon, the extent of adsorption is proportional to the specific surface area which is defined as that portion of the total surface area that is available for adsorption. Thus more finely divided and more porous is the solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent

The physicochemical nature of the adsorbent drastically affects both rate and capacity of adsorption. The solubility of the solute greatly influences the adsorption equilibrium. In general, an inverse relationship can be expected between the extent of adsorption of a solute and its solubility in the solvent where the adsorption takes place. Molecular size is also relevant as it relates to the rate of uptake of organic solutes through the porous of the adsorbent material if the rate is controlled by intraparticle transport.

The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption according to the adsorbate functional groups. Another important parameter is the temperature. Temperature seems not to influence the biosorption performances in the range of 20–35 °C(Kaushik, 2015). Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature.

Finally, the adsorption can be affected by the concentration of organic and inorganic compounds. The adsorption process is strongly influenced by a mixture of many compounds which are typically present in water and wastewater.

2.13. Anaerobic Digestion of Vinasse

Vinasse is the wastewater resulting from the production of ethyl alcohol by fermentation. It is strongly acidic and contains abundant organic matter. This type of waste can be very efficiently purified by anaerobic digestion, which avoids the use of large amounts of oxygen and produces biogas, thus allowing some of the energy contained in the waste to be reclaimed. The process produces little sludge, which facilitates its disposal. Anaerobic digestion is the most suitable option for the treatment of high strength organic effluents. In anaerobic degradation of vinasse, microorganisms are used to degrade the organic matter in the fluid in the absence of oxygen. After digestion, the following are produced: a clearer liquid, sludge, and methane gas.

The anaerobic digestion encompasses the following stages: (i) Hydrolysis of the large molecules by the bacteria; (ii) Acidogenesis: The acidogenic bacteria convert sugars and amino acids into CO_2, H_2, NH_3, and other organic acids; (iii) The acetogenic bacteria convert carboxylic acids into simpler organic acids, acetic acid, as well as more CO_2, H_2, and NH_3. (iv) Then the methanogen microbes produce CH_4 and more CO_2 (Mulat, 2015).

The following chemical reaction represents hydrolysis of simple sugar glucose, as an example (Kuusisto, 2013):

$$2C_6H_{12}O_6 + H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

With the formation of acetic acid, carbon dioxide and hydrogen, methane is then formed by the following two pathways:

$$2CH_3COOH \longrightarrow 2CH_4 + 2CO_2$$

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$$

2.14. Operating conditions and factors regulating biogas production in AD process

There are a number of reactor conditions that are important in ensuring a stable, productive anaerobic digestion process. These reactor conditions include (but are not limited to): temperature, pH, organic loading rate, moisture content, and retention time(Gamble, 2014). Temperature and pH are the most important variables as the methane producing bacteria are sensitive to these as well.

2.14.1. Temperature

The temperature of the reactor is one of the more important decisions that must be made in designing an AD system. There are three primary temperature ranges in which AD can occur: psychrophilic (0-20 °C), mesophilic (25-40 °C) and thermophilic (50-65 °C) conditions. Most industrial biogas plants are operated either at mesophilic or thermophilic temperatures. (Mulat, 2015).

2.14.2. pH

Anaerobic reactions are highly pH dependent. The optimal pH range for methane producing bacteria is 6.7-7.4(Gamble, 2014) while low pH (5 to 6.5) is generally optimum for the growth of fermentative bacteria, which are responsible for enzymatic hydrolysis of polymers to monomers and subsequent conversion to acids(Rajeshwari et al, 2000). The pH of an anaerobic system is typically maintained between methanogenic limits to prevent the predominance of the acid-forming bacteria, which may cause VFA accumulation. Methanogens are known to be more sensitive to pH changes than the fermentative bacteria.

2.14.3. Organic loading rate (OLR)

In anaerobic wastewater treatment, loading rate plays an important role. Organic loading rate (OLR) represent the amount of feed added into a digester per unit of time. Depending on substrate, temperature and reactor design, different range of OLR are employed. Typical well-functioning thermophilic digester can be loaded in the range of 4-5 kg VS $m^{-3}d^{-1}$ whereas mesophilic digester has a load of 2-3 kg VS $m^{-3}d^{-1}$ (Mulat, 2015).

2.14.4. Hydraulic retention time (HRT)

The hydraulic retention time (HRT) is a term commonly used to represent the statistically average residence time of the soluble substrate in the digester. The HRT, which depends on the characteristics of feedstock, reactor design temperature of the digester and environmental conditions, should be long enough to allow metabolism by organisms for the degradation of organic material to biogas. For slowly degradable substrates, the HRT is normally longer to allow the solubilization of the organic material efficiently and in this case, hydrolysis is considered as a rate limiting step. Continuous stirred tank reactor (CSTR) is operated at longer HRT (10-60 days)(Mulat, 2015).

2.14.5. Effect of nutrients

The presence of ions in the feed is a critical parameter since it affects the granulation process and stability of reactors like UASB. The bacteria in the anaerobic digestion process requires micronutrients and trace elements such as nitrogen, phosphorous, sulphur, potassium, calcium, magnesium, iron, nickel, cobalt, zinc, manganese and copper for optimum growth. Although these elements are needed in extremely low concentrations, the lack of these nutrients has an adverse effect upon the microbial growth and performance. The required optimum C:N:P ratio for enhanced yield of methane has been reported to be 100:2.5:0.5(Rajeshwari et al., 2000).

3. Materials and Methods

3.1. Experimental Framework

This research is conducted to devise appropriate treatment technique of distillery wastewater to minimize its environmental impact through adsorption and anaerobic digestion. The studies of all experiments were planned according to this framework.

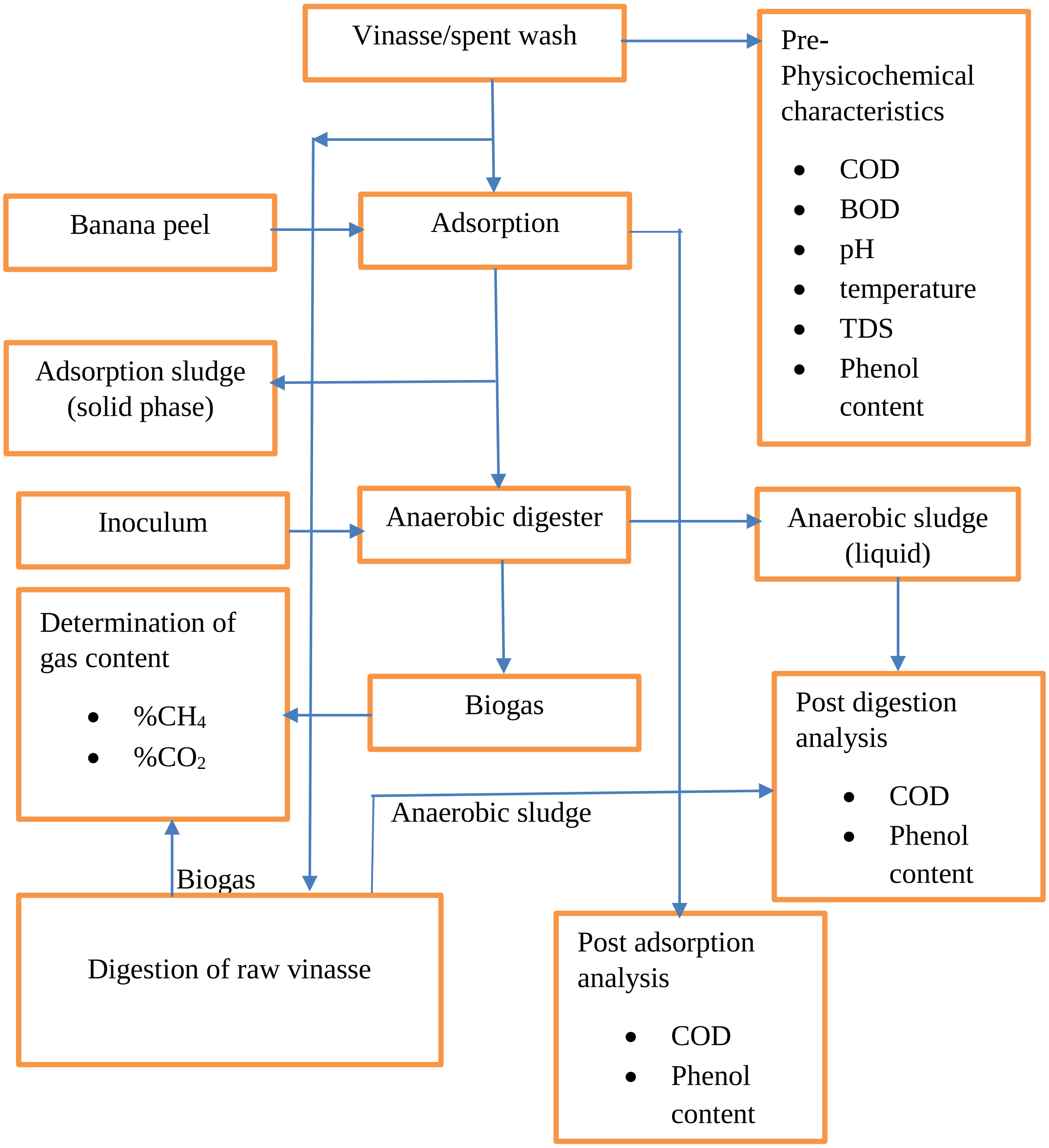


Fig. 3.1 Experimental Framework of the study

3.2. Materials

Raw material: Vinasse samples were collected from Balezaf alcohol and liquor Factory immediately after drainage from the factory pipelines. Cow dung was used as a source of methanogenic bacteria to inoculate the wastewater. The banana peel used as biosorbent was obtained from local fruit market.

Characterization of wastewater: The wastewater used in this work was the distillery Wastewater from Balezaf alcohol and liquor Factory located in Alemgena, Oromia regional state, 25 Km from capital. After sampling, the samples were immediately taken to the laboratory for physicochemical characterization such as BOD, COD, pH, phenol content and total solid content. The sample was stored at 4°C until it were utilized for the batch experiments.

i) Phenol content determination

The concentration of phenolic in vinasse was determined by spectrophotometric method, which is a photometric test method, based on the reaction of steam-distillable phenolic compounds with 4-aminoantipyrine at a pH of 10.0 ± 0.2 in the presence of $K_3Fe(CN)_6$. The antipyrine color formed in an aqueous solution was measured at 510 nm. The concentration of phenolic compounds in the sample was expressed in terms of milligrams per liter of phenol (C_6H_5OH).

Calibration: A series of 100-mL phenol standards containing 0, 10, 20, 30, 40 and 50 mL of intermediate phenol solution (1 mL = 0.01 mg phenol) were prepared in distilled water. In the series of prepared standards color was developed by adding 4-aminoantipyrine and potassium ferricyanide in a basic condition. After 15 min reaction time the absorbance of each standard was measured at 510 nm against the reagent blank as zero absorbance. Finally, concentration against absorbance was plotted.

