Characterization of Sugar Industry Effluent and Reduction of BOD and COD Contributing Pollutants by using Sugarcane Bagasse Fly Ash (SBFA), Case Study: Wonji -Shoa Sugar Factory

By:

Yisak Negewo

Thesis Submitted to Department of Applied Chemistry

School of Natural Science

Presented in Partial Fulfillment of the Requirements for Degree of Master of Science in Applied Chemistry (Specialization in Industrial Chemistry)

Office of Postgraduate Studies

Adama Science and Technology University

Adama, Ethiopia

September, 2018

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Advisor: Tegene Desalegn (PhD)

Co-Advisor: Dereje Tsegaye (PhD)

Adama, Ethiopia

September, 2018

Approval of Board of Examiners

We, the undersigned, members of the Board of Examiners of the final open defense by Yisak Negewo have read and evaluated his thesis entitled "Characterization of Sugar Industry Effluent and Reduction of BOD and COD Contributing Pollutants from Sugar Industry Effluent by using Sugarcane Bagasse Fly Ash (SBFA), Case Study: Wonji -Shoa Sugar Factory" and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of Master's

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_______________	_______________	_______________
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_______________	_______________	_______________
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Internal Examiner	Signature	Date
_______________	_______________	_______________
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DECLARATION

I hereby declare that the work which is being presented in this thesis entitled "Characterization of Sugar Industry Effluent and Reduction of its BOD and COD Contributing Pollutants by using Sugarcane Bagasse Fly Ash (SBFA), Case Study: Wonji -Shoa Sugar Factory'' is original work of my own, has not been presented for a degree in this or other universities and all sources of materials used for this thesis work have been fully acknowledged.

Name: Yisak Negewo Signature: ____________________

Place: Adama Science and Technology University

Date of submission: ____________________

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

Dr. Tegene Desalegn	____________________	__________
Advisor' Name	Signature	Date
Dr. Dereje Tsegaye	____________________	__________
Co-advisor	Signature	Date

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I dedicate this thesis work to my family specially my mother W/ro Amane Nure who has encouraged me during my study time by encouraging me day and night from beginning to end of the study.

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LIST OF ABBREVIATION AND ACRONOMYS

AOP	Advanced Oxidation process
ASTM	American Standard Testing Method
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
FTIR	Fourier Transform Infrared
NEQS	National Environmental Quality Standard
SBFA	Sugarcane Bagasse Fly Ash
SEM	Scanning electron microscopy
SS	Suspended Solid
TDS	Total Dissolved Solid
TH	Total Hardness
TOC	Total Organic Carbon
TSS	Total Suspended Solid
UN	United Nations
XRD	X-ray diffractometry

ABSTRACT

The aim of this study was to characterize sugar industry effluent and reduction of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of wastewater from industrial sugar effluent by using sugarcane bagasse fly ash (SBFA) (sugar industry solid waste). Sugar industry is one of the most polluting industries producing huge amount of wastewater effluents. These industries have been recognized to cause pollution by discharging effluent into receiving environment especially to the nearby rivers. . Industrial wastewaters result from spills, leaks, and product washing and water resulting from cooling processes. pH and conductivity of effluent were measured on site while other were determined in laboratory. The complete study was done in batch mode to investigate the effect of operating parameters. Proximate analysis of SBFA shows ash content percentage is high. Characterization of the SBFA by Fourier transform infrared spectroscopy (FTIR) showed the presence of hydroxyl, silanol and other functional groups, whereas X-ray diffraction analysis indicated its amorphous nature. Moreover, scanning electron microscopy analysis showed a heterogeneous and irregular shape of pores. Adsorption isotherm was also studied besides the calculation of optimum treatment parameters for maximum reduction of COD and BOD concentration from effluent of sugar industry. The maximum COD removal recorded was 67.14% at the optimum condition of adsorbent dose of 4 g in 100 mL, contact time of 60 min, pH 8 and initial COD concentration 1750 mg/L, whereas the BOD of effluent removal was 44.82% at adsorbent dose of 4 g, contact time 60 min, pH 6 and initial BOD concentration 879 mg/L. In order to understand the mechanism of the adsorption process, the sorption data were analyzed using Langmuir and Freundlich isotherm models. The linear form of both models was fitted with the data and resulted in good conformation with both models. Finally, the rate of the adsorption process was investigated using Pseudo-first order kinetics and Pseudo second-order kinetic models. Both kinetics models were found to be well fitted to the data obtained (both Pseudo-first-order kinetic and pseudo-second-order kinetics). The finding of the study revealed that SBFA is effective adsorbent for reduction of organic pollutants.

Keywords*: Bagasse fly ash, BOD, COD, Adsorption, wastewater, Isotherm*

1 INTRODUCTION

1.1 Background of the study

Environmental pollution has been recognized as one of the major problems of the modern world. The problem of environmental pollution on account of essential industrial growth is, practical terms, the problem of disposal of industrial water, whether solid, liquid or gaseous(Abraham *et al*.,2014).

Water is important for life and for processing various materials in industry. Living organisms cannot exist without water, and almost all industries require water to operate. However, in the 21stcentury the growing population and industrial sector have contributed significantly to a reduction in quality of water and its availability as result of discharge of untreated wastewater to the environment (Oljira, 2016).

Sugar industry is one of the main sources of pollutants to surface water bodies and the adverse impacts of sugar mills effluents are well known. These effluents carry load of oxygen demanding wastes and suspended matters which may result in depletion of dissolved oxygen and shocking of fish gills resulting in the extinction of aquatic life. The sugar effluent is the most complex caramelized and cumbersome waste having very high BOD, COD, TSS and TDS contents (Buvaneswari *et al*., 2013).

In the recent era great concern has been given throughout the universe regarding the environmental pollution from so many aspects since of rapid industrialization and subsequent urbanization. But as for the earlier concept of disposal of treated/untreated wastewater from the industry, treated/untreated wastewater has been drained into the rivers, nearby lakes or streams and by that river body it may spreading over a huge area till that water reaches its final destination (Shiva and Srikantaswamy, 2015). Therefore, the polluted water directly or indirectly affects the lives of flora and fauna which are situated nearby the water sources not only in the industrial area but also in agricultural fields, river and river beds(KNath *et al*., 2005).

Industries are the largest user of water and causes water pollution. In recent years, increasing awareness of the environmental impact of chemical and biochemical oxygen demands (COD and BOD) has prompted a demand for the purification of industrial wastewaters prior to discharge into natural waters. Pollution of water by organic chemicals has become serious environmental concern (Lakdawala, 2016). The conventional wastewater treatment technologies being adopted in industrialized nations are quite expensive to build, operate and maintain. Moreover, to comply with stringent environmental regulations and for restoration of safe environment, it has become imperative to find less costly and easily adaptable treatment technologies for the wastewater (Rani *et al*., 2008). Cane sugar bagasse is an industrial waste which is used worldwide as fuel in the same sugar-cane industry. The combustion yields ashes containing high amounts of unburned matter, silicon and aluminum oxides as main components. These sugar bagasse fly ashes (SBFA) have been chemically, physically and mineralogically characterized, in order to evaluate the possibility of their use as an adsorbent in surface chemistry (Milan, *et al*., 2012). The carbon content of fly ash plays a significant role during the adsorption of organic compounds. The adsorption capacity of an adsorbent was found to increase with its carbon content (Rani and Dahiya, 2006). The annually production of sugarcane fly ash at world level is 47,800 million tones. It has good porous structure and adsorption capacity (Abdulkarim *et al*., 2014).

The organic content of wastewater is traditionally measured using lumped parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS). Pollution is the contamination of earth‘s environment with materials that interfere with human health, the quality of life or the natural functioning of ecosystem (living organism and their physical surroundings) (Birendra and Inder, 2015).

1.2 Statement of the problem

Most industries in Ethiopia lack efficient effluent treatment plants. Therefore they discharge their effluents into water bodies without adequate treatment prior to the discharge. The nature of sugar mill effluents poses the most critical danger to the natural ecology of the local water bodies absorbing the wastewaters, with more muted impacts also likely for the fertility of the agricultural land irrigated with the effluents and the populations exposed through using contaminated groundwater. The most notable revelation of the chemical analysis, the presence of an extremely high BOD and COD levels, portends acute adversity for the survival of aquatic life through a diminished oxygen supply and the production of toxic hydrogen sulfide. The resultant foul-smelling septic conditions would also render the water body a nuisance for local residents and spoil any aesthetic value of the natural environment (Saranraj and Stella, 2014).

The technologies for removal of pollutants from waste water include coagulation, flocculation process, membrane filtration and oxidation process. These methods are expensive, complicated, time consuming and required skilled personnel. Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutant removal. For removal of the organic contaminants from industrial waste water adsorption has become one of the best effective and economical methods. The method of adsorption using commercial activated carbon is costly, especially for developing countries such as Ethiopia. Other conventional processes for removing organic pollutant compounds include extraction, steam distillation, bacterial and chemical techniques, oxidation with ozone/hydrogen peroxide , ion-exchange, electrochemical oxidation, reverse osmosis and photo catalytic degradation. The various disadvantages associated with these techniques are 1) treated effluent quality not satisfactory 2) high cost of operation 3) used of large amount of chemicals for oxidation processes, ion-exchange etc. becoming source of secondary pollution 4) difficulty in regeneration causing disposal problems (Laxmi.S and Ahmaruzzaman, 2010). This study has effort to develop an industrially viable, cost effective and environmentally compatible adsorbent sugarcane bagasse fly ash (SBFA) for sugar industry effluent treatment. In an attempt to address the cost problems associated with commercial adsorbents; the use of abundant, locally available, low cost adsorbents derived from industrial solid wastes are proposed in this study. This adsorbent is cheaper and readily available. As there is little or no literature report on the characterization of effluents and removal of BOD and COD from sugar industries in Ethiopia, this study is designed to tackle this issue taking Wonji- Shoa sugar factory as study site.

1.3 Objectives

1.3.1 General objective

The general objective of this study is to characterize sugar industry effluents and reduction of COD and BOD contributing pollutants from sugar industry effluent using sugar bagasse fly ash. Case Study: Wonji /Shoa Sugar Industry,Oromia, Ethiopia.

1.3.2 Specific objectives

The specific objectives of this study are:

1. To characterize sugar industry effluents.

2. To characterize sugarcane bagasse fly ash

3. To determine the effects of operating conditions such as solution pH, adsorbent dose, contacting time and initial COD and BOD concentration on the adsorption capacities in batch adsorption.

4. To evaluate the adsorption capacity of sugarcane bagasses fly ash (SBFA) for removal of BOD and COD contributing pollutants.

5. To study kinetics of adsorption and adsorption isotherm mechanism

1.4 Significance of the study

The sugar industry effluent which is untreated exhibits high COD and BOD contents and low contents of dissolved oxygen which is toxic to plants, so it is not permissible for irrigation. Treated effluent of sugar industry which is well balanced of chemicals if it is diluted with other fresh water, was suitable for irrigation purposes. The treated effluents of sugar industry are not highly polluted and they satisfy the irrigation values. This study could help sugar industries on how to reduce wastes. The significance of this study for the community is, when treated effluent released from the industry the community can use the effluent for irrigation and other purpose. It will certainly help in resolving waste water pollution economically to a large extent. It could be used as base line for further study.

1.5 Scope and limitation of study

This study mainly concentrates on characterization of effluent and reduction of BOD and COD contributing pollutant from sugar industry wastewater using sugarcane bagasse fly ash.

- Characterization of adsorbent is limited to only XRD, FTIR and SEM.
- Removals of pollutants were limited to BOD and COD.

2 REVIEW OF LITERATURE

2.1 Pollution of the Environment

Contamination of air, water and soil by human activity is the largest cause of disease and death in low- and middle-income countries (Philip, 2015). Rapid economic growth inevitably increases resource consumption and pressure on the environment. As is reflected in the history of most developing and newly industrialized countries, environmental deterioration and resource exhaustion restrict economic and social sustainable development. On one hand, economic growth increases pollutants and leads to environmental deterioration; on the other hand, environmental deterioration and resource exhaustion restrict economic growth (Wan, 2013). Environmental pollution due to increase of industrial activities are one of the most significant problems of the century. Pollution in soil and water is strictly related to human activities such as industry, agriculture, burning of fossil fuels, mining and metallurgical processes and their waste disposal(Ladwani *et al*., 2013). Today industries are the major source of pollutants to the ecosystem(Neethu and Thankamani, 2016)

2.2 Industrial wastewater

Industries are major sources of pollution in all environments. Based on the type of industry, various levels of pollutants can be discharged into the environment directly or indirectly through public sewer lines. Wastewater from industries includes employees' sanitary waste, process wastes from manufacturing, wash waters and relatively uncontaminated water from heating and cooling operations (Asia and Akporohonor, 2007). Many modern industries have the serious problem of disposal of their effluent. Unwanted chemical from these industries enter water resources. Most of these industrial wastes are oxygen demanding that lead to the depletion of dissolved oxygen(Buvaneswari *et al*., 2013).

Sugar industries generate large volumes of effluent, these effluents are discharged during manufacture of sugar and they contain high polluted contents. Thus the effluent of sugar industries contains higher amount of suspended solids, dissolved solids, BOD, COD, chloride sulphate, nitrates, calcium and magnesium (Bhutiani *et al*., 2015).

2.3 Sugar industry wastewater

Wastewater from sugar industry, if discharged without treatment, poses pollution problems in both aquatic and terrestrial ecosystems (Shiva and Srikantaswamy, 2015). Wastewater with varying levels of pollution load is generated at nearly all stages of sugar production.

In sugar process production water leaving the mill does so in the following ways

1. Together with the products of the mill: in molasses and in filter cake.

2. In the form of vapor in: boiler gases, which may or may not be saturated, depending on whether a wet scrubber is used; vapor evaporated in cooling towers or spay pond; flash vapor from the heated juice flash tank; evaporation from diffuser or mills.

3. In liquid form as: surplus condensate; overflow from the cooling water circuit; boiler blow down; drift loss from the cooling towers or spray pond; effluent (wash down or spillage) from drains.

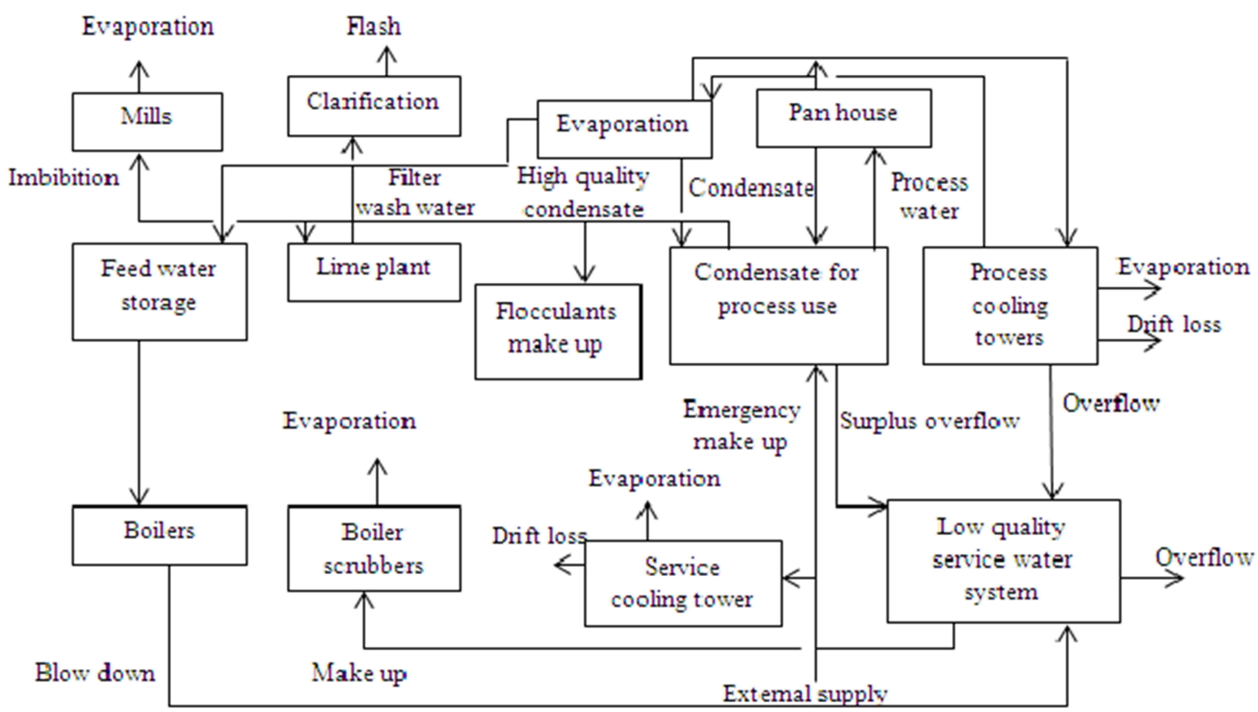

Figure 2.1 Water flow in a sugar mill (Chetan and Vikas, 2015)

Wastewater is generally generated in sugar mill from each section and finally disposed of in combined from for outside settlement. The wastewater which is generated from process house mainly results from floor and equipment washing and is highly contaminated with additives and other chemicals used at different processing stage. Boiler house mainly contributes to the production of air and have little share in water pollution. Sugar industry is large water consumer and there is no stage in sugar production where water is not requiring (Abdulrehman *et al*., 2006).

Table 2.1 wastewater generation from each unit in a sugar factory (Abdulrehman *et al*., 2006)

Main Input	**Unit house**	**Wastewater generated**
Sugarcane	Mill House	Wastewater from bearing house of the mills contains Suspended Solids and oil contents. Also includes washing water used for floor cleaning, which contains sugar contents.
Sugar Juice	Process House	Washing of different components such as, Evaporator, Juice heater, Vacuum pan, clarifiers, generates aggressive effluents having high BOD5, aggressive effluents having high BOD5, COD and TDS concentrations.
Bagasse/ Furnace oil	Boiler House	Wastewater of wet scrubbers

2.3.1 Sources of effluents of sugar industry

Effluent discharges from agro based industries like sugar are characterized by high COD due to their high level of organic contents and this effluent contains milk and milk products with wash water (Chetan *et al*., 2016). The wastewater generated from different process in the industry can be classified as follows:

(1) **Mill House**: The effluent consists of water used from cleaning the mill house which is likely to be converted by spills and pleased sugar juice. Water used for cooling of mills

also forms part of the waste water from this source. Basically this water contains organic matter like sucrose, bagacillo, oil and grease from the bearings fitted in to the mills.

(2) **Wastewater from Boiling House**: The waste water from boiling house results from leakages through pumps, pipelines and the washings of various sections such as evaporators, juice heaters, clarification, and pans.

(3) **Wastewater from Boiler Blow-down**: The water used in boiler contains suspended solids dissolved solids like calcium salts, magnesium salts, sodium salts, fatty salts etc.

(4) C**ondensate water**: The excess condensate does not normally contain any pollutant and is used as boiler feed water and the washing operations. Sometimes it gets contaminated with juice due to entertainment of carryover of solids with the vapours being condensed in that case if goes in to the waste water drain (Chidanand *et al*., 2015).

(5) **Condenser cooling water:** Condenser cooling water is re-circulated again unless it gets contaminated with juice, which is possible due to defective entrainment separators, faulty operation beyond the design rate of evaporation etc. if gets contaminated the water should go into the drain invisibly. This volume of water is also increased by additional condensing of vapour of trained from the boiling juice the pan (Chidanand *et al*., 2015).

(6) **Soda and Acid Wastes**: The heat exchangers and evaporator are cleaned with caustic soda and hydrochloric acid in order to remove the formation of the deposits of scales on the surface of the tubing. The soda and acid wash contribute considerable amounts of organic and inorganic pollutions and may cause shock loads to waste water treatment (Chidanand *et al*., 2015).

Wastewater with varying levels of pollution load is generated at nearly all stages of sugar production. Cane washing becomes necessary when the cane is harvested mechanically, generating waste water that has a high concentration of suspended solids and may have a significant sugar concentration due to damage incurred by the cane during mechanical harvesting. Relatively mild effluents from the mill house, containing oil, grease, and some sugar content, are generated from the lubricating and cooling systems, floor washings, the large quantity of water used for juice extraction, and some leakage and spillover (Nadia and Mahmood, 2006).

2.4 Industrial wastewater characteristics

The characteristics of individual and combined effluents vary from mill to mill and from time to time. All the individual effluents excluding spray pond overflow are acidic and coloured posters disagreeable older, high BOD and suspended solid. The oil and grease content is also high (Shiva and Srikantaswamy, 2015).

2.4.1 Physical characteristics of sugar industry effluents

The physicochemical analysis of Sugar industry effluent affected soil revealed the presence of higher amount of minerals, toxic pollutants and soil organic matter. The effluent not only affects the plant growth but also deteriorate the soil properties when used for irrigation (Pradeep and Omprakash, 2015).

Colour:

Colour is a qualitative characteristic that can be used to assess the general condition of wastewater. The effluent released from the main outlet of sugar mill was brown in color and had a smell of decaying (Pradeep and Omprakash, 2015).

Odour

Industrial waste generally has a strong odour. The substances responsible for causing odour and taste are phenol compounds, sulphur compounds, iron, manganese, sodium chloride, calcium chloride, magnesium salts, acids, and hydrocarbons, often present in wastes from gas and wood industries, refineries and various chemical industries (Pradeep and Omprakash, 2015).

Conductivity:

Conductivity is a parameter which is simple to measure and can easily be measured with continuous measurement device. This parameter is a general indicator of water quality, especially a function of the amount of dissolved salt, and can be used to monitor processes in the wastewater treatment that causes changes in total salt concentration and thus changes the conductivity (Seema, 2015).

2.4.2 Chemical characteristics:

Inorganic chemicals

The principal chemical tests include free ammonia, organic nitrogen, nitrites, nitrates, organic phosphorus and inorganic phosphorus. Nitrogen and phosphorus are important because these two nutrients are responsible for the growth of aquatic plants. Other tests, such as chloride, sulphate, pH and alkalinity, are performed to assess the suitability of reusing treated wastewater and in controlling the various treatment processes (Esra, 2012)

Organic chemicals

Laboratory methods commonly used today to measure gross amounts of organic matter (greater than 1 mg/L) in wastewater include (1) biochemical oxygen demand (BOD), (2) chemical oxygen demand (COD) and (3) total organic carbon (TOC). Trace organics in the range of 10^{-12} to 10^{3}mg/L are determined using instrumental methods including gas mass spectroscopy and chromatography (Esra, 2012).

Heavy metals and inorganic species

Sugar factory is one of the biggest factory manufacturing sugars for consumption of mankind. The factory uses fertilizers to produce sugar cane and chemicals to process cane juice. Hence at different stages of sugar processes there are chemicals in use that can contribute metal ions directly or indirectly to the sugar products (Yadata, 2014). Several industries discharge heavy metals (Suresh *et al*., 2015).

pH

Generally sugar industry effluent is acidic in nature. The pH is acidic in nature because of the use of phosphoric acid and sulphuric acid during clarification of sugarcane juice. The lime is added to the effluent to increase pH value so effluent become alkaline in nature, and then it will easy to treat (Chidanand *et al.,* 2015).

BOD (Biochemical oxygen demand)

Biochemical oxygen demand (BOD) is defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. The BOD test measures the amounts of dissolved oxygen organisms are likely to need to degrade wastes in wastewater. Common incubation periods are: five, seven, or twenty days, five days (or BOD_5) is the most common. At the end of the incubation period, the dissolved oxygen is measured again. The amount that was used (expressed in milligrams per liter) is an indication of wastewater strength (Chhaya *et al*., 2015)

COD (Chemical Oxygen Demand):

The chemical oxygen demand (COD) test is used to measure the total organic content of industrial wastes and municipal and natural wastewaters. During the determination of COD, organic matter is converted to carbon dioxide and water using a strong chemical oxidizing agent (dichromate) in the presence of a catalyst and strong acid. In the COD test, organic materials are oxidized regardless of the biological assimilability of the substances. As a result, COD values are greater than BOD values and may be much greater when significant amounts of biologically resistant organic matter are present (Esra, 2012).

2.5 Environmental impact of effluents from sugar mills

Waste water from sugar mills with its high BOD rapidly depletes available oxygen supply when discharged into water bodies endangering fish and other aquatic life. The high BOD also creates septic conditions, generating foul-smelling hydrogen sulfide, which in turn can precipitate iron and any dissolved salts, turning the water black and highly toxic for aquatic life. A high COD, a measure of the inorganic and partly organic non-biodegradable content of the effluents, has effects on the receiving water body similar to that of a high BOD (Saranraj and Stella, 2014).

2.6 Methods of COD and BOD reduction from wastewater

2.6.1 Oxidation

This is achieved by oxidizing the wastewater independently by two oxidants viz. Fenton reagent (Fe^{2+}/H_2O_2) and Sodium Hypochlorite (NaOCl) and comparing the results of COD and BOD reduction between them. Such advanced physico-chemical processes, can take much higher fluctuating load and characteristics of inlet effluent as compared to conventional biological treatment methods (Parshant *et al*., 2013).

2.6.2 Electrocoagulation technique

Electro coagulation (EC) is a process in which the anode material undergoes oxidation with formation of various monomeric and polymeric metal hydrolyzed species. These metal hydroxides remove organics from wastewater by sweep coagulation and/or by aggregating with the colloidal particles present in the wastewater to form bigger size flocs which ultimately are removed by settling. Sugar industry effluent is conventionally treated by adopting various physico-chemical and biological methods. These conventional processes suffer the disadvantage that the reagent costs are high and the soluble COD removal is low. Moreover, chemical treatments could induce a secondary pollution due to the fact that chemical additives may contaminate the treated water (Shivayogimath and Rashmi, 2013).

2.6.3 Ozonation in combination with biological treatment

The chemical method is used to oxidize organic materials using oxidizing agents such as ozone, H_2O_2, UV light or combinations of such oxidants, which are known as Advanced Oxidation Processes (AOPs). Most factories use this method to reduce COD and colour. But, it cannot satisfy the environmental discharge standard by itself alone and the cost is relatively high. The combination of ozonation and biodegradation seems to be a promising unit process to remove the residual colour, COD and BOD of wastewater (Abidin *et al*., 2016).

2.7 Adsorption

Adsorption is an effective method for the separation of effluent pollutants and effluents treatment (Abdulkarim *et al*., 2014). Adsorption is one of the most efficient wastewater treatment technologies because of its low cost, compared to the other technologies, its simple operation and it does not produce a large amount of sludge. Adsorption is defined as a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid solid interface (Milan and Yogesh, 2012). The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The materials used as adsorbents must have high content of carbon or oxygen for efficient adsorption.