Phenol determination: 300 ml of the filtrate after batch adsorption was transferred to a distillation apparatus to collect a clear condensate. After 275 ml of distillate was collected, 50ml of distilled water was added to distillate apparatus and distillation was continued until a total of 300ml has been collected. 100 ml of distillate was transferred to a beaker and pH was adjusted between 9.8 and 10.2 with ammonium buffer. 2ml of 4-amino antipyrine and 2ml potassium ferricyanide were added and the solution was mixed well. The reagent mixed sample were then diluted with dilution water. After 15 min the solution was transferred to absorption cell and the absorbance was measured against the zero absorbance of the reagent blank at 510 nm.

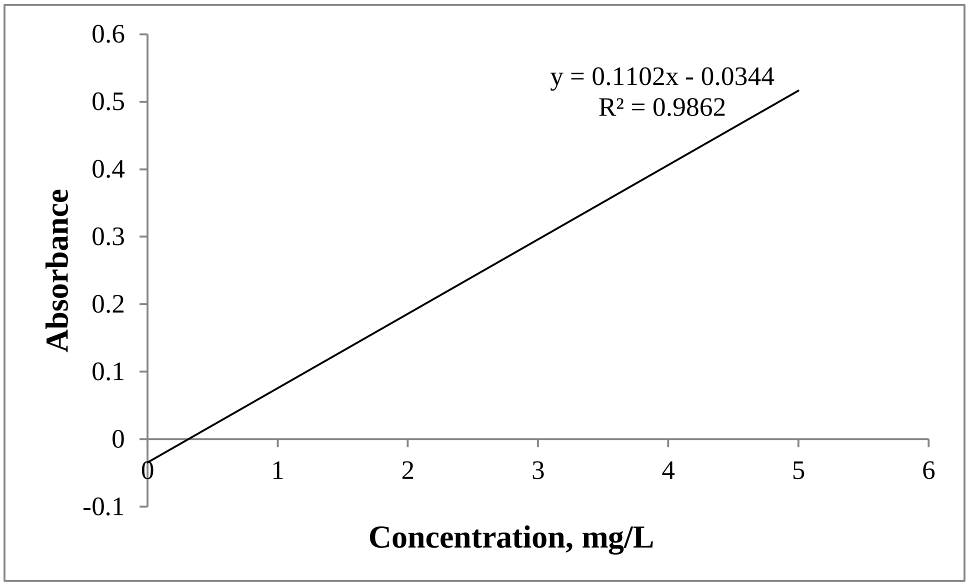


Fig 3.2 Calibration curve of phenol standard

Calculation: Calculate the phenolic content of the sample, in milligrams per liter as follows:

$$\boldsymbol{Concentration\ of\ phenolic\ in\ original\ sample\ mg/L\ =\ W\ *1000/V}$$

Where

W = phenolic, in aliquot of sample diluted to 100 mL, as determined from calibration curve, mg,

V = original sample, present in 100 mL of the solution reacted with 4-aminoantipyrine, ml

ii) pH

The sample pH measurements were carried out using a pH meter. The pH meter was kept in a standard buffer solution at pH of 4.0 and calibrated against a buffer solution of pH of 7 before each use.

iii) Total solid (TS)

Total solids (TS) concentrations were measured gravimetrically by weighing dried samples from known initial volume according to APHA 2540 B standard. The samples of known volume were dried for 48 h at 103-105^{0}C in pre-weighted ceramic crucibles. The crucible and remaining dried sample were then immediately placed in desiccators and allowed to cool to room temperature. The cool crucibles with dried samples were weighted to determine the TS concentration. The TS concentration was determined as the mass of dry samples over the initial volume of the sample. The drying procedure was repeated until constant weigh was obtained or weight loss was less than 0.5mg. Finally, the TS was calculated as follows:

$$\text{Total residue}, \frac{\text{mg}}{\text{l}} = \frac{(A-B)*1000}{C} \qquad (3.1)$$

Where, A= weight of sample + dish in mg

B= weight of dish in mg

C= volume of sample in ml.

iv) Chemical Oxygen Demand (COD)

The COD of the sample was determined according to APHA 5220 B for water and wastewater by Open Reflux Method. Before digestion the preparation block was placed into refrigerator to avoid loss of volatile compound while preparing the sample, and then the digester was switched on and preheated to the required temperature, which was 150^{0}C. then the rack was placed on cold preparation block and digestion tube was placed in it. 25 mL of 0.25N of $K_2Cr_2O_5$ was added and mixed. The known amount of sample was transferred to COD digestion tube and 10 mL $K_2Cr_2O_5$ solution was added and mixed well. After that 25 mL of sulphate-sulphuric acid solution was added slowly with mixing. The cooling water bath was turned on and immediately the condenser was placed on sample tube and fixed. Then the mixture was refluxed for 2 hours and cooled. Finally, the reflux condenser was disconnected and the mixture was diluted to about twice its volume with distilled water and further Cooled to room temperature and 2 ml of Barium Diphenyl amine sulphonate, (BDS), was added and the sample was titrated with excess $K_2Cr_2O_7$ with ferrous ammonium sulphate (FAS), using 0.15 mL (2 to 3 drops) ferroin indicator. The end point of the titration will be taken as the first sharp color change from blue-green to reddish brown that persists for 1 min or longer. The technique and quality of reagents was evaluated by conducting the test on a standard potassium hydrogen phthalate solution. At the end, COD was calculated as:

$$COD\ as\ mg\ of\ \frac{O2}{L} = \frac{(A-B)*N*8000}{mL\ of\ sample} \tag{3.2}$$

Where, A= mL FAS used for blank

B= mL FAS used for sample

N= normality of FAS, and

8000 Milliequivalent weight of oxygen × 1000 mL/L.

v) Biological Oxygen Demand (BOD)

BOD of the sample was determined according to standard method of 5210 D by Respirometric method which provides direct measurement of oxygen consumed by microorganism in closed vessel under constant temperature condition. Thus, following that the sample temperature was adjusted to 20 ± 3^0c before making dilution and pH was adjusted to 7±0.2. After that the sample was diluted with the dilution water and 157 mL of the diluted sample was transferred to prepared BOD bottles. 5-drop of Nitrification inhibitor was added. The sample was then incubated at $20^0C\pm1^0C$ and after 5 days the consumed oxygen was recorded.

Preparation of biosorbent: In the present work banana peel without any chemical pre-treatment was employed in the adsorption studies experimentations. Banana peels were obtained from banana fruits bought from local fruit market. The fruit was peeled and the peels were collected. The collected biomaterial was extensively washed under tap water to remove any particulate matter and sun dried to remove free moisture. The dried peels were size reduced manually with stainless steel knife. To this end, the banana peels were oven dried at 105^0C for 24 h. After drying, the banana peels were ground to average size in a grinder. After grinding, banana peels powder was once again washed with distilled water and dried in an oven for 24 h. Finally, the samples of banana peels were sieved to different mesh size and stored in air tight bags.

Characterization of produced biosorbent: The moisture content present was found by heating a known amount of the sample, before sun drying and after sun drying, inside an oven kept at a temperature of 105^{o}C until a constant weight was obtained.

The chemical functionality of the peel was qualitatively determined by Fourier Transform Infrared (FTIR) spectroscopy and the spectra were recorded between wave lengths of 4000 to 400 cm^{-1}. This is a proven technique for investigating various functional groups and structural variations in biomass. It can detect a wide variety of functional groups which are present in banana peels structure. These wavelength variations provide accurate and many information about porous structure of banana peel and helps in concluding the adsorption properties of the adsorbent.

3.3. Methods

A combined effect of adsorption and anaerobic digestion for vinasse treatment was used in this research. The efficiency of banana peel as a biosorbent for removal of phenolic compounds from vinasse was investigated, in which the effects of various operating parameters on biosorption such as sorbent dosage, particle size and contact time were monitored and optimal experimental condition was determined. Adsorption pretreated vinasse was then undergo a biodegradation process to reduce its organic content. Phenol removal capacity was the selected response variables for adsorption process.

3.4. Experimental Design

The experiments were designed to determine the effect of coupling adsorption with anaerobic digestion to treat distillery wastewater in which adsorption pre-treated wastewater undergo anaerobic digestion. A fully randomized experimental design was conducted to determine the optimum adsorption condition. Randomization ensures that the conditions in one run neither depend on the conditions of the previous runs nor predict the conditions in the subsequent runs. Randomization is essential for drawing conclusions from the experiment, in correct, unambiguous and defensible manner. Adsorbent dosage, particle size and contact time were taken as experimental factor. ANOVA was performed using Design expert® (V.7.0.0) trial version. Response surface methodology (RSM), which is the most widely used statistical technique for bioprocess optimization(Annadurai et al, 2002), was used to study the influence of operational parameters on the adsorption of phenol by a natural and low cost adsorbent from distillery wastewater. RSM is one of the powerful statistical experimental design techniques that is applied to build models and investigate individual and interaction effects of the selected operating condition on the given response in a given experiment(Kassahun et al, 2017). Box-Behnken Design (BBD), which require fewer runs than the others RSM designs, was the selected experimental design used to determine the optimal response of phenol adsorption by this biosorbent. The Box-Behnken design is based on the construction of balanced incomplete block designs and requires at least three levels for each factor(Tekindal et al, 2012). BBD can provide a maximum amount of complex information with minimum experimental time. Moreover, Box–Behnken design allows calculations of the response function at intermediate levels and enables estimation of the system performance at any experimental point within the range studied through careful design and analysis of experiments(Li et al., 2010). The optimization process with this design involves three major steps; i.e. performing the statistically designed experiments, estimating the coefficients in a mathematical model, and predicting the response and checking the validity of the model(Annadurai et al., 2002). For statistical calculations the variable x_i was coded X_i according to Eq. (1):

$$X_i = \frac{(x_i - x_0)}{\Delta x},\ i = 1;\ 2;\ 3 \ldots k \qquad (3.4)$$

where X_i is coded (dimensionless) value of the variable x_i, x_0 is the value of x_i at the center point, and Δx is the step change.

The response variable was fitted to the following second-order polynomial model (Equation (2)) which is generally able to describe relationship between the responses and the independent variables.

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \qquad (3.5)$$

where Y is the predicted response, b_0 the offset term, b_i the linear effect, b_{ii} the square effect, and b_{ij} the interaction effect.

This design consisted of fifteen randomized runs with three replicates at the central point to minimize the error. Each variable was studied over three level: low, middle and high. The level of each variable were selected based on the preliminary experiment-trials (5, 10 and 15 gm adsorbent dose; and 60, 90 and 120 min contact time), and also on the available literatures. The factors and levels are given in Table 3.1.

Table 3.1 The levels of variables chosen for the trials

Variables	Levels		
	Low	Middle	High
Adsorbent dosage, g	10	20	30
Particle size, mm	0.5	1	1.5
Contact time, min	60	120	180

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

$$N = K^2 + K + Cp \qquad (3.6)$$

where k is a number of factors, and Cp is a central replication point. Table 2 shows the 15 experimental runs that are arranged according to BBD.