2.7.1 Mechanism of adsorption

In the case of wastewater treatment, adsorption is the interface is between the adsorbent solid surface and the liquid phase of the wastewater

2.7.1.1 Physical adsorption

It is a general incident and occurs in any solid/liquid or solid/gas system. Physical adsorption is a process in which binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction. The electronic structure of the atom or molecule is hardly disturbed (Oscar, 2012).

2.7.1.2 Chemical adsorption

It is a kind of adsorption which involves a chemical reaction between the adsorbent and the adsorbate. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds (Covalent, Ionic) (Oscar, 2012). Chemical adsorption is also referred as activated adsorption. The adsorbate can form a monolayer. It is utilized in catalytic operations.

2.7.2 Adsorption isotherm

Adsorption is a function of both the characteristic and concentration of adsorbate and temperature

$$qe = \frac{(C0-Ce)V}{m} \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.1)$$

Where qe = adsorbent phase concentration after equilibrium, mg adsorbate (BOD or COD) contributing pollutant /g adsorbent

C_0 = initial concentration of the adsorbate, mg/L

Ce = final equilibrium concentration of the adsorbate after adsorption has occurred, mg/L

V = volume of liquid in the reactor, L and m = mass of adsorbent, g

To optimize the design of an adsorption system for the adsorption of adsorbents, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those of Freundlich, Langmuir have been used to describe the equilibrium characteristics.

2.7.2.1 Langmuir isotherm

The Langmuir isotherm has been used by various workers for the sorption of variety of compounds. The model assumes uniform energies of adsorption on to the surface. This isotherm suggests that uptake occur on homogeneous surface by monolayer adsorption without interaction between the adsorbed materials (Oscar, 2012).

$$qe = \frac{qmKLCe}{1+KLCe} \dots\dots\dots\dots\dots\dots (2.2)$$

Where, K_L is the Langmuir adsorption (L/mg) related to the energy of adsorption and

$\mathbf{q_m}$ signifies the adsorption capacity of the adsorbent (mg/g),

$\mathbf{C_e}$ is the equilibrium liquid – phase concentration of the adsorbate and

qe is the equilibrium adsorbate loading on to the adsorbent (mg/g).

Langmuir adsorption parameters were determined by transforming the above equation into linear For.

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{qmKLCe} \dots\dots\dots\dots\dots\dots (2.3)$$

Where: qe = amount of COD or BOD adsorbed per gram of the adsorbent at equilibrium (mg/g). qm = maximum monolayer coverage capacity (mg/g), Ce = equilibrium concentration of adsorbate (mg/L), KL = Langmuir isotherm constant (L/mg)

The values qm and KL can be computed from the slope and intercept of the Langmuir plot of 1/qe versus 1/Ce. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimensionless constant referred to as separation factor or equilibrium parameter.

$$R_L = \frac{1}{1(1+KLCo)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.4)$$

Where: RL= Langmuir equilibrium parameter

C_0 = initial concentration (mg/L)

K_L = constant related to the energy of adsorption, Langmuir Constant (L/mg)

RL value indicates the adsorption nature to be either unfavorable if RL>1, linear if RL =1, favorable if 0< RL<1 and irreversible if RL=0.

2.7.2.2 Freundlich isotherm

The Freundlich isotherm represents the most widely nonlinear adsorption models. This model proposes monolayer sorption with a heterogeneous energy distribution of actives sites, accompanied by interaction between adsorbed molecules (Lakdawala and Nimavat, 2011).

The Freundlich equation can be represented as follow (Zeinab *et al*., (2014)

$$q_e = KfCe^{\frac{1}{n}}$$

$$\log qe = \frac{1}{n}\log Ce + \log Kf \dots\dots\dots\dots\dots (2.5)$$

Where: K_f is Freudlinch adsorption (L/mg), $\frac{1}{n}$ = Freundlich intensity parameter

2.8 Factor affecting adsorption

2.8.1 pH

The pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, the large number of H^+ ions present neutralizes the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion, and a better adsorption is obtained. If the surface charge of the adsorbent is positively charged, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed (Ushakumary, 2013).

2.8.2 Contact time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions (Bansode *et al*., 2015)

2.8.3 Concentration

Whatever be the mechanism of adsorption from the solution, it is certain that the extent depends mainly on the available surface of the adsorbent. The process of adsorption is almost invariably reversible and a definite equilibrium is reached in a short time dependent on the concentration of the solution and quantity of the adsorbent (Bansode *et al*., 2015).

2.8.4 Surface area (particle size)

The adsorbents with smaller particle size have a higher ability in the adsorption process with large external surface. The adsorption increases as the particle size decreases, because the surface area increases when the particle size decreases. Such an effect is probably due to the inability of the large ions to penetrate all the initial pore structure of the adsorbents.

2.9 Sugarcane Bagasse Fly ash as an Adsorbent

Sugarcane bagasse fly ash (SBFA) is industrial solid waste generated from burning of bagasse in steam boilers to generate electric energy in the sugar industry. In most developing countries, SBFA is not commercialized and remains as a waste that causes great problems for environmental disposal. Studies have shown that it is a carbon- and silica-rich industrial waste which is cheap and available in large quantities in many sugar industries (Nure *et al*., 2017). The high percentage of silica and alumina in bagasse fly ash make it a good candidate for utilization as an inexpensive adsorbent for bulk use. It has been used previously for the COD removal from sugar mill and paper mill effluents (Gebremeskel, 2016). Adsorption capacity depends upon the interface of effluent pollutants with the prepared material from sugarcane bagasse fly ashes. The presence of inorganic salts could enhance the adsorption of organic species to carbon (Abdulkarim *et al*., 2013).

Instead of using commercial activated carbon or zeolites, a lot of researches have been conducted using fly ash for adsorption of NOx, SOx, organic compounds, and mercury in air, and cations, anions, dyes and other organic matters in waters. Adsorption Studies for Organic Matter Removal from Wastewater by using Bagasse Fly ash in batch and column operations was carried out by Sunil and Ajaygiri, 2013. It is recognized that fly ash is a promising adsorbent for removal of various pollutants. Chemical treatment of fly ash makes conversion of fly ash into a more efficient adsorbent for gas and water cleaning (Suhas *et al*., 2013). Bagasse fly ash, a waste generated in local sugar industries, has been converted into a low cost adsorbent. The product obtained has been characterized and used for the removal of COD and BOD contributing pollutants from sugar industry effluents. Bagasse fly ash mainly consists of unburned carbon, SiO_2 - 51 to 55%, Al_2O_3,10 to 11%, CaO -5 to 6 %, Fe_2O_3 -4 to 5%, and trace of MgO (Milan and Yogesh, 2012). Chemical composition of Wonji –Shoa sugarcane bagasse fly ash is; SiO_2, 71%, Al_2O_3, 8.16%, Fe_2O_3 5.12%**,** Cao, 1.68% and MgO, 1.24% (Tadese, 2018).

2.9.1 Availability of bagasse fly ash in Ethiopia

Assessment of the availability of bagasse fly ash can be made by rough estimation of the bagasse fly ash generated in the currently operating sugar factories in the country. These are Wonji/Shoa, Metehara and Fincha. On average, the amount of sugar produced from a certain amount of cane sugar is only 12.4%. The bagasse produced from processing cane sugar is about 30% while out of that 8% of the bagasse is returned as bagasse fly ash from the boiler (Gebremeskel, 2016)

3 MATERIALS AND METHODS

3.1 Description of Study Area

The Wonji-Shoa Sugarcane Estate lies downstream of the Koka Dam in the Central Rift Valley of Ethiopia in the upper Awash River basin around 114 km from Addis Ababa and 10km from Adama with in the geographical boundaries of 80 21' to 80 29' N latitudes and 390 12' to 390 18' E longitudes at an altitude of about 1,540 m above sea level.

3.2 Chemicals and Equipment

All chemicals used in this study are reagent grade and purchased from local markets of Addis Ababa city, Kirkos sub city: include; hydrochloric acid, sodium hydroxide, Nutrients, sulfuric acid, starch indicator, potassium dichromate, silver sulphate, mercuric sulphate, Alkali-iodide-azide and sugarcane bagasse fly ash.

The major equipment used were: FTIR spectrometer(spectrum 65FTIR, Perkin Elmer), Oven((101-0, Biobase Biodustry(Shandong)Co.Ltd)), photo lab(S6), COD heater (CR 4200), BOD incubator, X-ray diffraction (XRD-7000S, South Korea), Scanning electron microscopy, pH meter, digital balance, COD digestion tubes and sieving equipment. The laboratory wares used were volumetric flask, vacuum filter pump, Erlenmeyer flasks, desiccators, beaker, conical flask, micropipettes and burette.

3.3 Sampling of effluents of sugar industry

Samples were collected between April, 2018 and May, 2018. Sample of the sugar industry effluent was taken on effluent discharge flow from the factory around 200m from point of discharge. The actual samplings were done midstream by dipping sample container below the water surface, projecting the mouth of the container against the flow direction. The effluent samples were collected in a pre-cleaned acid washed, plastic container from the point of disposal from Sugar industry located at Wonji Shoa district, Oromia and was be analyzed at giz Adama hub Laboratory. For the reduction of BOD and COD contributing pollutants and characterization of sugar industry effluent, the effluent was brought into the laboratory and kept below 4°C.

3.4 Characterization of effluent samples

The pH and electrical conductivity (EC) was measured by the method of pH meter and electrical conductivity meter respectively. The analysis was carried out in the laboratory. Using titrimetric methods, the analysis of total hardness as $CaCO_3$ (TH) was performed. While nitrate was analyzed by spectrophotometric method (Chhaya *et al*., 2014).These experiments were done at room temperature ($25^{O}C$)

Sugar industry effluent characterization procedure

Determination of pH

The pH of the samples was determined using the pH meter, by calibrating the pH meter using the buffer solutions of (4, 7 and 10) pH values.

Alkanity (as $CaCO_3$)

A known volume of the sample (50 mL) is taken in a beaker and a pH probe was immersed in the sample. HCl acid (0.1NHCl in 1000 mL distilled water) added drop by drop until the pH of the sample reached 3.7. The volume of the acid added was noted (Abdrie and Tesfalem, 2017).

Calculation: $$\text{Alkanity (mg/L)} = \frac{\text{50000xNHCl x mL acid titrated value}}{\text{Volume of sample taken}}$$

Determination of Total solid

Empty crucible was dried and weighed (initial weight, w1), 50 ml of sample was added to the crucible, kept in in oven (105°C) for at least 1 hour, and put in desiccator, took final weight of dish(Abdrie and Tesfalem, 2017).

Calculation

$$\text{Total solid (mg/L)} = \frac{\text{final weight(w2)} - \text{intial weight(W1)}}{\text{volume of sample}} \times 1000 \times 1000$$

Determination of total dissolved solid

Empty crucible was dried and weighed (initial weight (W1), sample was filtered and around 50mL of filtered effluent sample was added to the crucible, kept in oven at $105^{o}C$ for at least 1 hour, then the crucible was put in desiccator and final weight (W2) was taken (Abdrie and Tesfalem, 2017).

Calculation

$$\text{Total dissolved solid (mg/L)} = \frac{\text{final weight(W2)} - \text{intial weight(W1)}}{\text{volume of sample}} \times 1000 \times 1000$$

3.5 Collection and pretreatment of bagasse fly ash

Sugarcane bagasse fly ash was produced from sugarcane and was collected from Wonji/Shoa sugar factory located in Oromiya Regional State North Eastern Ethiopia. The sample was then washed with tap water to remove dust, dirt, clay and other non-bagasse material. After that it was soaked into distilled water for 24h and then dried for 24h at $100^{0}C$. The fine powdered ash was treated by physico-chemically method. In 1^{st} instant, the ash samples were washed with warm distilled water for 5 minutes. Then diluted solution of sulfuric acid (10% concentrated) was prepared for the washing of ash samples. For the modification process, $H_2SO_4$was used to try to increase the proportion of active surfaces and to eliminate soluble components, such as tannins, resins, reducing sugars, and colouring agents (Abdulkarim *et al*, .2013). This chemical washing was performed for 5 minutes using vacuum filtration system. The dried SBFA was ground and sieved to the desired particle size. Afterwards, pretreated fly ash was stored in desiccator till use.

3.6 Characterization of the Sugarcane bagasse fly ash (SBFA)

3.6.1 Proximate analysis of SBFA

Proximate analysis is used to identify the amount of fixed carbon and non-carbon sources in the adsorbent. The ash content indicates the amount of inorganic substance that remains after the sample was burned off at high temperature whereas the amount of fixed carbon is the non-volatile carbon source of the adsorbent.

Determination of Ash contents

1g of dried SBFA was weighed into crucible (W1) and incinerated at 600^{o}C for 2h in furnace. The crucible was coaled in desiccator and reweighted (W2).

$$\text{Ash content (\%)} = \frac{W2}{W1} x100 \text{....................................} 3.1$$

Determination of volatile matter

1g of SBFA sample was weighed into crucible (W1) and incinerated at 850^{o}C for 10minute in furnace. The crucible was coaled in desiccator and reweighted (W2).

$$\text{Volatile matter (\%)} = \frac{W1-W2}{W1} x100 \text{.......................} 3.2$$

Determination of moisture content

The moisture content of the sample was determined by weighing 1 g of sample into a pre-weighed crucible and drying it in an oven at a temperature of 105°C till the constant weight dry matter was obtained. The percentage moisture content was computed as follows:

$$\text{Moisture content} = \frac{W1-W2}{W1} X100 \text{……………..} 3.3$$

Where:

W1 = weight of sample before drying (gram)

W2 = weight of sample after drying (gram)

Determination of fixed carbon

Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture content, ash content, and volatile matter content subtracted from.

Fixed carbon (%) =100% - [moisture content (%) + ash content (%) +volatile matter (%)]…….3.4

3.6.2 Surface functional group analysis by Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was carried out in order to identify the functional groups that might be involved in the binding of organic pollutants such as BOD and COD contributing pollutant. The functional groups of sugarcane bagasse fly ash were determined using FTIR Spectrometer (Spectrum 65 FT-IR, PerkinElmer) at wave number range of 4000-400 cm^{-1}. First, the dried adsorbent was mixed with KBr particles to make it suitable to infrared analysis. The mixture was then pressed to a small thickness, slightly below 1 mm, required for FTIR analysis. FTIR analysis was done at Addis Ababa University, College of Natural Science, Chemistry department Laboratory.

3.6.3 XRD (X-ray diffraction) analysis

X-ray powder diffraction (XRD) was used for phase identification of the crystalline nature of SBFA. XRD analysis of the SBFA sample was conducted using an XRD-**7000S** powder diffractometer instrument. The x-ray diffractograms were taken using Cukα radiation at a scanning rate of 3°/min in the range 10−80°, 2θ at continuous mode of measuring. The XRD diffractometer was switched on at initialization power 40kV and 30 mA; and the wavelength of the analysis were fixed at 1.541 nm. XRD analysis was done at Adama Science and Technology University, School of Engineering, Material Science Engineering Laboratory.

3.6.4 SEM (Scanning electron microscope) analysis

A surface morphology of adsorbent (SBFA) was determined using SEM resolution 1.0 nm guaranteed at 2.00kV. The sample was applied on carbon tape, and measured at a working distance of 8 mm. The sample preparation and analysis were done as per standard operating procedure which was operated at 2.00 kV and a current of 10A under different magnifications

The overall work of this study was:

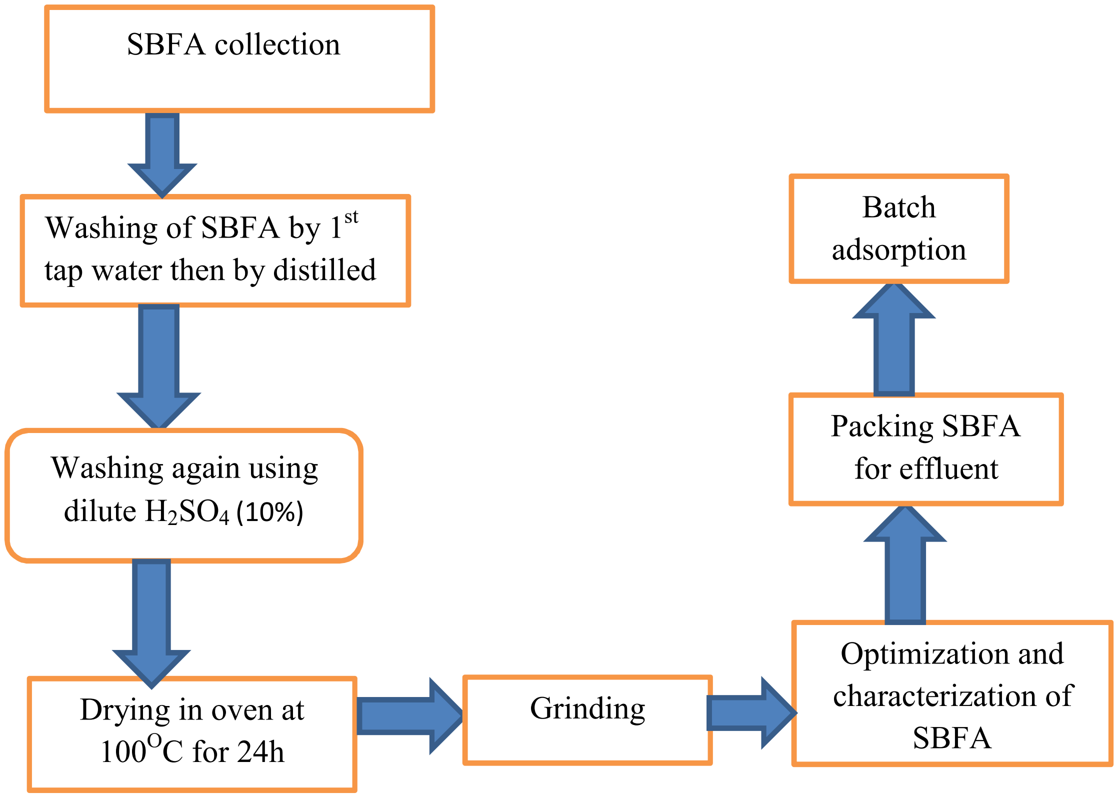

Figure 3.1 the overall experimental procedures

3.7 BOD (Biochemical Oxygen Demand) determination of sugar industry effluent

Principle

The sample is filled in an airtight bottle and incubated at specific temperature (20°C) for 5 days. The dissolved oxygen (DO) content of the sample is determined before and after five days of incubation at 20°C and the BOD is calculated from the difference between initial and final DO.

Dilution water preparation

BOD dilution water will be made up by adding to each liter air saturated distilled water:

Ferric chloride solution: 0.25g $FeCl_3.6H_2O$ was dissolved in distilled water and diluted to 1L. Calcium chloride solution: 36.5g $CaCl_2.2H_2O$) was dissolved in distilled water and diluted to 1L. Magnesium sulfate solution: 22.5g $MgSO_4.7H_2O$ was dissolved in distilled water and diluted to 1L. Phosphate buffer: (8.5g KH_2PO_4 and 1.7g NH_4Cl in 100ml distilled water). The sample was brought to 20^0C and distilled water was aerated until saturation about 1-2 h.

Testing of sample

Four 300mL glass stoppered BOD bottles (two for the sample and two for the blank) was taken. 10mLof the sample was added to each of the two BOD bottles and the remaining quantity was filled with dilution water. The remaining two BOD bottles were for blank, to these bottles the dilution water was added alone. After addition glass stopper was placed over the BOD bottles. Then one blank solution bottle and one sample solution bottle were preserved in a BOD incubator at 20^oc for five days. The other two bottles (one blank and one sample) was analyzed immediately.

Determination of DO using Winkler method:

2mL of $MnSO_4$ and 2mL of alkali-iodide-azide was added in BOD bottle in the same manner. After precipitation 2mL of H_2SO_4 (2N) was added and titrate with sodium thiosulphate (N=0.025). 203mL of solution measured out from bottle and transferred to an Erlenmeyer flask. Titration was continued until yellow color of liberated iodide is almost faded out (pale yellow color) and then 2-3 drops of starch indicators was added and titration was continued until the blue color disappears to colorless. The volume taken from sodium thiosoulphate equivalent to amount of dissolved oxygen required.

Chemical reaction that was involved in Winkler method

$$2Mn^{2+} + 2OH^- + \frac{1}{2}O_2 \rightarrow Mn_2O_{2(s)} + H_2O \ldots\ldots\ldots\ldots\ldots (1)$$

$$MnO_2 + 2I + 4H \rightarrow Mn^{2+} + I_2 + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (2)$$

$$NaN_3 + H^+ \rightarrow HN_3 + Na^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$HN_3 + NO_3 + H^+ \rightarrow N_2 + N_2O + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The released iodine can then be titrated with sodium using starch as indicator.

$$I_2 + 2S_2O_3 + 2H^+ + \frac{1}{2}O_2 \rightarrow S_4O_6^{2-} + 3H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The overall reaction is:

$$2S_2O_3 + 2H^+ + \frac{1}{2}O_2 \rightarrow S_4O_6^{2-} + 3H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

BOD is calculated as follows:

$$BOD = \frac{DO1 - DO5}{P} \ldots\ldots\ldots\ldots (3.4)$$

Where: DO1=initial DO of the diluted waste sample in mg/L

DO_2 =DO of diluted sample after incubation for five days in mg/L

P= dilution factor

Dilution factor=V sample before dilution)/V (diluted sample)

3.8 COD (Chemical oxygen demand determination)

Principle

The organic matter present in the sample produces CO_2 and H_2O by oxidizing completely with $K_2Cr_2O_7$ in the presence of H_2SO_4, Ag_2SO_4 and Hg_2SO_4. The sample is refluxed with a known amount of potassium dichromate ($K_2Cr_2O_7$) in the sulfuric acid medium and the excess potassium dichromate ($K_2Cr_2O_7$) is determined by titration against ferrous ammonium sulphate, using ferroin as an indicator. The dichromate consumed by the sample is equivalent to the amount of O_2 required to oxidize the organic matter.

Reagents Preparation for COD:

Standard potassium dichromate solution 0.25N(0.0416M): 12.25g of $K_2Cr_2O_7$ was dissolved in distilled water and dried at 150^{o}C for 2h and was diluted to 1000mL, sulfuric acids added to overcome the nitrites interference.

Sulfuric acids reagent: Ag_2SO4 was added as the rate of 5.5 Ag_2SO_4 /500mL of H_2SO_4. Ag_2SO_4 acts as catalyst for oxidation straight chain aliphatic compound.

COD measurement using spectrophotometer (photo lab instrument)

The effluent sample was homogenized, about 3mL of effluent sample was taken from sample container using pipette and 3.5mLof sulfuric acid and 1.5mL of potassium dichromate reagents were added respectively and vigorously mixed. Then the sample was refluxed for 2h at 148^{o}C in COD digester instrument (CR 4200). After 2 hours the sample was taken from the COD digester and cooled at room temperature for around 10 minutes. Then the sample was shaken very well and inserted in COD measurement instrument (photo lab S6).

BOD and COD adsorption study

Adsorption experimental setups

Batch adsorption experiment was performed by contacting a certain concentration of COD and BOD contributing pollutants with the SBFA at specified process conditions. For this set of experiments, sugar industry effluent was taken and initial concentration was measured and the needed concentrations were diluted from it in 250 ml volumetric flask. The pH of the solution was adjusted by using 0.01 M HCl and 0.01 M NaOH to bring to the required pH. The appropriate concentration of the BOD and COD were mixed with the SBFA and put on stirrer at 800 rpm for different times.

3.9 Experimental optimization

The experimental optimization was done for batch adsorption studies on different amount of sugarcane bagasse fly ash (SBFA) samples in order to find out the best maximum adsorption capacity. Simultaneously, the parameters which include pH, adsorbent dosage, contact time and initial concentration were optimized.

$$q_e = \frac{Co-Ce}{m} xV \ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

$$\text{Removal }\% = \frac{Co-Ce}{CO} X100 \ldots\ldots\ldots\ldots\ldots\ldots 3.7$$

Where, C_0 is the initial concentration of COD or BOD (mg L^{-1}) of the wastewater sample and **Ce** is the final concentration of COD or BOD (mg L^{-1}) after addition of adsorbent, **qe** = adsorbent phase concentration after equilibrium, mg adsorbate /g adsorbent

The effect of contact time: contact time was ranged from 10-90 minutes, initial concentration was 1750 mg/L and 879mg/L, for COD and BOD respectively initial pH solution was 4 and adsorbent dose was 2- 6 g/100mL for both.

The effect of initial pH and initial concentrations: pH was ranged from 4 to 10. The initial concentration was ranged from 1250 to 1750 mg/L for COD, and 479 to 879mg/L adsorbent dose was 4g/100mL. The suitable condition to remove COD and BOD: Equilibration time was determined at the optimum initial pH and initial concentrations.

The effect of adsorbent dose: adsorbent dose was ranged from 2g to 6g/100mL at optimum contact time.

Adsorption isotherms for BOD and COD contributing pollutants onto sugarcane bagasse fly ash: Experiment was set at the suitable condition. All experiments were done triplicate.

The mean and standard deviation for BOD and COD was calculated as follow:

Since the experiments was done triplicate

For BOD: 875,884 and 878ppm and for COD: 1745, 1735 and 1770 ppm

Standard deviation for BOD:

$$SD=\sqrt{\sum\frac{(X-\mu)2}{n}}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.3.8$$

For BOD: SD=$\sqrt{14}$= 3.74

Mean $\pm$standard deviiation= 879$\pm$3.74

Standard deviation For COD: SD= $\sqrt{216.66667}$=14.72

Mean $\pm$sdandard deviation $= 1750 \pm 14.72$ for COD

Where: SD=Standard deviation

X= mean of the data

μ=each measured value

n= number of measurement

Standard deviation measures the dispersion of data. The greater the value of the standard deviation, the further the data tends to be dispersed from the mean.

4 RESULTS AND DISCUSSION

4.1 Characteristics of sugar industry effluent

pH: In this study the pH value of effluent was recorded as 6.2. The pH of tested sample was found to be less than the acceptable range of WHO guidelines (WHO, 2006) for drinking (6.5-8.5). Relatively low pH values of sample are due to use of phosphoric acid and Sulphur dioxide during cleaning of sugar cane juice.