3.5. Experimental Procedures

Sample preparation: The original distillery wastewater was passed through screening system by using filter paper, for the removal of any visible materials and dirt. The clean wastewater sample was stored in polyethylene container as stock feed wastewater. The initial pH of the feed stock is measured using pH meter.

Biosorption Process: Optimization of the amount of adsorbent dose, particle size and contact time are very important in the adsorption process. For this purpose, the batch biosorption experiments were carried out in 1 L beaker using 500mL of clean wastewater. The biosorption process was conducted at initial pH of the feed wastewater. The known amount of banana peel adsorbent with known particle size was added in the flasks at dosage ranging from 10 to 30 g with increment of 10 g. The flasks with mixture of wastewater and biosorbent was placed under stirrer and agitated at the speed of 150rpm for constant contact time. At the end of the experiments, the flask was removed and the contents were filtered and the filtrate phenol contents were analyzed using double beam UV/Vis spectrophotometer. Similarly, the effects of contact time and adsorbent particle size were optimized by changing one parameter at a time and keeping the others constant. The biosorption process is carried out at room temperature.

Anaerobic Digestion process: Three 500 mL Batch lab-scale reactors were fed with 300 mL of vinasse and inoculated with 2 g/L of volatile suspended solids (VSS) (in these case 2 g/L of cow dung was used as a methanogenesis bacteria source). Two reactors were fed with pretreated samples and the third one was fed with raw vinasse. Prior to loading in the digester, the pH of the distillery wastewater was set around 7 units with pH buffer (NaOH 3%). The reactors were located in a constant temperature water bath with the thermostat set to a temperature of $35^0C \pm 2^0C$. few days later the sample starts generating biogas. The produced gas was collected in the plastic bag. The methane yield was measured with biogas 5000 gas analyzer with CH_4 and CO_2 accuracy of ±0.5% measurement reading. Both methane yield and biogas quality (CH_4, CO_2, H_2S and O_2), were investigated and recorded at the end of the incubation period of 8 days. The generated biogas volume was measured using the liquid displacement gas collecting and measuring system at the end of the digestion period. Finally, the percent COD reduction of the bio-digested vinasse was characterized as an indication of performance.

Adsorption isotherms and kinetics: Batch experimental run were conducted to determine adsorption performance and adsorption mechanism of the banana peel, through adsorption isotherm and adsorption kinetics, respectively. The experiments were conducted at constant temperature and contact time with varying adsorbent dose to determine adsorption isotherm followed. The equilibrium contact time of 129 min and particle size of 0.5 mm were used with variation of adsorbent dose from 5 to 30 g per liter of spent wash with an increment of 5 g.

On the other hand, experiments were also conducted at constant adsorbent dose of 20 g per liter of vinasse and particle size of 0.5 mm, with variation of contact time from 30 to 180 min with an increment of 30 min to determine the appropriate kinetic model corresponding to this biosorbent.

3.6. Adsorption isotherm

The adsorption performance of the biosorbent is evaluated using adsorption isotherms. Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by adsorbent. It is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of absorbable solute between the liquid and solid phases at various equilibrium concentrations(Agarwal et al, 2014).

The most commonly used models were Freundlich and Langmuir isotherms. Langmuir adsorption is isotherm commonly applied in solid/liquid system to describe the saturated monolayer adsorption, whereas Freundlich adsorption isotherm describes the adsorption equilibrium, based on adsorption on heterogeneous surface(Joshi & Pokharel, n.d.). The Langmuir isotherm is based on these assumptions, the adsorbate is chemically adsorbed at a fixed number of well-defined sites; each site can hold only one ion; all sites are energetically equivalent and; there is no interaction between the ions(Igwe & Abia, 2007). Whereas, the Freundlich isotherm, assumes the exponential distribution of active sites of biosorbent. This isotherm does not predict any saturation of the adsorbent surface; thus, infinite surface coverage is predicted, indicating physicosorption on the surface(Bousba & Hassen, 2014).

The applicability of the isotherm equations was compared by judging the coefficients of determination R^2. In the present study, the Langmuir and Freundlich isotherms were chosen to estimate the adsorption intensity of the adsorbent towards the adsorbate. The equilibrium distribution of adsorbate between the solid and liquid phases. The following equation represents the Langmuir adsorption isotherm.

$$q_e = (q_m\, b\, C_{eq})/(1 + b\, C_{eq}) \tag{3.7}$$

where q_e is milligrams of adsorbate accumulated per gram of the biosorbent material; C_{eq} is the adsorbate residual concentration in solution at equilibrium, q_m is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates.

The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and it’s equated by the following equation.

$$\frac{C_{eq}}{q_e} = \frac{1}{bq_m} + \frac{C_{eq}}{q_m} \tag{3.8}$$

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor R_L, which is expressed as:

$$R_L = \frac{1}{1+bC_0} \tag{3.9}$$

Where b is the Langmuir constant and Co is the initial concentration of the adsorbate. The value of R_L indicates the shape of Langmuir isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$), or favorable ($0 < R_L < 1$). Also the smaller R_L value indicates a highly favorable adsorption(Bousba & Hassen, 2014).

The Freundlich isotherm is represented by the equation:

$$q_{eq} = K_F\, C_{eq}^{1/n} \tag{3.10}$$

Where C_{eq} is the equilibrium concentration (mg/l), q_{eq} is the amount adsorbed (mg/g) and K_F and n are Freundlich constants related to the multilayer adsorption capacity and the surface heterogeneity, respectively. The linearized form of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as.

$$Log\, q_{eq} = Log\, K_F + \frac{1}{n} Log\, C_{eq} \tag{3.11}$$

The equilibrium data were obtained from batch experiments. The amount of phenol adsorbed (q_e) was calculated by using the following mass balance equation:

$$qe = \frac{(Co-Ce)}{m} * V \tag{3.12}$$

Where q_e (mg/g) is the amount of adsorbate per mass unit of adsorbent at equilibrium condition, C_0 and C_e (mg/L) are the concentration of adsorbate at initial and at equilibrium, respectively, V is the volume of the solution (L), and m is the mass of adsorbent (g).

The removal efficiency of phenol was calculated as follows:

$$Removal\ (\%) = \frac{Co-Ce}{Co} * 100 \tag{3.13}$$

3.7. Adsorption kinetics

Adsorption kinetics has been proposed to elucidate the adsorption mechanism. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transport process (Achak et al, 2009). In order to investigate the mechanism of adsorption, kinetic models such as the pseudo first and second order model were applied to study the adsorption dynamics, and is helpful in prediction of adsorption rate constants, equilibrium adsorption capacity and adsorption mechanism(Bousba & Hassen, 2014). The capability of pseudo-first-order, pseudo second-order and diffusion kinetic models were examined in this study.

The pseudo-first-order equation is given as:

$$ln(q_e - q_t) = ln(q_e) - k_1 t \qquad (3.14)$$

where q_e and q_t refer to the amount of phenolic compounds adsorbed (mg/g) at equilibrium and at any time, t (min), respectively, k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order sorption. k_1 and q_e values were determined from the slope and intercept of the plots of $ln(q_e-q_t)$ versus t.

On the other hand, a pseudo-second-order equation based on the adsorption capacity is expressed in the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3.15)$$

where k_2 is the rate constant for pseudo-second-order kinetics (g/mg min). The values of q_e and k_2 were determined from the slope and intercept of the plot of $\frac{t}{q_t}$ versus t.

Since neither the pseudo-first-order and pseudo-second-order kinetic model can identify the diffusion mechanism, the intraparticle diffusion model was also used to analyze and elucidate the diffusion mechanism(Achak et al, 2009). The intraparticle model is expressed as:

$$q_t = k_p t^{1/2} + C \qquad (3.16)$$

where q_t is the amount of phenolic compounds adsorbed (mg/g) at time t (min), C is the intercept and k_p is the intraparticle diffusion rate constant (mg/g $min^{1/2}$).

4. Result and Discussion

4.1. Characterization of wastewater

The characteristic of wastewater was presented in Table 4.1.

Table 4.1 Physicochemical characteristics of distillery wastewater

Colour	Dark brown
pH	4.6
Temperature, ^{o}c	90-95
COD, mg/l	92,500
BOD, mg/l	53,550
Total solid, mg/l	85,500
Phenol, mg/l	52.8

4.2. Characterization of biosorbent (Banana peel)

Moisture content: The moisture content of the biosorbent was determined based on both dry matter basis, after removing free moisture with sun drying, and wet basis, without removing free moisture. The results show that the adsorbent has high water content based on wet basis, which was 86.7%. whereas, after sun drying it was found to be 14.6% which agrees with the value obtained by Achak et al, 2009.

Functional group of biosorbent: Fourier transform infrared (FTIR) transmission spectra were obtained to characterize the functional group on the peel before and after adsorption as shown in Figure 4.1 and 4.2, respectively. The spectrum revealed the presence of a number of characteristic bands in the range of 400–4,000 cm^{-1}. A broad band noticed from 3650-3120 cm^{-1} corresponds to hydroxyl functional group (OH stretching vibration), and may be also the characteristic peak of carbonyl and phenolic hydroxyl groups, while the weak bands at 2920 cm^{-1} assigned to asymmetric C-H stretching. The bands observed in the region between 1700 cm^{-1} and 1490 cm^{-1} were attributed to C=C symmetrical stretching of pyrone groups and C=O of carboxylic groups. This may also be the band attributed as a result of amides groups and aromatic carbon–carbon stretching vibration. Moreover, the band observed at 1,632 cm^{-1} was assigned to carbonyl C–O present in carbonyls, ketones, aldehydes or ester groups and to C–C present in olefinic vibrations in aromatic region(Hegazy, 2014).

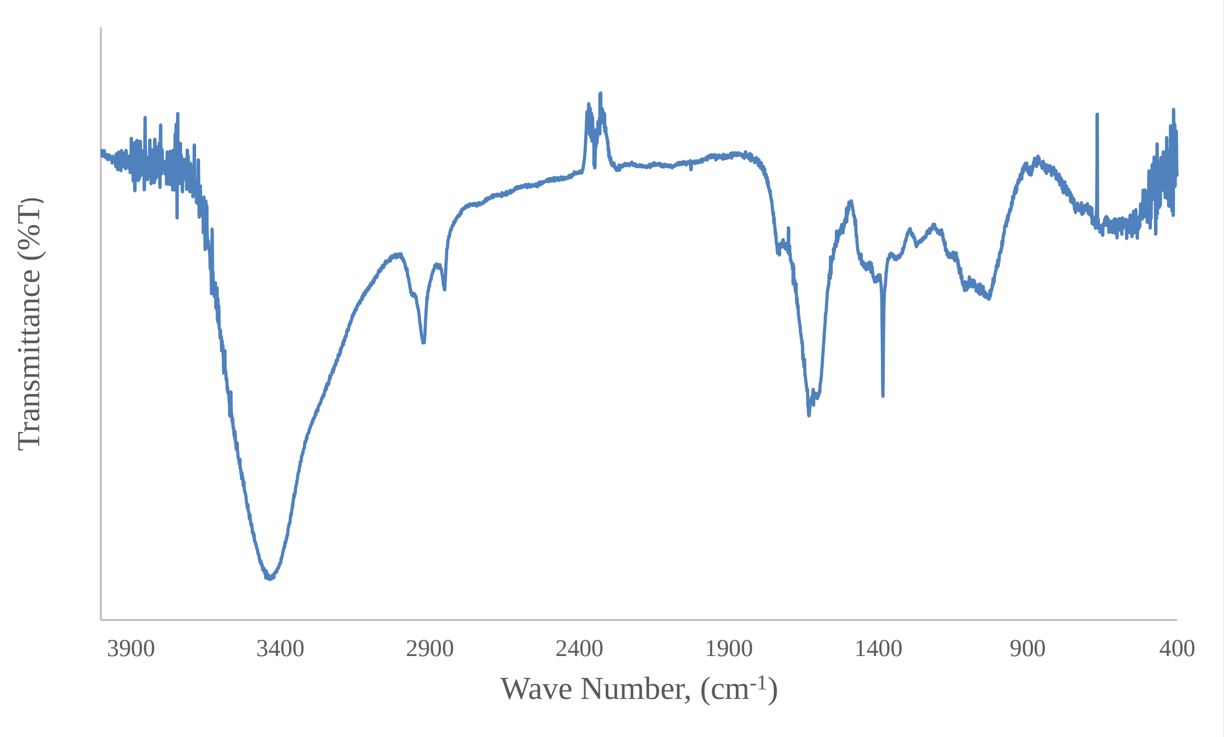


Fig 4.1 FTIR graph of raw banana peel before adsorption

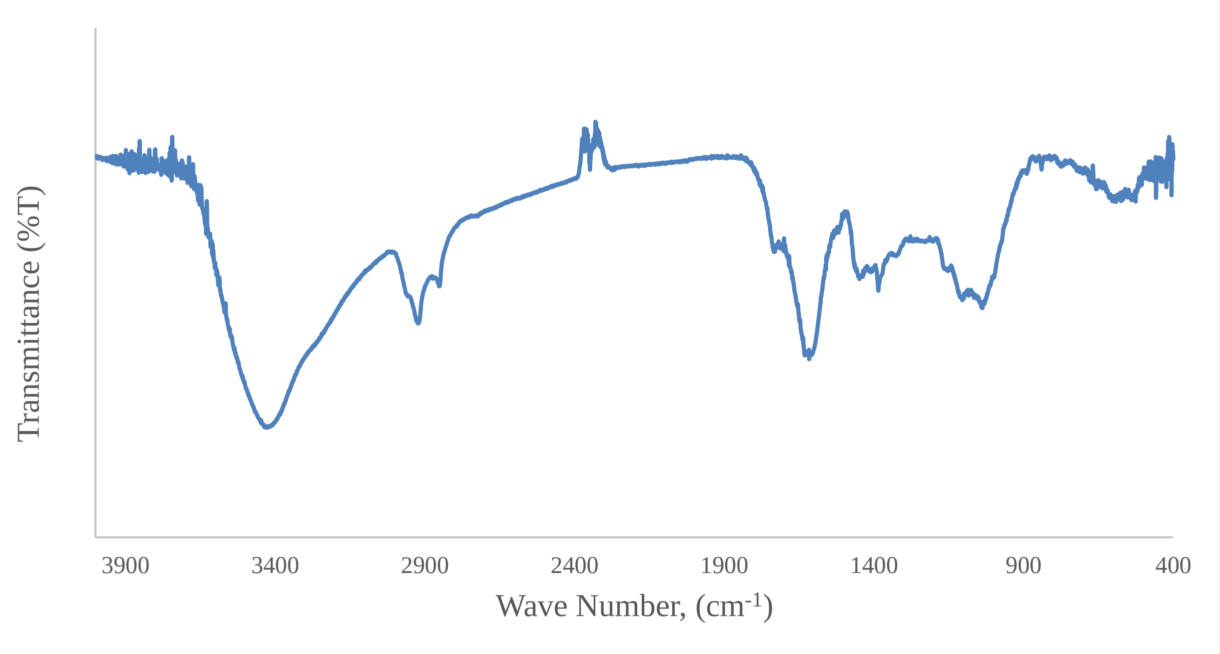


Fig 4.2 FTIR graph of raw banana peel after adsorption

The bands in the range of 1200-900 cm^{-1} have also been attributed to either Si-O or C-O stretching in alcohol, ether or hydroxyl groups. The bands in the region 450-800 cm^{-1} were also suggested to be due to alkaline groups of cyclic ketones and their derivatives, the in plane and out-of-plane aromatic ring deformation vibrations, and the out-of-plane C-H bending mode.

After adsorption, a significant reduction was observed for a series of complex bands for biosorbent. Some weak bands were also observed. Fig. 4.2 shows that many functional groups shifted to different frequency level or disappeared after adsorption, indicating the possible involvement of those groups for uptake of adsorbate. It can be observed that the sharp and intense peak at around 3,434 cm^{-1} was shifted to a lower frequency level of 3,423 cm^{-1} and after adsorption it was broad, which represented that the hydrogen bonded -OH group was involved for binding adsorbate from wastewater. The peak at 1632 cm^{-1} that corresponds to carbonyl C–O present in carbonyls, ketones, aldehydes or ester groups and to C–C present in olefinic vibrations in aromatic region was slightly decreased to 1616 cm^{-1} after adsorption. However, the minor peak of 1030 cm^{-1} shifted to slightly higher wave number of 1038 cm^{-1} after adsorption. The minor peaks at around 1270 cm^{-1} were disappeared after adsorption. The large perturbation of the adsorption band in the range of 720 cm^{-1} to 400 cm^{-1} observed on the biosorbent before adsorption and that may be due to inside structure was become weaker after adsorption. In general, shifts in adsorption bands of functional groups to lower or higher energies shows that there were a binding process taking place at the surface of the biosorbent.

4.3. Batch adsorption result

Response surface methodology (RSM), which is a collection of statistical and mathematical techniques was applied to optimize conditions for phenol adsorption. By analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which describes the chemical processes within the experimental range(Tilahun & Chun, 2016). The application of response surface methodology offers on the basis of parameter estimate, an empirical relationship between the response variable and the test variable. Box-Behnken experimental Design with three numeric factors on three levels was used. Based on BBD a total of 15 experimental runs were performed including the central point that measures process stability and inherent variability. Details of the experimental runs with the set of input parameters that conducted were given in Table 4.2. Most importantly, parameters corresponding to the central point were repeated three times to establish that the experimental data is within the normal dispersion, and repeatability is ensured. The developed BBD shows that phenol removal efficiency (% R) values obtained under different conditions varied from 39.5 to 82.8%.

Table 4.2 BBD with actual and predicted values of phenol reduction efficiency (%R)

Order		Independent variables			Investigated response (%R)	
Std.	Run	Adsorbent dosage, g	Particle size, mm	Contact time, min	Experimental result	Predicted result
1	15	10.00	0.50	120.00	61.7	62.35
2	10	30.00	0.50	120.00	82.6	80.62
3	1	10.00	1.50	120.00	54.2	55.68
4	11	30.00	1.50	120.00	75	73.95
5	8	10.00	1.00	60.00	39.5	38.29
6	3	30.00	1.00	60.00	56.4	56.56
7	4	10.00	1.00	180.00	64.3	63.39
8	9	30.00	1.00	180.00	78.8	81.66
9	14	20.00	0.50	60.00	52.6	54.01
10	7	20.00	1.50	60.00	47.7	47.34
11	6	20.00	0.50	180.00	80.1	79.11
12	5	20.00	1.50	180.00	73.4	72.44
13	2	20.00	1.00	120.00	71.2	71.40
14	13	20.00	1.00	120.00	70.3	71.40
15	12	20.00	1.00	120.00	71.8	71.40

4.4. Model fitting and response surface analysis

Data were modeled by Linear regression analysis and the statistical significance of the terms was examined by analysis of variance. The statistical analysis of the data and three dimensional plotting were performed using design expert software (V7.0.0.) trial version. The adequacy of regression model was checked by R^2, Adj R^2, Pred R^2, Adeq precision and F-test. The significance of F value was judged at 95% confidence level. The regression coefficients were then used to make statistical calculation to generate three dimensional plots from the regression model. All statistical analysis including ANOVA test, Post ANOVA statistics, lack of fit test, normal plot of residuals etc. were done for the phenol adsorption data, as shown in Table 4.3. All the tests indicated that the model is statistically acceptable. From ANOVA test, the model F-value was 175.08 with P value of less than 0.0001, which implies that the model is significant. The three factors were significant, which shows that all variables affect significantly the biosorption process. The interaction effects of the three variable were not significant, and were omitted.

Table 4.3 Analysis of variance (ANOVA) of the fitted second-order polynomial model for %R.

Source	Sum of Squares	DF	Mean Square	F-Value	Prob > F	Remark
Model	2291.85	5	458.37	175.08	< 0.0001	Significant
A	667.95	1	667.95	255.13	< 0.0001	
B	89.11	1	89.11	34.04	0.0002	
C	1260.02	1	1260.02	481.28	< 0.0001	
A^2	39.23	1	39.23	14.99	0.0038	
C^2	248.23	1	248.23	94.81	< 0.0001	
Residual	23.56	9	2.62			
Lack of Fit	22.42	7	3.20	5.62	0.1593	Insignificant
Pure Error	1.14	2	0.57			
Cor Total	2315.41	14				

The "lack of fit f-value" of 5.62 implies the lack of fit is not significant relative to the pure error. Non-significant lack of fit is good -- we want the model to fit. The regression coefficient of the model was presented in Table 4. 4. The model adequacy was further investigated using coefficient of determination, R^2. The coefficient of determination (R^2) was 0.9898, which could explain 98.98% variability of the response variable. The experimentally found and the predicted values were in a good agreement as depicted in Table 4.2. The Predicted R^2 show that the model equations %R gives good prediction with 96.82 variability. In addition, the adj-R^2 of 98.42 was in a reasonable agreement with Predicted R^2 value. The degree of precision and reliability can be explained by the low values of CV, which was 2.48. "Adeq precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 42.386 indicates an adequate signal. It indicated a good agreement between experimental and predicted values and implied that second order model equation could describe the effect of adsorbent dosage, particle size and contact time on the adsorption process very well (All the above values were based on the significant model terms and can be changed if insignificant model terms were included).

Table 4.4 The regression coefficients of the model

Std. Dev.	1.62	R-Squared	0.9898
Mean	65.31	Adj R-Squared	0.9842
C.V. %	2.48	Pred R-Squared	0.9682
PRESS	73.61	Adeq Precision	42.386

Based on regression analysis the quadratic model is suggested by the design program for this response to test for its adequacy and to describe its variation with independent variables, and can be written by considering the significant terms as follows by omitting insignificant model terms:

$$R(\%) = -11 + 2.21375\, dosage - 6.675\, particle\ size + 0.75417\, contact\ time - 0.0325\, dosage^2 - 2.2708 * 10^{-3}\, contact\ time^2 \qquad (4.1)$$

According to particularly high value of coefficient of multiple determinations (R^2) for %R (0.9898) (Table 4.4) second-order polynomial model equation provides good representation of experimental values. Moreover, for the response, mathematical model was statistically acceptable due to significant regression for the model ($p < 0.05$) (Table 4.3). Lack of fit testing confirmed adequacy of fitting experimental data to a second-order polynomial model, where p-value for lack of fit was insignificant ($p > 0.05$) (Table 4.3). Therefore, as suggested by ANOVA, Equation (4.1) would be able to adequately describe behavior of %R.