BOD: Biochemical Oxygen Demand (BOD) is defined as amount of oxygen required by microorganism while stabilizing biological decomposable organic matter in water under aerobic conditions. The found value of BOD is higher than the standard values of 80 mg/L (Jadhav *et al*., 2013). In this study the BOD of the untreated effluent was 879 mg/L. The effluent needs treatment before discharge.

COD: The chemical Oxygen demand test determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The COD is a test which is used to measure pollution of industrial waste. In this study the COD of the untreated effluents was 1750 mg/L. These values were found much higher than EPA standard limits for COD of 250mg/L for the discharged (Mulu and Ayenew, 2015). This indicated high organic pollutants in the sample as compared with standard.

TSS: The total suspended solids affect the light intensity of water; suspended solids are the cause of suspended particle inside the water body influencing turbidity and transparency. According to this study the suspended solids of untreated effluent was 200 mg/L.

The values obtained for TSS was again found to be higher than the standard limit value of 150 mg/L for TSS (Jadhav *et al*., 2013). So industrial effluent must treated before discharge to the environment.

Electrical Conductivity: The electrical conductivity which is the measure of total ion concentration. The ionic concentration of the sugar industry effluent has distinctly high EC value. The measured EC value of effluent is 320μS/cm. The result shows that the effluent sample fall within the WHO permissible limit for drinking. The maximum limit of EC for discharge is 1000 μS/cm (WHO, 2006).

Table 4.1: characteristics of sugar industry effluent

Parameters	Effluent
pH	**6.62**
Hardness(mg/L)	**150**
EC(μS/cm)	**320**
Nitrate(mg/L)	**292**
Total Alkanitiy(mg/L)	**650**
COD(mgO_2/L)	**1750**
BOD(mg/L)	**879**
TS(mg/L)	**1000**
TDS(mg/L)	**800**
Color	**Dark brown**
Odour	**Unpleasant burnt sugar**
TSS(mg/L)	**200**

4.2 Proximate analysis of SBFA

As shown in the table 4.2 sugarcane bagasse fly ash had high ash content (86%) and low volatile matter (4.31%) which are in good agreement with the literature of (G/meskel,2016).

Table 4.2: Proximate analysis of sugarcane bagasse fly ash

Proximate analysis	**Percentage (%)**	**Comparison with other investigation (G/meskel, 2016)**
Moisture content	3%	6%
Ash content	86%	81.63%
Volatile matter	4.31%	4.9%
Fixed carbon	6.69%	7.47%

Sugarcane bagasse fly ash consists of trace metals, with the main constituents being oxides, silicates, and aluminosilicates of calcium, iron, and other bases (G/meskel, 2016). Because these constituents who are responsible for the adsorption process, the particle size of SBFA that has the high ash content is used for the experiments.

4.3 Characteristics of SBFA as detected by FTIR

In the case of adsorption from liquid phase, the type of surface functional groups influences the process to a large extent changing the character of interactions between the solute molecules and carbon surface.

The adsorption capacity of SBFA can be influenced by the chemical structure of the surface. The FTIR technique is an important tool to identify some of the characteristic functional groups, which are capable of adsorbing COD and BOD contributing pollutant. FTIR data provides the information of some functional groups that may form chemical bonds, beside to van der Waals bond. The infrared spectrum of SBFA includes strong and weak peaks in the region of 4000-400 cm^{-1}. Absorption bands in the region between 3100 and 3400 cm^{-1}indicates the presence of both free and hydrogen bonded OH groups on the adsorbent surface. The peak obtained at in range of 3650-3200cm^{-1} indicates presence of aliphatic alcohol group. This stretching is due to both the silanol (Si–OH) groups and adsorbed water (peak at 3428 cm^{-1}) on the surface. The stretching of the OH groups bound to methyl radicals presented a very light signal 2922 cm^{-1}. The peak at 1075cm^{-1} is due to C-O-H stretching. A relatively intense peak has been observed in sugarcane bagasse flyash. The presence of these bands confirmed the adsorption of organic pollutant (BOD and COD).

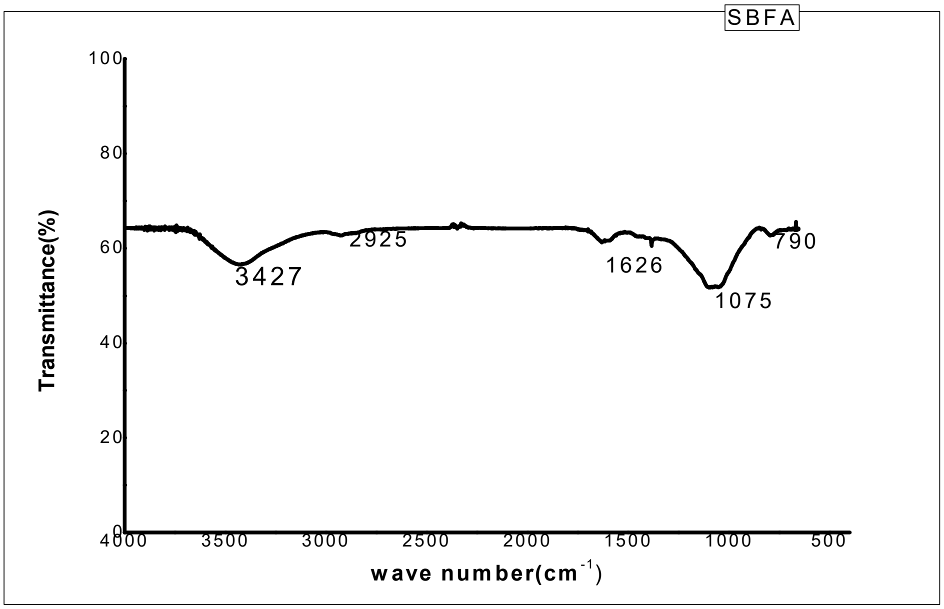

Figure 4.1 FTIR analyses for SBFA

4.4 Characteristics of SBFA as detected by XRD

X-ray diffraction analysis of SBFA was conducted at 2θ in the range 10–80°, which indicated the amorphous nature of the SBFA sample with low content of inorganic constituents. Main ingredients of SBFA are SiO_2 and Al_2O_3, as shown in figure 4. 2. There are peaks characteristic of SiO_2 on the value of 2θ = 26.5796°, 27.7514° and 30.7832° corresponding to the standard JCPDS No.88-2302. Al_2O_3 peaks characteristic at 2θ = 34.74°, 50.26°, and 59.82° according to the standard (JCPDS No. 88-0107).

Th activation process caused crystallinity of SBFA is reduced and more amorphous, that mean increasing the capacity of adsorption.

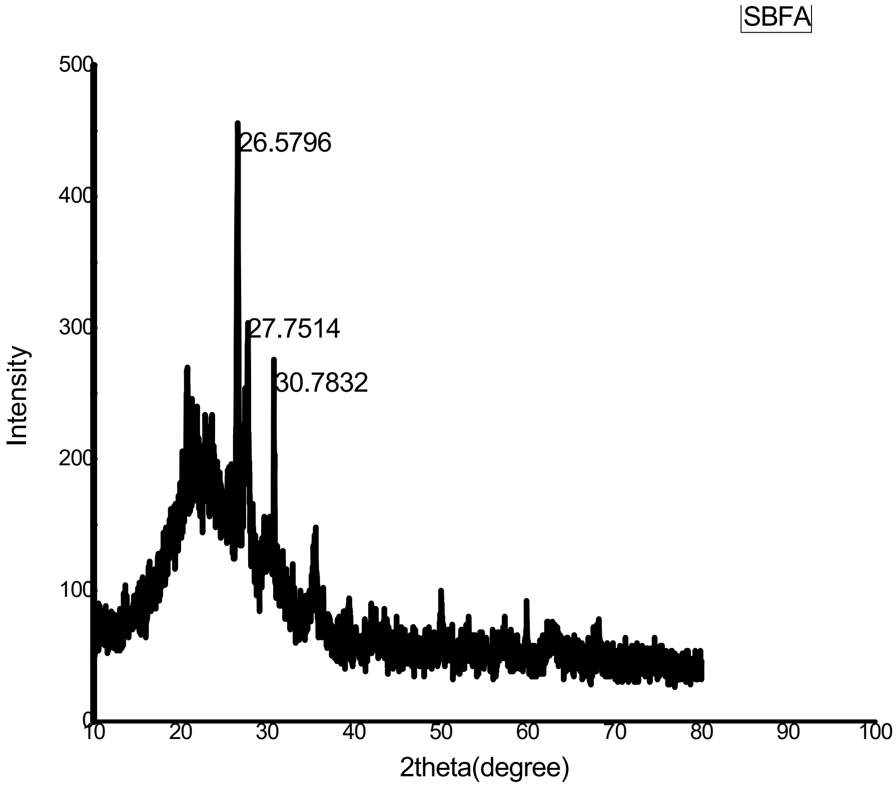

Figure 4.2 XRD analyses for SBFA

4.5 SEM analysis for SBFA

SEM analysis of SBFA was performed before treatment with sugar industry wastewater. Shape and the pore size on the surface of SBFA were not uniform but heterogeneous and irregular in shape. In particular, the larger-sized pores were rough with a lot of cracks which indicated binding sites for adsorbates of different sizes. This was a good indicator of the development of surface porosity and the readiness of the adsorbent to interact with adsorbates, but the chemical nature of the SBFA surface is another important factor to be considered. The surface of the sugarcane bagasse fly ash appears rough and porous as seen in the SEM micrograph in Fig. 4.3; this facilitated the high adsorption achieved. This could be attributed to the adsorption of organic molecules contributing to the COD and BOD in the wastewater.

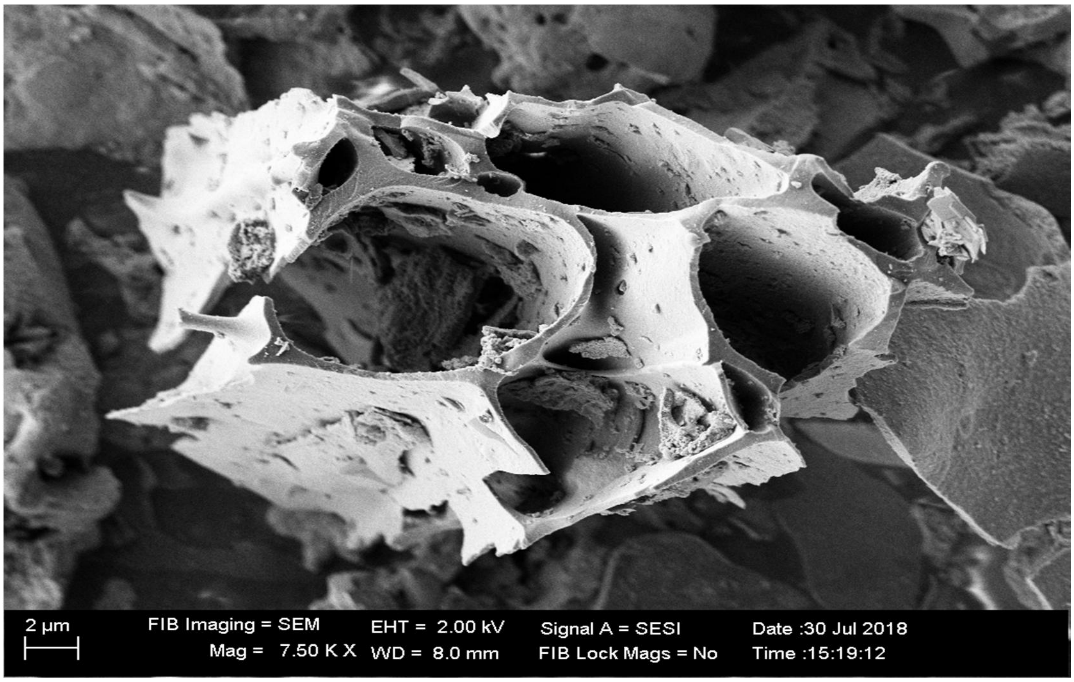

Figure 4.3 SEM analyses for SBFA

4.6 Effect of process variables on performance of SBFA for COD and BOD reduction

Effect of COD and BOD concentration

The effect of the initial concentration of COD and BOD contributing pollutants on the adsorption efficiency of the sugarcane bagasse fly ash was evaluated at concentrations of 1750,1500,1250 ppm and 879,679,479ppm respectively. When the concentrations of COD contributing pollutants increased from 1250 to 1750 ppm the adsorption capacity of adsorbent (qe, (mg/g), at constant adsorbent dose of 4gram, pH of 8 and 60 minute, increased from 9.125 mg/g to 29.375mg/g and when the concentrations of BOD increased from 479ppm to 879ppm adsorption capacity of the adsorbent (qe, (mg/g), at constant adsorbent dose of 4gram, pH of 6 and 60 minute, increased from 3.35 mg/g to 9.825mg/g. These may be due to the greater availability and interaction of the sorbent molecules with the existing pores at higher concentration of the sorbent.