From acquired experimental data and developed model the three dimensional response surface were constructed to illustrate the interactive effect of independent variables on the response and shown in Fig. 4.3. These figures reflect the relative effects of two variables while keeping the third variable constant. The interaction effects and optimal levels of adsorbent dosage, particle size and contact time were determined by plotting the response surface curves.

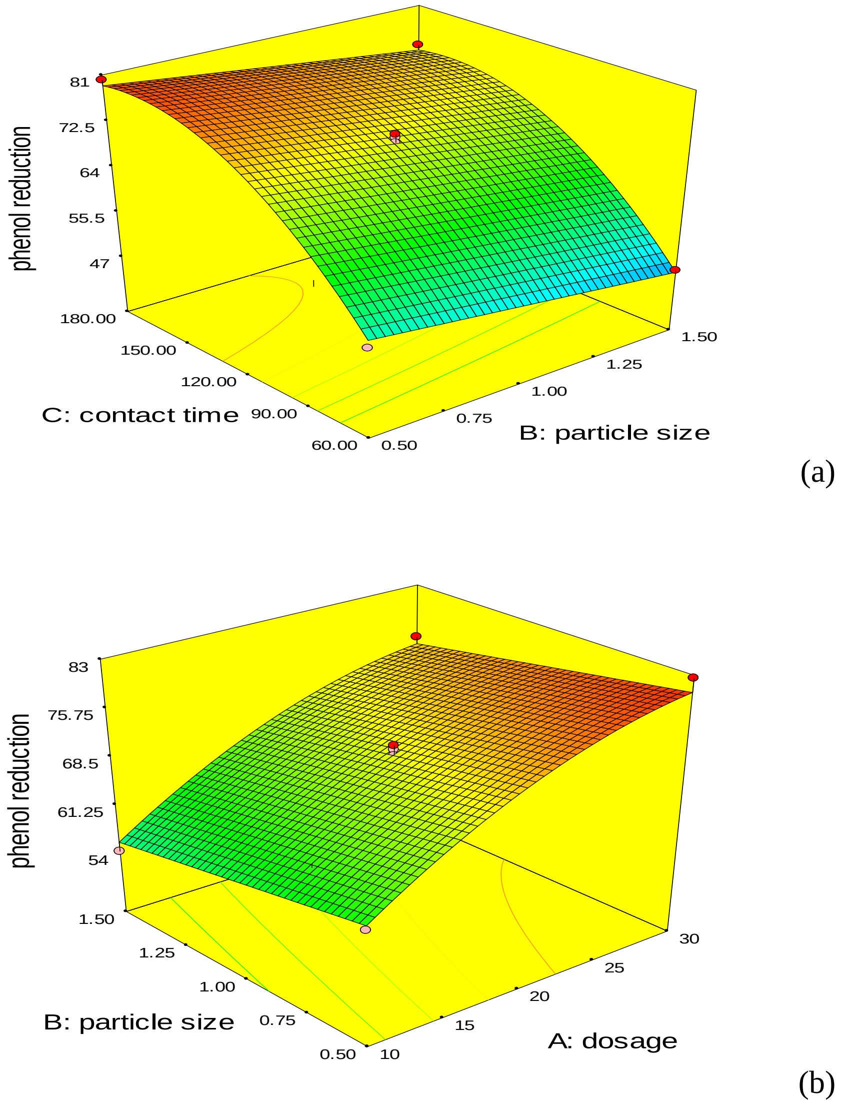
Table 4.5 Sequential model fitting for %R

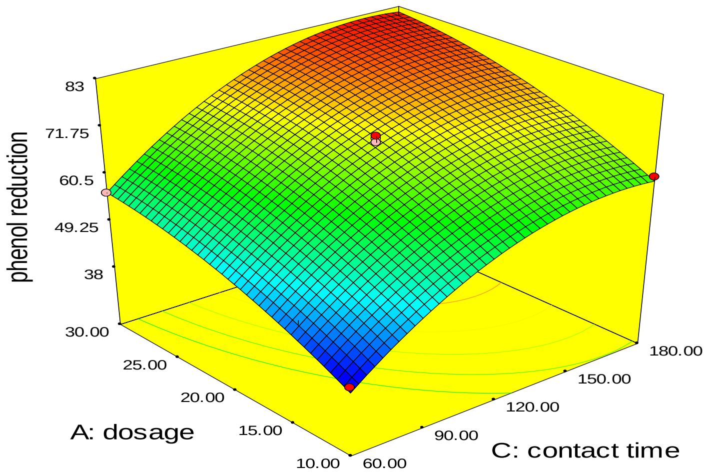
Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	R^2	Adj-R^2	Pred-R^2	Press	Remark
Linear	297.19	9	33.02	57.93	0.0171	0.8712	0.8360	0.7678	537.71	
2FI	294.93	6	49.16	86.24	0.0115	0.8721	0.7762	0.5027	1151.34	
Quadratic	19.29	3	6.43	11.28	0.0825	0.9912	0.9753	0.8656	311.25	Suggested
Cubic	0.000	0				0.9995	0.9966		+	Aliased
Pure Error	1.14	2	0.57							

The response surface curves representing the interaction effects of two variables, i.e. particle size with contact time, adsorbent dosage with particle size and adsorbent dosage with contact time on the phenol reduction were plotted as shown in Figures 4.3. Figure 4.3a shows that a maximum phenol reduction was attained at a high contact time and at considerably low particle size (0.5 mm). On the other hand, Figure 4.3b shows a maximum phenol reduction at relatively low particle size (0.5 mm) and at high adsorbent dosage (30 g/L). Effect of contact time and adsorbent dosage on adsorption of phenolic compounds by banana peel is presented in Figure 4.3c. The adsorption equilibrium of phenolic compounds was obtained after 140 min contact time and 25 g adsorbent dose with an adsorption of approximately 76% of the phenolic compounds. Almost, no remarkable improvement was observed after longer contact time and high adsorbent dose. This can explain the decrease of adsorption rates which is well illustrated by the plateau line (red shaded area) after 140 min and 25 g adsorption.

In general, at sufficient contact time and low particle size, the increment in adsorbent dose from 10 to 30 g/l results in increment of phenol removal efficiency, from 39.5 % to 82.6%, whereas the adsorption capacity decreased from 3.26 to 1.45 mg/g. It is readily understood that the number of available adsorption sites increases with the increase in the adsorbent dosage and it, therefore, results in the increase in the amount of adsorbed phenolic compound. The adsorption capacity was found to be high at low dosages. This decrease in adsorption capacity with the increase in the adsorbent dosage is mainly attributed to the non-saturation of the adsorption sites during the adsorption process.

Fig. 4.3. Three dimensional response surface plots representing interaction effects: (a) particle size with contact time, (b) adsorbent dosage with particle size and (c) adsorbent dosage with contact time



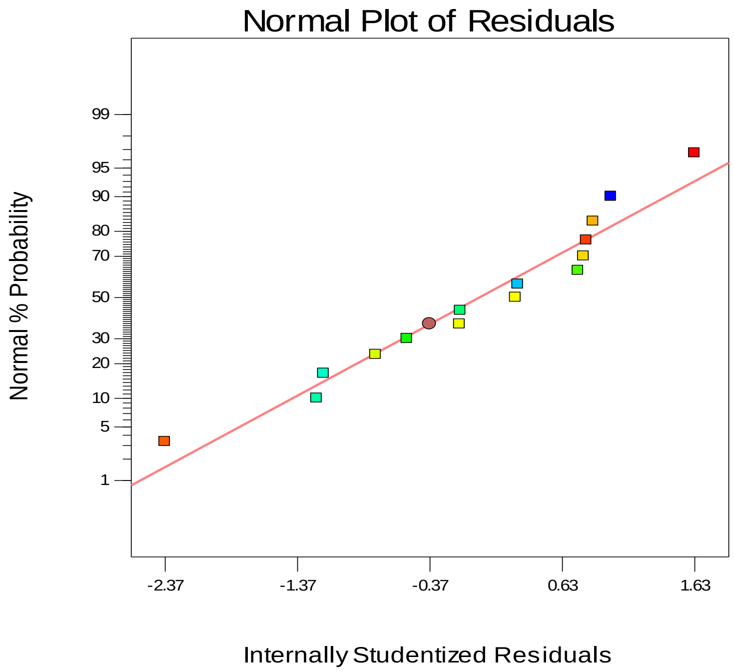


(c)

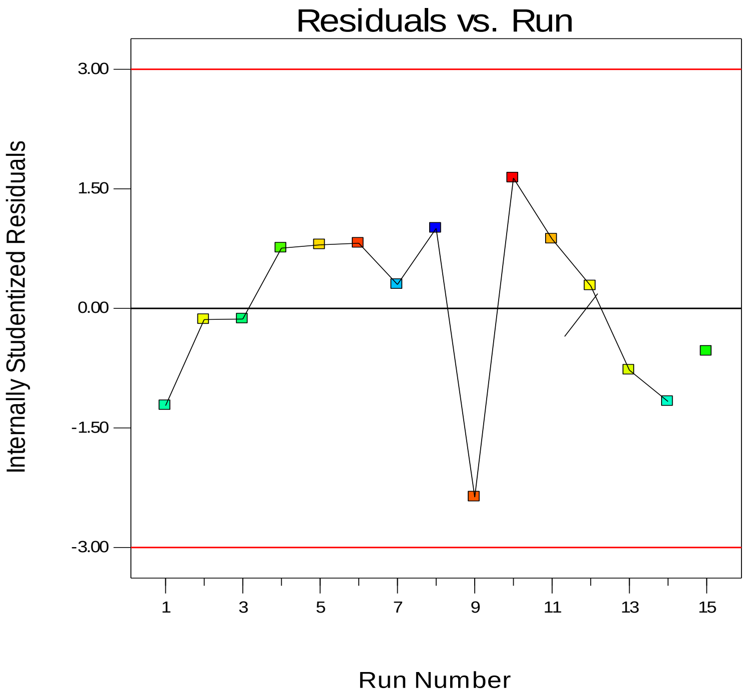
4.5. Diagnostics of model adequacy

The adequacy of the model was checked by constructing different diagnostic plots shown in Figure 4.4. The normal % probability plot of residuals for response was normally distributed, as they lie reasonably close to the straight line and shows no deviation of the variance (Figure 4.4a). The analysis of residuals, difference between the predicted and experimental responses, is another important diagnostic tool for judging adequacy of the fitted model for predicting the response. Thus, internally studentized residuals plot was constructed to facilitate the satisfactory fit of the developed model and the plot (Figure 4.4b) shows that, all the data points lie within the limits (±3). This indicates that the plot of percentage phenol removal predicted versus residual did not show any outliers, all the points were found to fall in the range of +3 to -3, which indicated that the model presents a minimal deviation of the fitted value from the observed. In another word, there was close correlation between the experimental and predicted values. The predicted values obtained from the developed model were quite close to the experimental values and lie reasonably close to the straight line and indicated the adequate agreement with real data (Figure 4.4c).

The correlations between the theoretical and experimental responses, calculated by the model, are satisfactory. Therefore, the "R^2" are in reasonable agreement with the "R^2 Adj". It can be seen that, more than 96% of the response can be well predicted by the models, indicating that the terms which were considered in the proposed models are significant enough to make acceptable predictions.

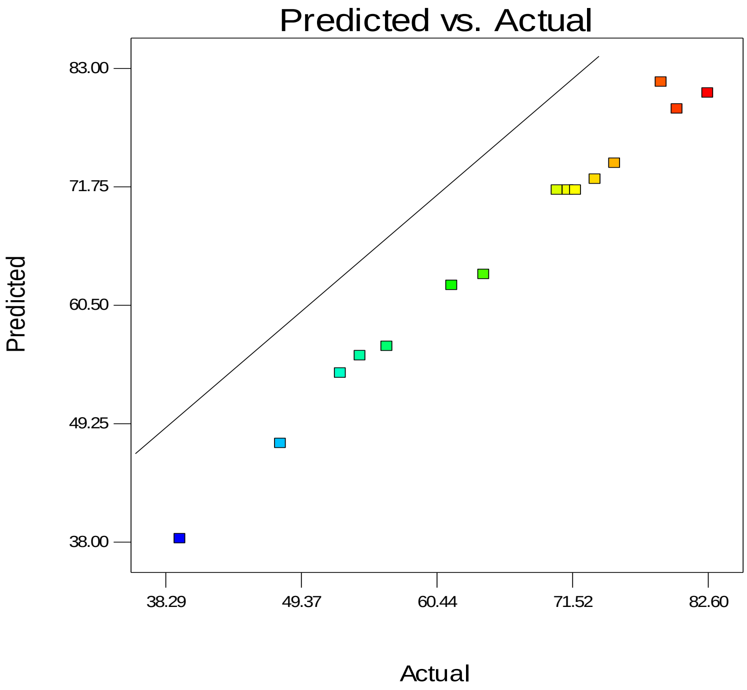

Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-2.37
-1.37
-0.37
0.63
1.63
Internally Studentized Residuals

(a)


Residuals vs. Run
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
3
5
7
9
11
13
15
Run Number

(b)

Fig. 4.4. Diagnostic plots for the adequacy of proposed model: (a) Normal vs Residual plot, (b) residual vs run plot and (c) predicted vs actual plot



(c)

4.6. Optimization and verification of the model

Derringer's desired function methodology was employed to optimize the adsorption process conditions. This function searches for combination of independent parameter levels that simultaneously satisfy the requirement for response in the design(Tilahun & Chun, 2016). The desired set of adsorption parameters were determined through optimization of the response from the obtained model equation (eq. 4.1). So in order to obtain the maximum %R, the predicted combination of parameters was as follows: adsorbent dosage of 20.0 g, particle size of 0.53 mm and contact time of 129.98 min. Under these conditions, the model predicted %R of 76.4259% with a desirability value of 1. To validate the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized process conditions and mean %R value of 75.3 ± 0.34% was obtained. The results are closely related with the data obtained from optimization analysis using desirability functions, indicating BBD incorporate with desirability function could be effectively used to optimize the parameters that affect phenol reduction efficiency (%R).

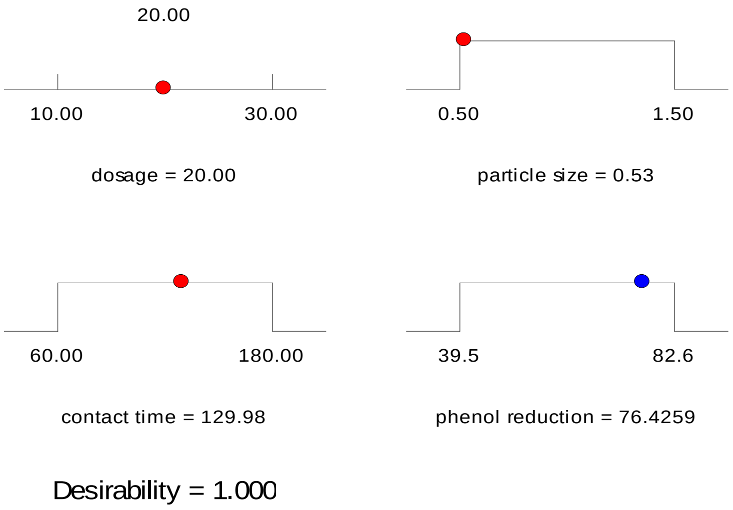


Fig.4.5: Ramp display of desirability at and corresponding optimum values

4.7. Adsorption isotherm

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Several models have been published in the literature to describe the equilibrium adsorption systems. In this paper the two classical models, Langmuir and Freundlich, were fitted to determine equilibrium relationship.

The batch adsorption characteristics of phenol by banana peel were studied at varying adsorbent dosage range from 5 to 30 g. The studies were performed at 0.53 mm particle size and 129.98 min contact time, which is the optimum value for adsorption as indicated by ANOVA. The data obtained from the study was used to determine best adsorption isotherms that fits the pattern.

The linear regression equation was calculated from linear plots of Ceq/q vs Ceq (fig 4.6) for Langmuir isotherm, and Log C_{eq} vs Log q_{eq} for Freundlich isotherm. From these linear regression equations, the values of the Langmuir constants, b and q_m, and Freundlich constants, K_F and n, were calculated from the intercepts and slopes of the plots, respectively, and are shown on Table 4.6. The correlation factor value R^2 of 0.959 which is more close to unity for the Langmuir isotherm model shows a better fit of the experimental data by means of this isotherm, i.e. Langmuir isotherm is the best adsorption isotherm that fits banana peel phenol adsorption data than the Freundlich isotherm. In addition, the R_L values of 0.19 shows the adsorption process is favourable and banana peel is good adsorbent for phenol removal. This proves the monolayer adsorption and the adsorbate is chemically adsorbed at a fixed number of well-defined sites of biosorbent.

Table 4.6 Langmuir and Freundlich isotherms parameters for phenol adsorption by banana peel

Langmuir isotherm				Freundlich isotherm		
q_m, mg/g	b, l/mg	R^2	R_L	K_F, $(mg/g(l/mg)^{1/n})$	n	R^2
4.12	0.08	0.959	0.19	0.082	0.826	0.9083

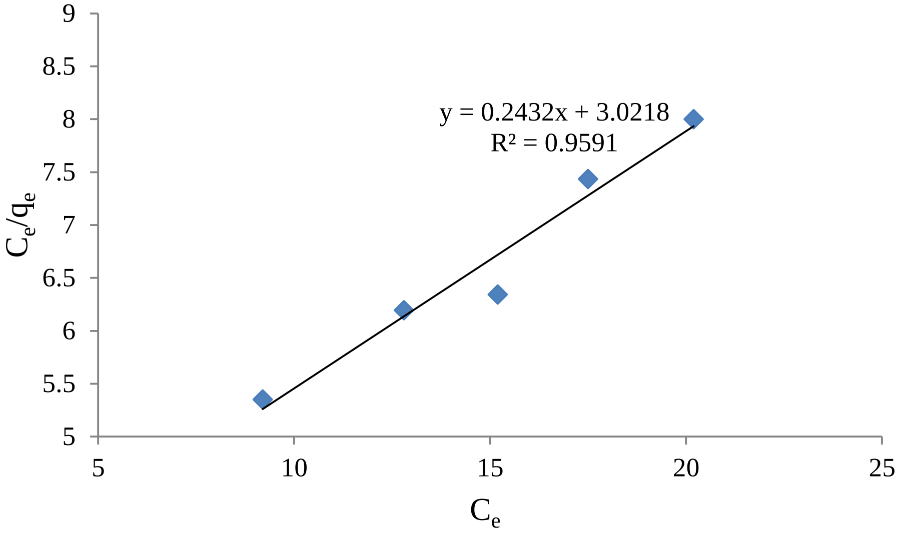


Fig 4.6 Langmuir isotherm plot for the adsorption of phenol on banana peel

4.8. Adsorption kinetics

The capability of pseudo-first-order (PFO), pseudo-second-order (PSO) and diffusion kinetic models were examined in this study at optimum parameter values (adsorbent dosage 20 g; particle size 0.5 mm; and contact time 129 min). The PFO, PSO and diffusion model constants, were determined from the slope and intercept of the corresponding plots and were listed in Table 4.7. As shown in Table 4.7, the correlation coefficient of pseudo second-order equation is higher than that of pseudo-first-order and diffusion model, and also the theoretical q_e value calculated from pseudo-second-order was more close to the experimental q_e value than pseudo-first order. In this case, the fitting of the experimental data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient (R^2=0.998).

Table 4.7 kinetic parameters for different kinetic models

$q_{e,exp}$, mg/g	Pseudo-first order			Pseudo-second order			Diffusion model		
	K_1, min^{-1}	$q_{e,cal}$, mg/g	R^2	K_2, min^{-1}	$q_{e,cal}$, g/mg.min	R^2	K_p, mg/g.min	C, mg/g.min	R^2
2.015	0.032	3.857	0.96	0.00576	2.84	0.998	0.149	0.201	0.961

An analysis of the data in Table 4.7 suggests that the kinetics of adsorption of phenol onto banana peel can be explained accurately by the PSO kinetic model. Therefore, pseudo-second order model is the best choice among the three kinetic models to describe the adsorption behavior of phenolic compounds onto banana peel, suggesting that the pseudo-second-order adsorption mechanism is predominant and the overall rate of the adsorption process appears to be controlled by the chemical reaction, which may be partly due to the hydrogen-binding between the hydroxyl groups of phenolic compounds and the active functional groups in the banana peel.

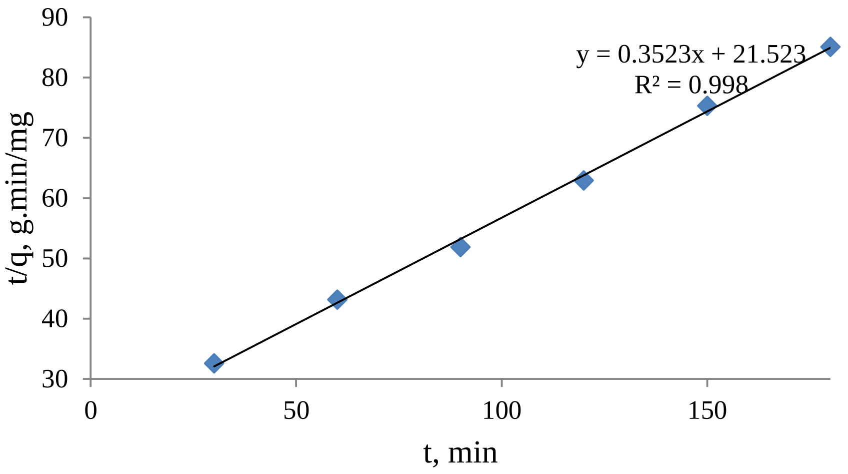


Fig 4.7 Plot of the pseudo second-order kinetic for the adsorption of phenol onto banana peel.