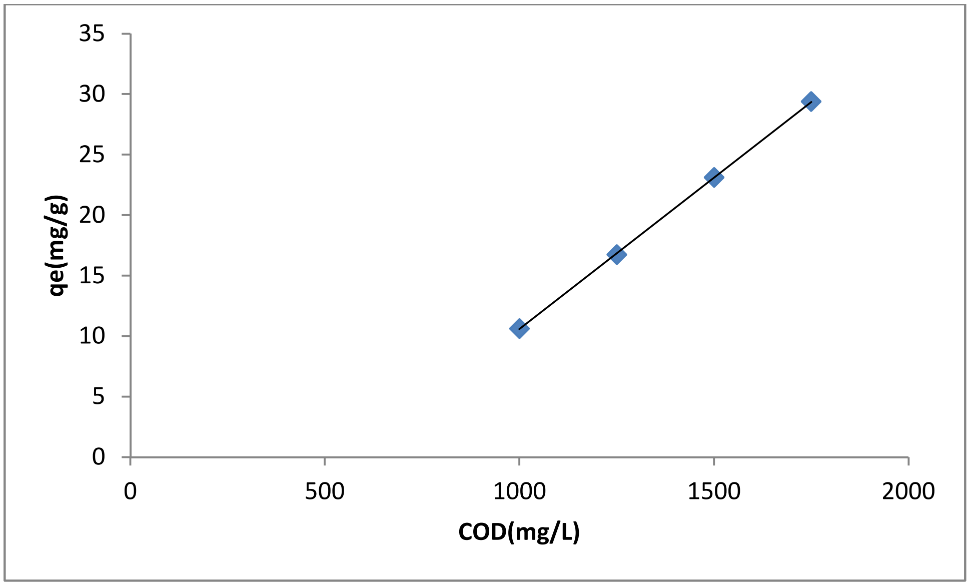

Figure 4.4 Effect of concentration on adsorption capacity of SBFA for COD

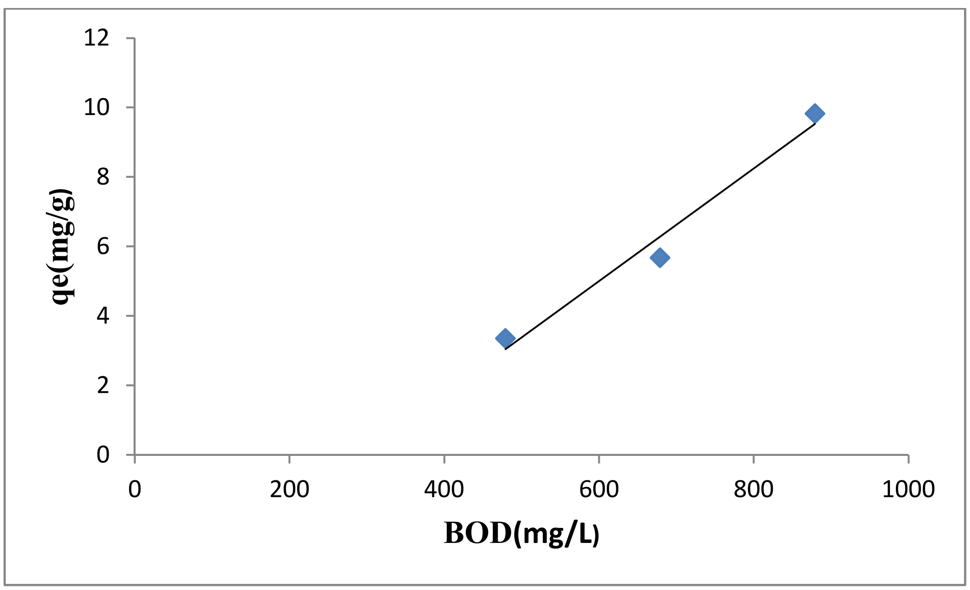

Figure 4.5 Effect of concentration on adsorption capacity of SBFA for BOD

Effect of contact time

The effect of contact time on the adsorption capacity of COD and BOD was investigated at initial COD concentrations of 1750 ppm and initial concentration of BOD of 879ppm. For the investigation, again 4gram per 100 mL of adsorbent dose and pH = 8 was used for COD and 4g/100mL of adsorbent dosage and pH=6 was used for BOD.

The results show an increase in the adsorption capacity as the time of contact increases (Fig.4.6). This is understandable because of the existence of equilibrium for the process of adsorption, the process will continue until all active sites (pores) are filled with COD and BOD contributing pollutants. In addition, the adsorption process will be fast at the beginning due to availability of large area then the process will slow down as more pores are filled by molecules. The adsorption capacity increased from 9.125mg/g to 29.375mg/g (67.14%) for COD and 3.144mg/g to 9.85mg/g (44.82%) as time increased from 10 to 90 minute. The maximum adsorption capacity was found at 60 minute and 1750 ppm for COD and 879ppm for BOD concentration respectively. This observed value of COD removal percentage by using SBFA was comparable with literature values of 64%Reported by Nure *et al*., 2017

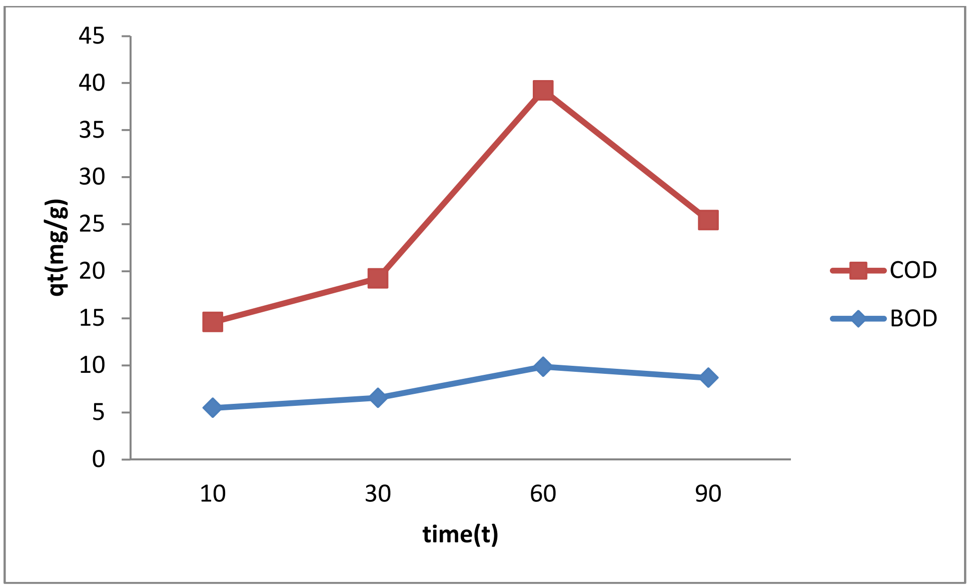

Figure 4.6 Effect of contact time on adsorption capacity of SBFA for COD and BOD

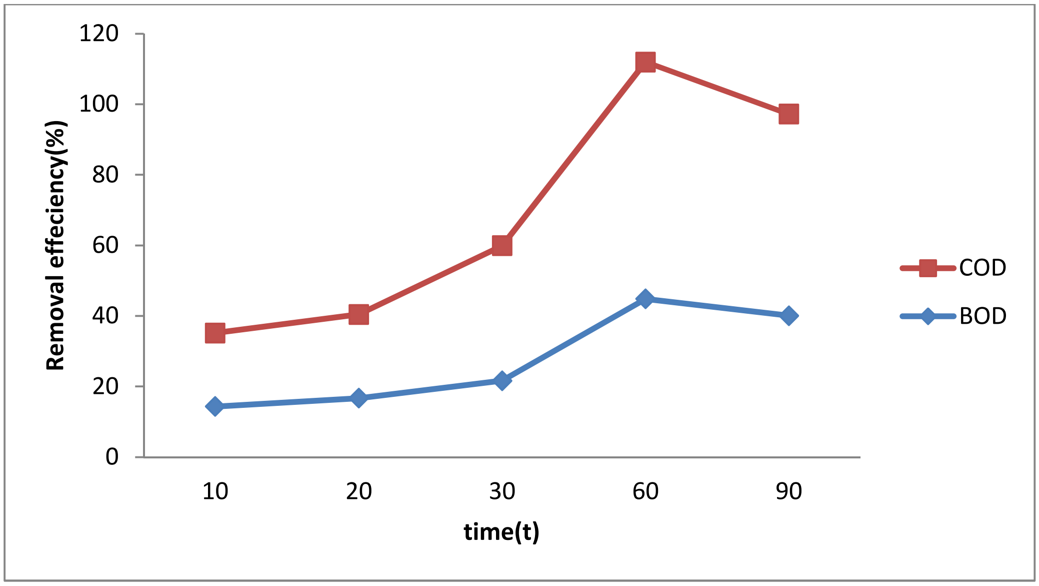

Figure 4.7 Effect of contact time on removal percentages of COD and BOD using SBFA

Effect of solution pH

The pH of the COD and BOD solution plays an important role in the adsorption process, hence on the adsorption capacity. To reveal the effect of solution pH on the adsorption capacity of SBFA, the adsorption process was carried out at different pH (4, 6, 8 and 10). The effect of pH on the COD and BOD removal was observed by keeping other parameters constant. Adsorption phenomenon is analogous to ion exchange process. The pH of the aqueous solution has significant effect on organic matter adsorption by the adsorbent. Effect of variation of pH on removal of COD and BOD is present in fig. 4.8

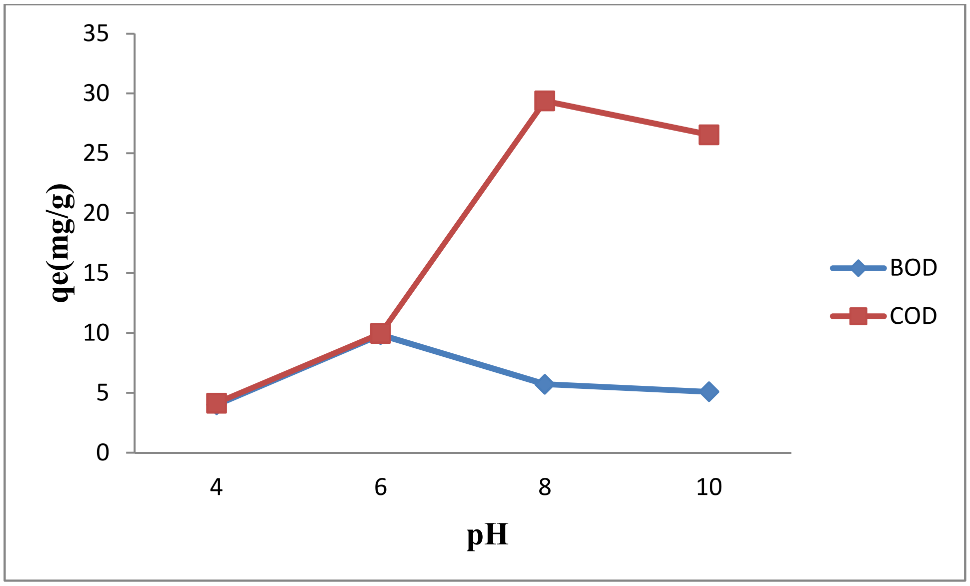

Figure 4.8 Effect of pH on adsorption capacity of SBFA for COD and BOD

Effect of adsorbent dose

In order to study the effect of adsorbent dose on the adsorption of the COD and BOD, a series of adsorption experiments were carried out with different adsorbent dosages (1, 2, 4, 6g) at constant initial COD and BOD concentration of 1750 ppm, 879ppm, pH 8 and pH 6 and shaking time 60 respectively. The result of the study is plotted in Fig. 4.9. The graph shows stable values for the adsorption capacity of higher doses than 4g per 100mL. The adsorption capacity decrease as the dose increases probably due to unused adsorption sites on the surface of the adsorbent.