4.9. Comparison of maximum phenol removal

The maximum removal of phenol by adsorption onto banana peel biosorbent was found to be 76.426 %. In the previous studies reported in the literature, the removal percentage of phenol was found to be 85% on activated carbon prepared from Rhazya stricta at 45 ^{0}C temperature, 3 pH and 0.5 g/L adsorbent dose(Hegazy et al, 2014); 87.6% on activated carbon produced from tobacco residues at 5 g/L adsorbent dose(Kilic et al, 2011) and the percentage removal of 2-chlorophenol was found to be 91.25% by banana peel biosorbent at 0.2 g adsorbent dose/10ml, 6 pH and 60 min shaking time(Ibrahim et al, 2013). The overall treating technique resulted in the global reduction of phenol less than 95% which is better than all the above results. And also the adsorption capacity from the present study was compared with another biosorbent from previous studies as indicated in the Table 4.8. The value obtained in this study was comparable with the literature value. However, this value was low as compared with the adsorption capacity of banana peel obtained by Achak et al, 2009. This is possibly due to the presence of other competing groups in the wastewater such as mineral component, other colorant component, and organic compounds for biosorbent active site. It may also be due to the low concentration of phenol in this spent wash as compared to that of olive mill wastewater, which is above 13.5 g/L. This low concentration indicates that there is low probability for phenol to reach adsorbent active site as it inhibited with another component.

Table 4.8: Comparison of adsorption capacities of biosorbent for phenol removal from waste water

Adsorbent	Adsorption capacity (mg/g)	Reference
SSBA activated with H_2SO_4	26.16	Bousba & Hassen, 2014
Fly ash	27.9	Grassi et al., 2012
Bagasse fly ash	23.83	Srivastava et al., 2006
Coal fly ash	17.1	Sarkar and Acharya, 2006
Rice husk	4.5	Ahmaruzzaman M. and Sharma D.K., **(2005)**
Tectona grandis sawdust	2.82	Mohanty et al, 2005.
Sterculia alata nutshell	2.8	Mohanty et al, 2006.
Evaluation of Barley	0.067	Maleki et al, 2010
Banana peel	2.015	This paper

4.10. Batch Anaerobic digestion result

A batch laboratory experiment was carried out to investigate the effect of biodegradation of adsorption pretreated distillery spent wash as an alternative treatment method. The treatment was evaluated in terms of the effluent-COD, and phenol content reduction and also in terms of biogas quality. The degradation process began rapidly, which suggests that the inoculum appropriately adapted with both raw and pretreated vinasse. The batch experiment started generating biogas on the first day. Less volume of gas was generated in the first 2 days. After day #2, there was sudden increase of collected gas volume. The process continued generating biogas during the next few days. However, after day #5 small amount of gas was generated. This may be due to the low COD concentration; the methanogens did not have enough food to grow to significant numbers to start generating substantial volumes of methane. After the 8th day, the batch stopped generating biogas altogether.

The COD removal of adsorption pretreated vinasse was higher than that of raw vinasse. At the end of the treatment method, the overall effluent COD removal percentage near to 69% for raw vinasse and 84% for pretreated vinasse were obtained, respectively. This shows that the raw vinasse is more resistance to degradation than pretreated vinasse, which can be attributed to higher phenol-compound content. On the other hand, in terms of biogas volume and its quality the pretreated sample shows a favorable result as compared to that of the raw one. i.e. the volume of generated biogas and its methane potential was higher than that of raw spent wash. The cumulative biogas volume generated by pretreated sample was 12.4 l/l of vinasse with average methane content of 59.6%. The raw sample yielded 11.7 l/l of vinasse with an average methane content of 56%. The methane percent values were reasonably agreeing with the value claimed by Tippayawong and Thanompongchart, (2010) and the value achieved by Patyal, (2016) which is 57%. And also the biogas yield of 12.4 l/l of vinasse was close to the theoretical value of 14 l/l of vinasse(Souza et al, 2011).

Table 4.9: Physicochemical properties of treated effluents

Sample	Property	Pretreatment		Anaerobic digestion	
		Before	After	Before	After
Pretreated	COD, mg/L	92,500	77,700	77,700	14,800
Pretreated	Phenol, mg/L	52.8	12.447	12.447	< 2.64
Raw	COD, mg/L	-	-	92,500	28,675

As observed above, the combination of the treatment process resulted in global degradation of COD from 92,500 to 14,800 mg/mL, whereas 92,500 to 28,675mg/L in COD reduction was achieved in raw sample, which indicates the combination process was an effective alternative for degradation of distillery wastewater to treat it. On the other hand, the generated gas has above 55% methane content, and it would be a valuable fuel. Thus, anaerobic digestion coupled with biosorption process have dual advantages of pollution control and production of fuel.

The Cumulative gas yields were also calculated as the ratio of cumulative gas volumes to cumulative COD reacted. In the present work the methane yield observed at the end of the batch digestion was around 0.129 mL-CH_4/mg-COD reacted for pretreated vinasse and 0.1032 mL–CH_4/mg–COD reacted for raw vinasse. This yield was low as compared to the theoretical methane yield, which is 0.350 mL-CH_4/mg-COD reacted, at standard temperature and pressure, when assuming that all COD reacted was converted to exit the reactor as methane(Stefen L.K., 2015). The value show that the removed COD in pretreated sample was efficiently converted to CH_4 than the raw one, which favors the pretreatment step.

The most remarkable result was the overall 95% reduction in total phenols content, whose final concentration was below the detection limit of the used technique. On the other hand, the chemical oxygen demand was reduced to nearly 84% with pretreated sample. The percent removal of these parameter was comparable with the value obtained in different researches. Lekshmi S.R. (2013), studied the performance of Hybrid Anaerobic Baffle Reactor (HABR) for the treatment of distillery wastewater and obtained an overall COD removal efficiency of 92% at the end of the whole cycle of process. Paz Pino et al, (2014), concluded a global diminution close to 93% in

BOD5; 83% in COD and up to 99% in phenol content by combining anaerobic digestion with another pretreatment method.

In terms of biogas quality, the adsorption pretreated vinasse also shows a favorable result with high amount of CH_4 and CO_2 contents and with trace amount of other gases, 4.1%. But, in case of raw vinasse the percentage of other gases was increased to 9.5%, which shows that biodegradation of the raw vinasse results in biogas with high content of impurity. This may limit the usage of these gas for different purposes which are sensitive to the percentage content of impurities.

Table 4.10: Biogas quality

Sample	Biogas quality, %		
	CH_4	CO_2	Other gases
Raw	56.2	34.3	9.5
Pretreated	59.6	36.3	4.1

5. Conclusion and Recommendation

5.1. Conclusion

Bio-sorbents are certain types of biomass used to bind and concentrate pollutants from even very diluted aqueous solution. In the present research the preparation of alternative biosorbent from banana peel as a cheap and locally available material was successfully achieved for phenolic wastewater decontamination. Banana peel, a discarded agricultural waste, was used to produce bio-adsorbent through easy and environmentally friendly processes. This natural bio-sorbent was evaluated for adsorptive removal of phenolic compound from distillery wastewater. The characterization results showed that this bio-sorbent has potential binding sites and functional groups which support the adsorption process. To determine the effects of various operating conditions (adsorbent dose, particle size and contact time) and their interactions on the adsorption of phenol, a Box-Behnken design was performed. ANOVA, F test showed that the three tested variables were statistically significant. However, adsorption was found to be highly influenced by adsorbent dosage and contact time. The prepared biosorbent showed that high adsorption efficiency for the removal of phenol from this wastewater and a value of 76.426% phenol reduction and 22% COD reduction was obtained. Equilibrium study show that the data fit very well in the Langmuir equation of monolayer adsorption, this result indicate the adsorbate is chemically adsorbed at a fixed number of well-defined sites. The values of R^2 obtained from pseudo second-order model was 0.998, indicating that the adsorption process obeyed the pseudo second-order model. Finally, the adsorption experiments indicated that Banana peel biosorbent was efficient adsorbent for the removal of phenol from distillery wastewater.

On the other hand, laboratory experiment was carried out to investigate the effect of biodegradation of adsorption pretreated distillery spent wash. The treatment was evaluated in terms of the effluent COD and phenol content reduction, and in terms of generated biogas volume and quality. The pretreatment step alone had 76.425% phenol reduction and relatively low COD reduction, which is 22%. However, the combination of treatments resulted in COD reductions of 84% and 95% of the effluent phenol content. The cumulative biogas volume generated by pretreated sample was 12.4 l/l of vinasse with 59.6% methane, which shows that it is a valuable fuel. Therefore, anaerobic digestion coupled with biosorption process have dual advantages of pollution control and production of fuel.

5.2. Recommendation

Distillery wastewater handling and treatment is the area that need to be given a paramount attention. In this paper, it is found that the combination of adsorption and anaerobic digestion is an effective treatment method for distillery wastewater. The following recommendations are made for further study.

- In the present work, prepared biosorbent is characterized only with FT-IR test, thus application of additional characterization method is recommended for further work.
- Adsorbent dose, particle size and contact time are the three parameter that have been optimized in the present work. However, there are parameter that have effects on the biosorption process such as solution pH and mixing rate. Further improvement of the process by taking in to consideration these parameters is recommended for further study.
- Banana peel is used as natural adsorbent with any modification in this paper. The adsorption capacity of this biosorbent can be enhanced through different activation process for further study.
- Following adsorption stage, the degradation process is conducted at specified condition. However, optimization of this process is required for further study.
- The anaerobic digestion effluent is expected to be rich in mineral composition such as potassium, phosphate, nitrate etc. which shows that the effluent has potential for using it for fertirrigation on cane plantation fields. However, the potential must be supported with further research so that constituents are exactly identified and appropriate technologies selected.
- Under the present study, only the technical feasibility of the process is considered. Thus, detail of economic feasibility should be studied to show whether the process is economically feasible.

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Appendices

Appendix A: List of Tables

Table A.1: Absorbance of the standard phenol solution used to plot calibration curve

Concentration, mg/l	Absorbance
0	0
1	0.037
2	0.187
3	0.284
4	0.310
5	0.428

Table A.2: Batch adsorption result

Label	Absorbance	Sample phenol concentration	Original sample phenol concentration, mg/l	%phenol reduction
1	0.188	2.02	20.2	61.7
2	0.067	0.92	9.20	82.6
3	0.232	2.42	24.2	54.2
4	0.111	1.32	13.2	75
5	0.316	3.19	31.9	39.5
6	0.218	2.30	23.0	56.5
7	0.173	1.89	18.9	64.3
8	0.089	1.12	11.2	78.8
9	0.240	2.50	25.0	52.6
10	0.269	2.76	27.6	47.7
11	0.081	1.05	10.5	80.1
12	0.119	1.40	14.0	73.4
13	0.133	1.52	15.2	71.2
14	0.138	1.57	15.7	70.3
15	0.129	1.49	14.9	71.8

Table A.3: Data for adsorption isotherms

Adsorbent dosage, gm	C_e, mg/L	q_e, mg/gm	Log C_e	Log q_e	C_e / q_e
5	39.88	5.10	1.436	0.7075	7.825
10	22.8	3.26	1.305	0.5132	7.592
15	17.52	2.356	1.243	0.3716	7.437
20	11.93	1.88	1.182	0.2742	6.345
25	9.92	1.60	1.107	0.2041	6.196
30	7.76	1.45	0.964	0.1614	5.35

Table A.4: Data for kinetic studies

Time, min	C_t, mg/L	q_t, mg/gm	t/q_t, min.gm/mg	ln(q_e-q_t)	$t^{1/2}$
30	34.43	0.92	32.61	0.0913	5.477
60	25.03	1.389	43.197	-0.4732	7.746
90	18.11	1.734	51.903	-1.2801	9.487
120	14.678	1.906	62.959	-2.2443	10.954
150	12.989	1.991	75.339	-3.8632	12.247
180	10.51	2.115	85.106	-	13.416

Table A.6. FTIR analysis of the cellulose, hemicellulose and lignin components (Chen et al, 2015)

Range of wave number, cm^{-1}	Absorption band
3460-3412	O-H stretching
3000-2842	C-H stretch in methyl and methylene group
2860-2970	$C-H_n$ stretching with alkyl, aliphatic and aromatic
1738-1709	C-O stretch in unconjugated ketone, carbonyl and ester groups
1675-1655	C=O stretching in conjugated aryl ketones
1605-1593	Aromatic skeleton vibrations plus C-O stretching
1515-1505	Aromatic skeleton vibrations
1470-1445	C-H deformations (asym in $–CH_3$ and $–CH_2$)
1430-1422	Aromatic skeleton vibrations combined with C-H in plane deformation
1370-1365	Aliphatic C-H stretching in CH_3 and phenol
1270-1266	Ring plus C+O stretching
1233-1214	C-C + C-O + C=O stretching
1166	Typical for lignin; C-O in ester groups (conjugated)
1140	Aromatic C-H in-plane deformation
1128-1125	Typical secondary alcohol and C-O
1110	Aromatic C-H deformation
1086	C-O deformation in secondary alcohol and aliphatic ether
1035-1030	Aromatic C-H in plane deformation plus C-O deformation in primary alcohols plus C-H stretching (unconjugated)
990-966	-HC=CH- out-of-plane deformation (trans)
925-915	C-H out-of-plane (aromatic ring)
895-885	C-H deformation vibration; CH_2 wagging
858-817	C-H out-of-plane in different positions
700-400	C-C, C-H and O-H stretching with out-of-plane bending mode of hydroxyl and methyl.

Appendix B: List of figures

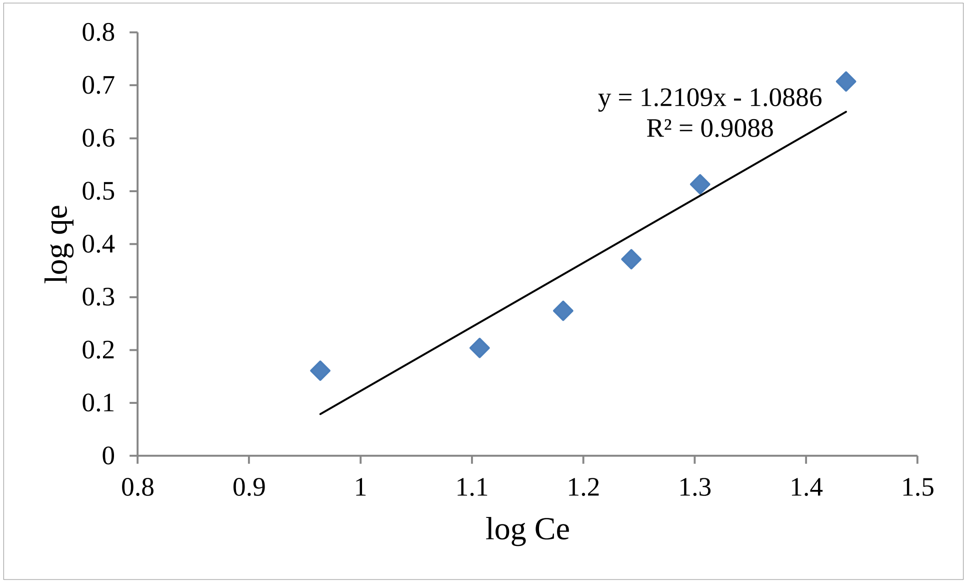

Fig B.1: Freundlich isotherm plot

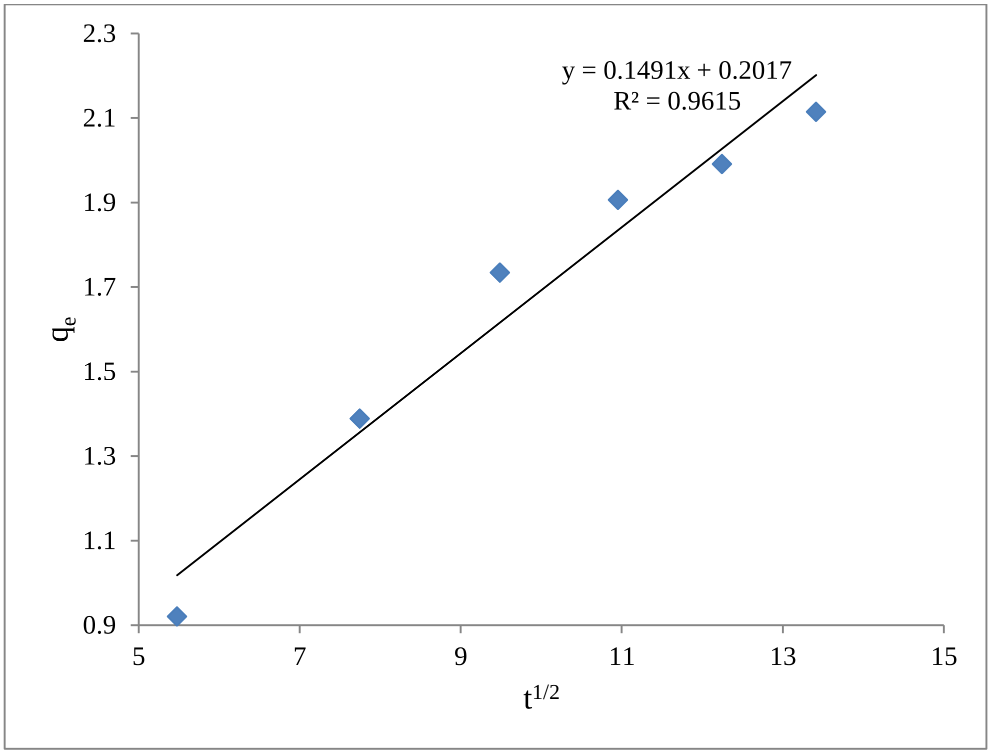

Fig B.2: Diffusion model plot

Appendix C: Lab work pictures

Fig C.1: Fresh and grounded Banana peel

Fig C.2: Batch adsorption process

Fig C.3: Distillation setup

```
OTO     510.0   nm    -0.000   Abs   PARA
   No.      Abs       K * Abs        (F 1
 1   -1    -0.000    -0.001          DELE
 2   -1    -0.000    -0.000          (F 2
 2   -2     0.037     0.371          SAMP
 2   -3     0.187     1.874          (F 3
 2   -4     0.284     2.836          PRIN
 2   -5     0.205     2.052          (F 4
 2   -6     0.264     2.644
 2   -7    -0.105    -1.054
 2   -8    -0.105    -1.053
ess START to measure                 16:2
                                     03/2
```

Fig C.4: UV-Vis determination of phenolic compound

Figure C.5 Laboratory scale Anaerobic digestion setup

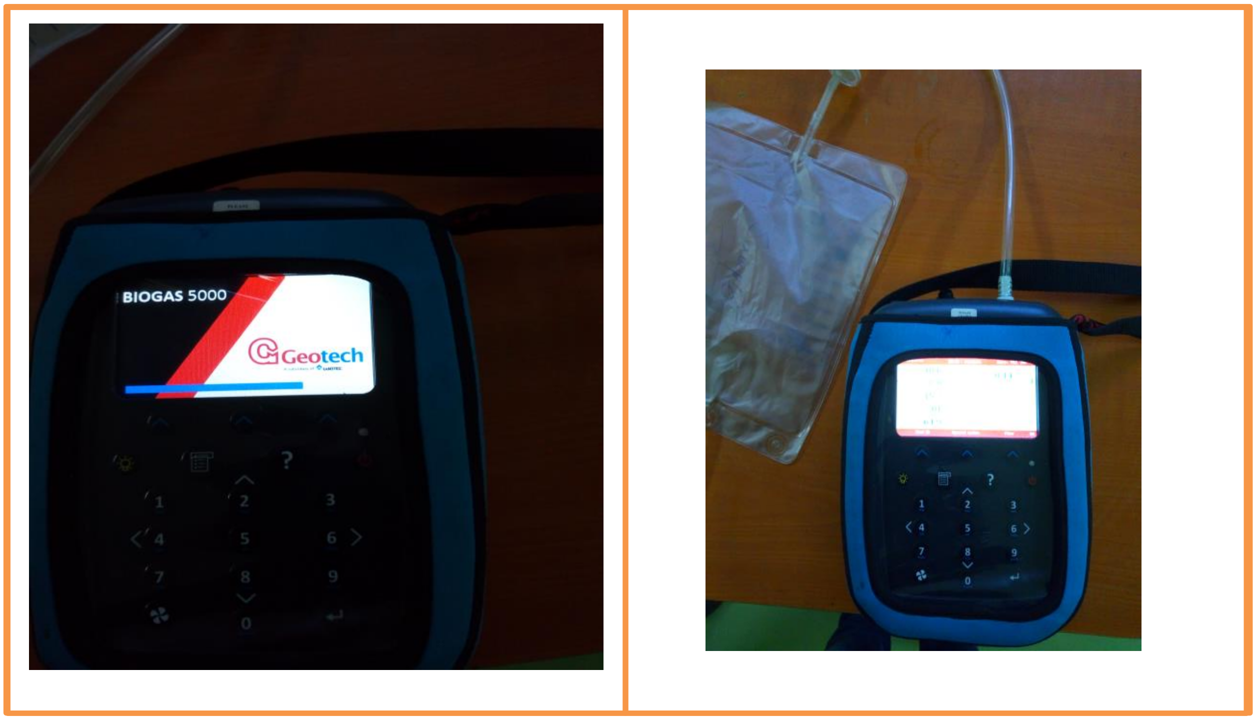

Fig C.6 Determination of biogas quality with gas analyzer