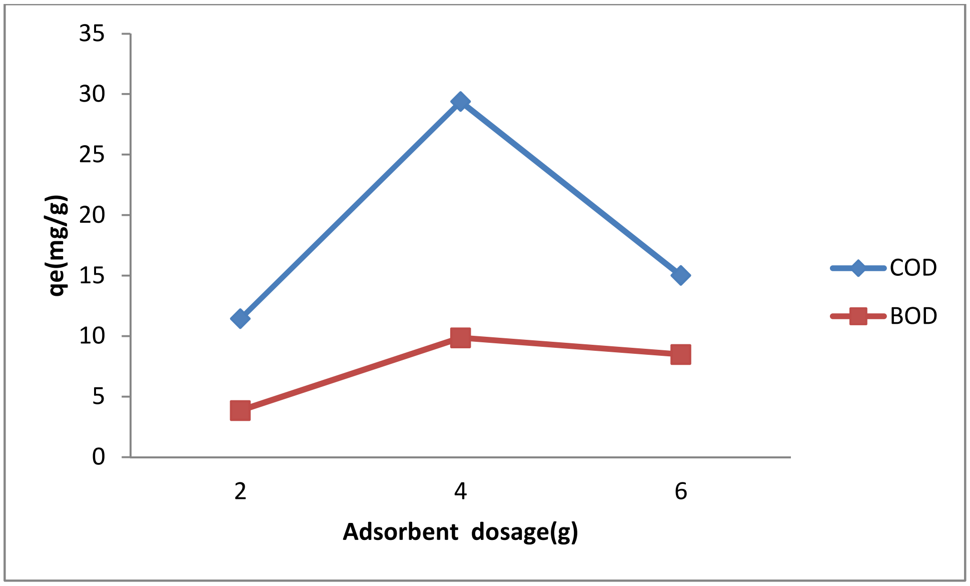

Figure 4.9 Effect of adsorbent dosage on adsorption capacity for COD and BOD

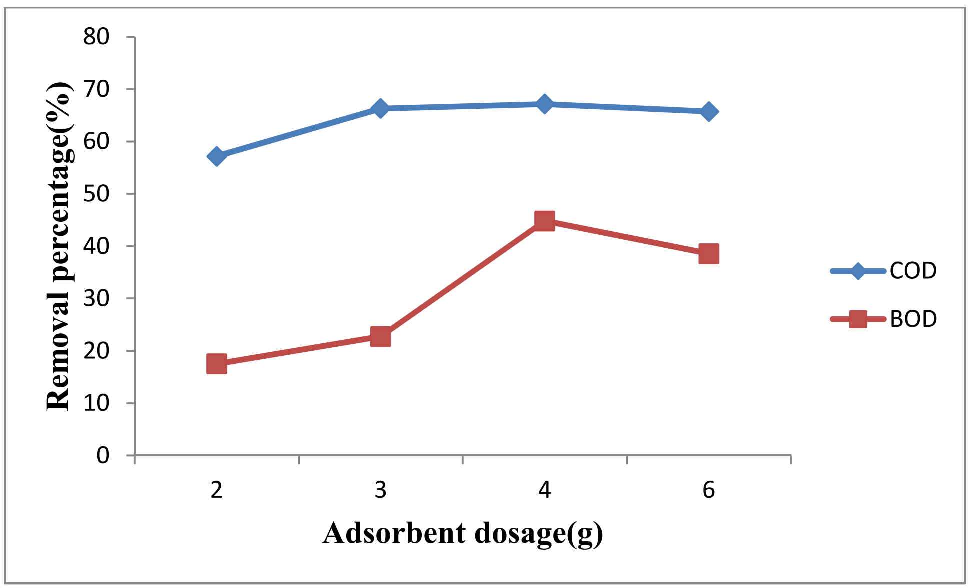

Figure 4.10 Effect of adsorbent dosage on removal percentage of COD and BOD using SBFA

4.7 Adsorption isotherm model

In order to understand mechanism of the process better and to optimize the design of an adsorption process, experimental data were analyzed to see if the process behaves similarly with the common adsorption models. In this study, Langmuir and Freundlich isotherm models have been tried to see if they could describe the adsorption process. These models are simple, well established and have physical meaning and are easily interpretable.

4.7.1 Langmuir isotherm model

Langmuir isotherm is a plot of the amount of impurity adsorbed by sugarcane bagasse fly ash against the amount of impurity that remains in solution.

In the Langmuir model is based on the simplest model of adsorption with the basic assumptions including: 1) Molecules are adsorbed at discrete active sites on the surface, 2) Energetically uniform adsorbing surface, 3) Each active site adsorbs one molecule only, 4) No interaction among the adsorbed molecules.

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmKLCe}$$

The values K_L and q_m were computed from the slope and intercept of the Langmuir plot of $\frac{1}{qe}$ Versus $\frac{1}{\mathrm{Ce}}$, respectively. In Figure 4.11, the result shows good correlation with the Langmuir isotherm model evidenced by the R^2 values (0.9977 for COD and 0.9371 for BOD) which is close to unity. These result works for COD and BOD, meaning that the overall process can be modelled as monolayer coverage of COD and BOD contributing pollutants.

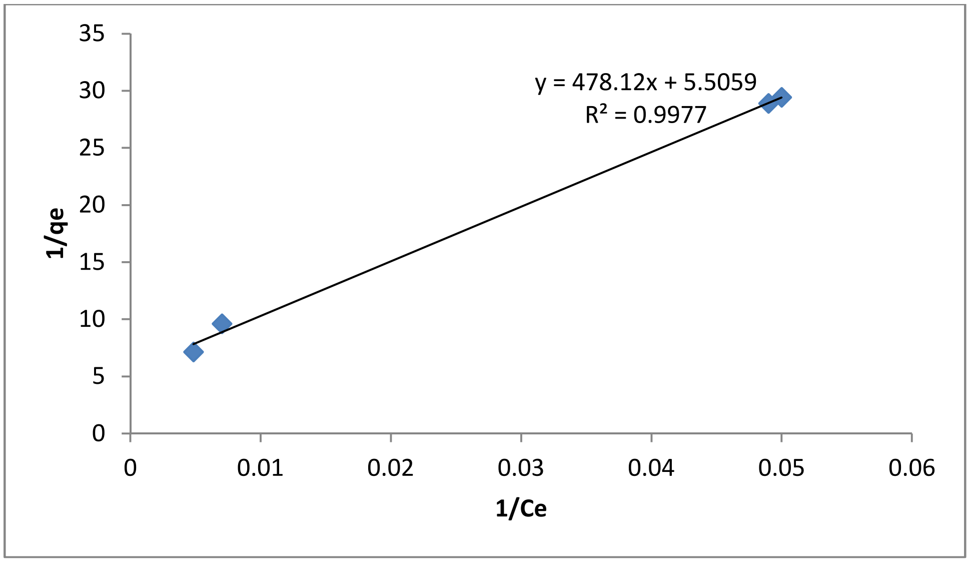

Figure 4.11 Langmuir isotherm model for COD

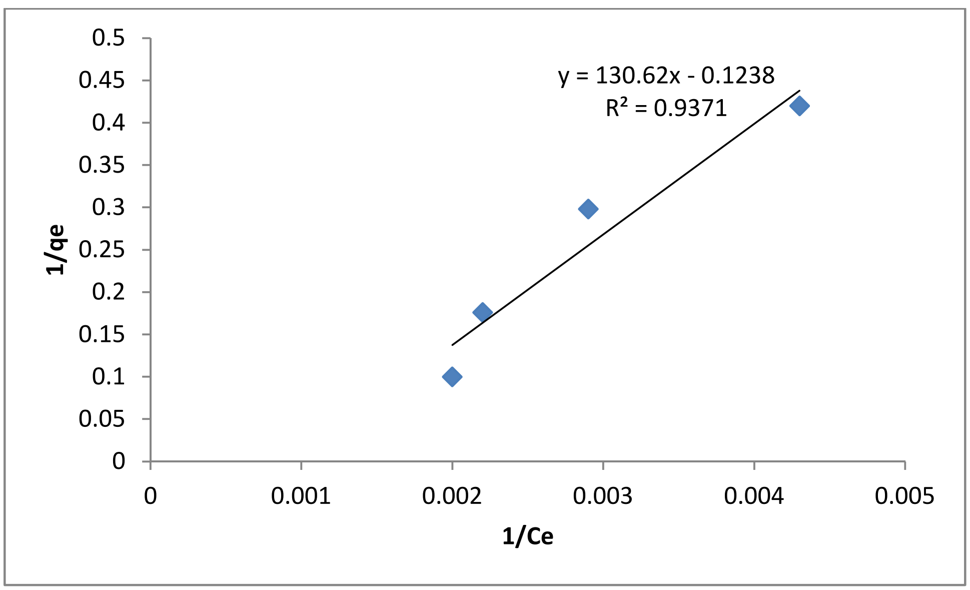

Figure 4.12 Langmuir isotherm model for BOD

4.7.2 Freundlich isotherm model

The Freundlich isotherm is one of the most popular isotherm which gives reasonable description of the adsorption of liquid molecules on solid surfaces. The Freundlich isotherm is derived by assuming that the amount of substance adsorbed at equilibrium has a power law dependence on the concentration of the solute. Freundlich Isotherm equation is given by equation 2.3

The Freundlich isotherm model constants, Kf and n, were computed from the slope and intercept of the equation for the graph ($\log_{qe}$) versus ($\log_{Ce}$), respectively. The fit of the data to the Freundlich isotherm was also tested by the R^2value of the plot, which gave satisfactory result.

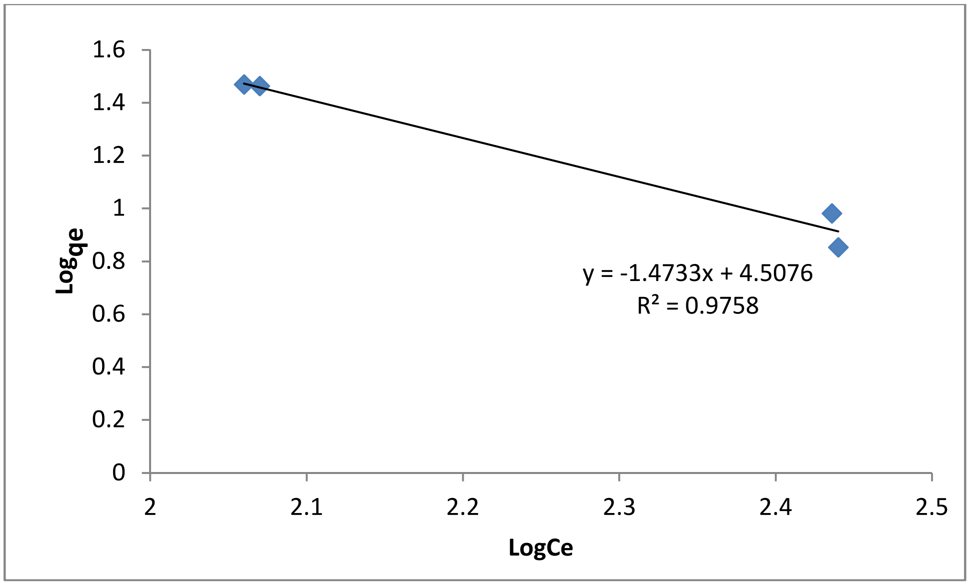

Figure 4.13 Freundlich isotherm model for COD

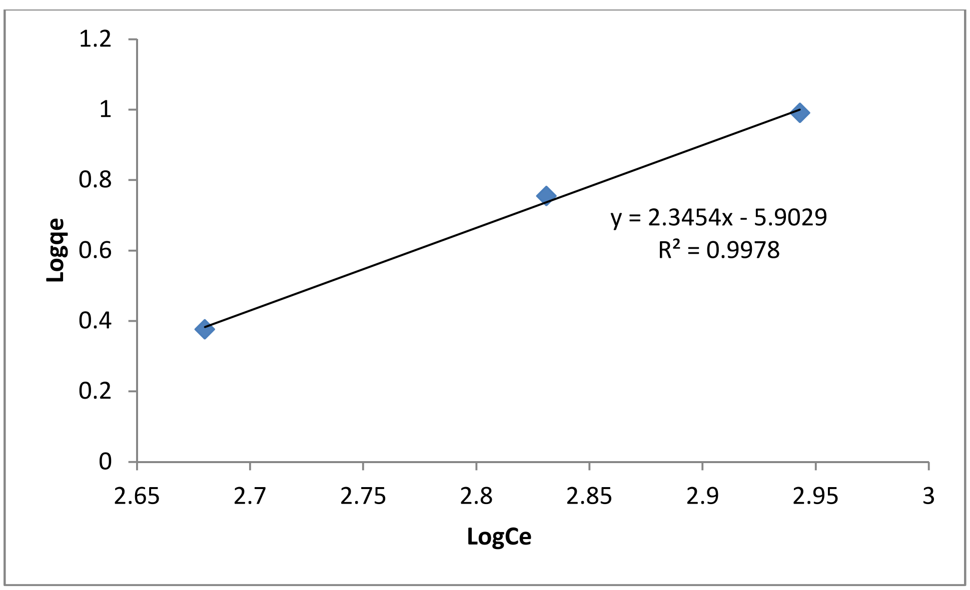

Figure 4.14 Freundlich isotherms for BO

Table 4.3 Langmuir and Freundlich isotherm constants for BOD and COD

Isotherm	Langmuir model			Freundlich model		
Paramere	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
BOD	8.08	$8.7x10^{-4}$	0.9371	4.097	0.426	0.9978
COD	0.18	0.0115	0.9977	$3.2x10^{4}$	0.679	0.9758

4.8 Adsorption kinetics model

Kinetic modeling of the adsorption data is essential for the prediction of adsorption rate, which gives important information for designing and modeling of the process (Laxmi, 2010).

In order to evaluate the kinetic mechanism which controls the process, the pseudo first order and pseudo second order models were tested and the validity of the models were verified by linear equation analysis log(qe-qt) versus t, ($\frac{t}{qt}$) versus t respectively. Good correlation with the kinetic data explains the organic pollutant adsorption mechanism in the solid phase.

4.8.1 Pseudo-first order model

The Pseudo first-order rate kinetics model based on adsorption capacity of adsorbent is generally expressed as:

$$\log(qe - qt) = \log qe - \frac{k1}{2.303}t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.3$$

Where k_1 (min^{-1}) is the pseudo-first-order adsorption kinetic parameter; qt is the amount adsorbed at time t(min); and qe denotes the amount adsorbed at equilibrium, both in mgg^{1}. The plot of the log (qe-qt) as a function of **t** provides the K1and qe values.

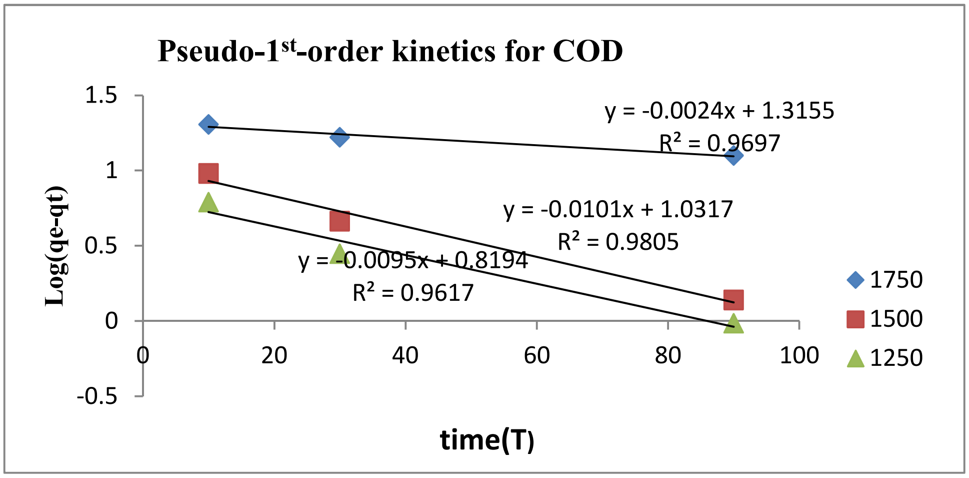

Figure 4.15 Pseudo-1st -order kinetics for COD

4.8.2 Pseudo second-order kinetics model

The Pseudo-second order kinetics model was tested in the same way by rewriting the equation in its linear form and plotting the appropriate variables. The equation that describes the pseudo-second order model is given in the following linear form:

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{qe} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.4$$

The constants, **qe** and $\mathbf{K_2}$, were computed from the slop and intercept of $\frac{\mathbf{t}}{\mathbf{qt}}$ versus **t** linear plot, respectively.

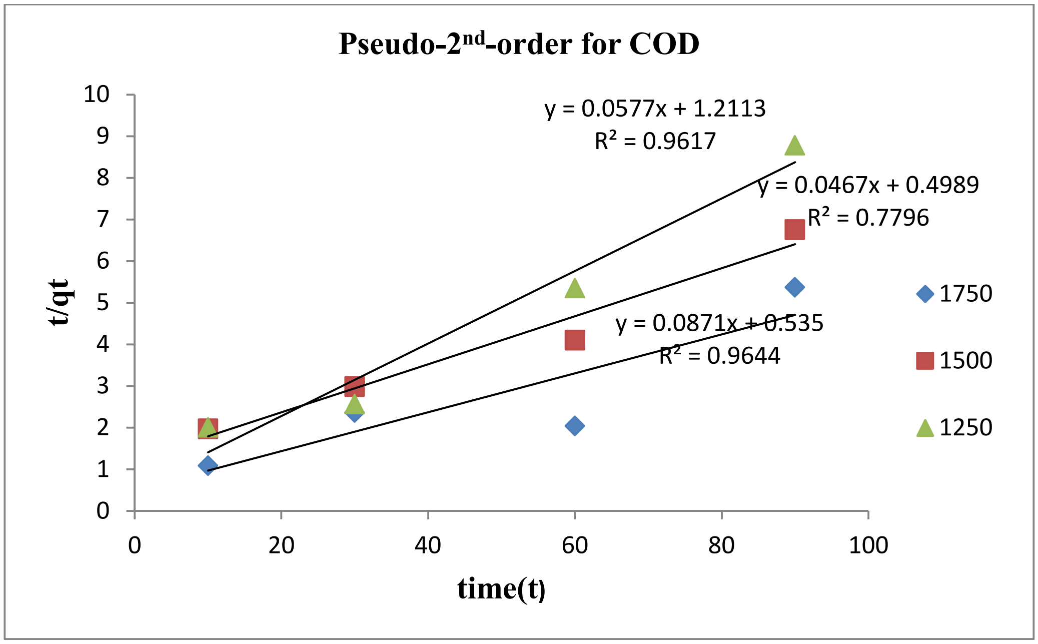

Figure 4.16 Pseudo 2nd -order kinetics for COD

The graph for COD gave satisfactory fit with both Pseudo first order kinetic and pseudo second order model implying the process of adsorption has first order and second order kinetics for COD (Fig. 4.16 & 4.15). Therefore, the adsorption of the COD contributing pollutant on the sugarcane bagasse fly ash follows both pseudo first and pseudo second order kinetics which is a better since it would result in a fast adsorption reaction.

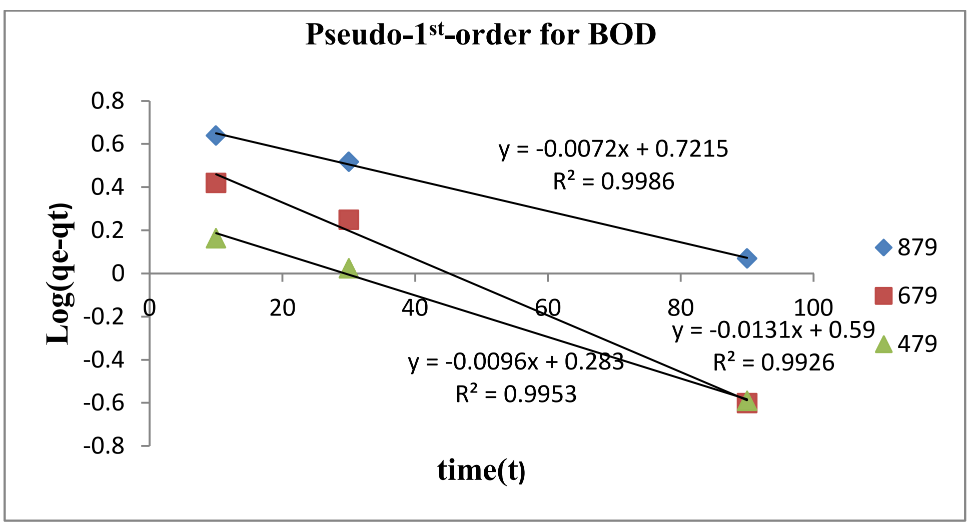

Figure 4.17 Pseudo 1st order for BOD

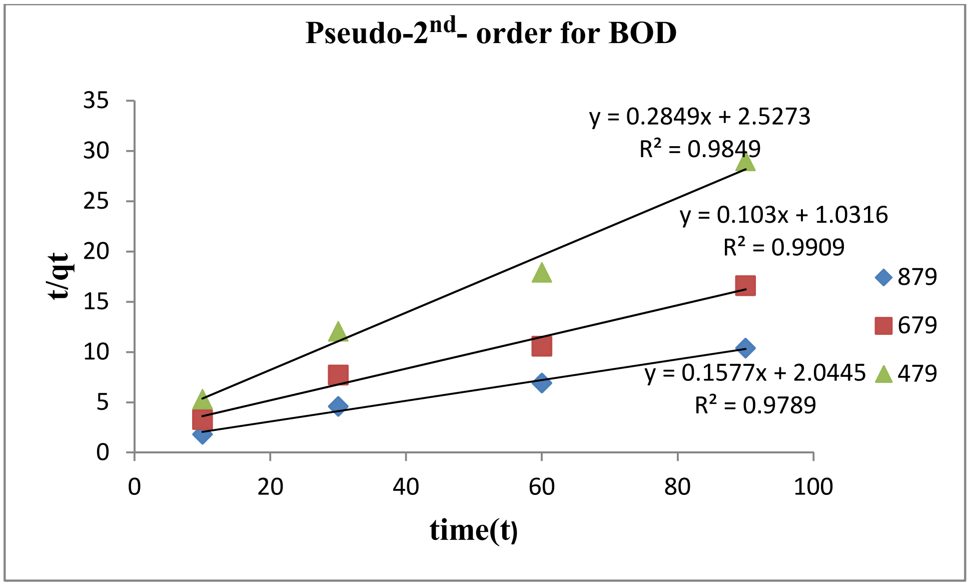

Figure 4.18 Pseudo 2nd order for BOD

Table 4.4 The Pseudo first and second-order constants for BOD and COD

Organic pollutants	Concentration(mg/L)	Pseudo 1st order			Pseudo 2nd Order		
		$K_{1(mg/g)}$	qe.calc (mg/g)	R^2	Qe,calc(mg/g)	K_2	R^2
BOD	879	0.0166	1.18	0.9986	6.3411	0.012	0.9789
	679	0.0302	3.89	0.9926	9.7087	0.01028	0.9909
	479	0.0221	1.92	0.9953	3.51	0.032	0.9849
COD	1750	0.00553	20.677	0.9697	11.481	0.014	0.9644
	1500	0.02326	10.757	0.9805	21.41	0.00437	0.7796
	1250	0.022	6.6	0.9617	17.33	0.0027	0.917

5 CONCLUSION

A simple and cost effective treatment procedure was proposed for the removal of organic matter through the adsorption on sugarcane bagasse fly ash.

In this study, the adsorption efficiency of sugarcane bagasse fly ash was investigated in detail by considering various factors that affect the adsorption process such as initial BOD and COD concentration, time, pH and adsorbent dose by starting from the proximate analysis of the SBFA. The raw bagasse fly ash was treated with H_2SO_4 to improve the efficiency of the material by removal of heterogeneously distributed organic matter and unwanted inorganic dirt materials. Sugarcane bagasse fly ash was characterized by using FTIR, SEM and XRD to know the adsorptive capacity of the material (SBFA). The effect of operating parameters was studied for concentration, time, pH and adsorbent dose. Increasing the concentration of the initial aqueous solution for the specified amount of 4 g adsorbent dose at different pH and time, also increased the adsorption capacity for an increase in concentration from 1250 ppm to 1750 ppm for COD and 479ppm to 879ppm for BOD. The sugarcane bagasse fly ash is found to be very effective adsorbent. Bagasse fly ash of sugar industry itself is a pollutant removes COD and BOD contributing pollutants up to 67.14% and 44.28% of sugar industry effluent respectively. The adsorbent dosage, pH, contact time and initial concentration of organic matter have significant effect on the removal. The optimum adsorbent doses for COD and BOD removal were observed to be 4 grams. The optimum contact times for these pollutants were 60 minute for both. The optimum pH values for the adsorption were 8 and 6 for COD and BOD respectively.

The kinetic and isotherm study was carried out in order to understand the mechanism of the adsorption process. The kinetics was also investigated to determine the rate of adsorption using pseudo-first order and pseudo-second order kinetics models. The data followed both Pseudo-first order kinetics and the Pseudo-second order kinetics. Langmuir and Freundlich isotherm was used and the experimental data were fitted for both model. The result indicated that the adsorption process followed both the Langmuir and Freundlich isotherm models.

6 RECOMMENDATIONS

This paper is only an initial work on the study of characterization of sugar industry effluent and the efficiency of sugarcane bagasse fly ash for use on the removal of organic pollutants such as BOD and COD of sugar industry effluent. It only entails the characterization of the effluents and removal efficiency of SBFA to remove organic pollutants and. But as most wastewater from sugar industry contain a lot of different species such as heavy metals, oil and grease there is a need to undertake further research on the material. The most important further research works are identified below.

- Characterization of the SBFA using advanced techniques such as BET; to visualize the pore structure of the material and EDAX-SEM to know morphology and elemental constituents.
- The regeneration potential of the used SBFA should be studied before the commercial application of the material.

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APPENDICES

APPENDIX A: Adsorption isotherm and kinetics models results.

Table A1: Pseudo 1st order kinetics data for BOD

Concentration							
479mg/L, qe=3.35				679mg/L, qe=5.675			
t(min)	qt	qe- qt	logqe-qt	t(min)	qt	qe-qt	logqe-qt
10	1.89	1.46	0.164	10	3.05	2.625	0.42
30	2.29	1.06	0.025	30	3.894	1.781	0.25
60	3.35	0	#Num	60	5.675	0	Num
90	3.094	0.256	-0.59	90	5.425	0.25	-0.6

Concentration BOD =879mg/L, qe=9.85			
t (min)	qt	qe-qt	logqe-qt
10	5.47	4.38	0.64
30	6.55	3.3	0.518
60	9.85	0	#Num
90	8.675	1.175	0.07

Table A2 Pseudo 2nd order kinetics data for BOD

Concentration					
479mg/l,			678mg/l,		
t(min)	qt	t/qt	t(min)	Qt	t/qt
10	1.89	5.29	10	3.05	3.2786
30	2.49	12.048	30	3.894	7.7
60	3.35	8.955	60	5.675	10.57
90	3.094	29	90	5.425	16.59

Concentration(879mg/L)		
t(min)	q_t	t/qt
10	5.47	1.828
30	6.55	4.58
60	9.85	6.916
90	8.675	10.37

Table A3 Pseudo 1st order data for COD

Concentration					
1250mg/L, qe=11.215			1500mg/L, qe=14.63		
t(min)	qe-qt	logqe-qt	t(min)	qe-qt	Logqe-qt
10	6.215	0.79	10	9.554	0.98
30	2.795	0.446	30	4.605	0.6632
60	0	#Num	60	0	Num
90	0.965	-0.01547	90	1.38	0.1398

Concentration 1750mg/L, qe=29.375		
t(min)	qe-qt	logqe-qt
10	20.25	1.306
30	16.686	1.222
60	0	Num
90	12.625	1.10

Table A4: Pseudo 2nd order data for COD

Concentration								
1250mg/L			1500mg/L			1750mg/L		
t(min)	qt	t/qt	t(min)	Qt	t/qt	t(min)	Qt	t/qt
10	5	2	10	5.07	1.97	10	9.125	1.096
30	8.42	3.563	30	10.025	2.99	30	12.689	2.364
60	11.215	5.35	60	14.63	4.10	60	29.375	2.042
90	10.25	8.78	90	13.32	6.7567	90	16.75	5.373

Table A$_{5}$: R_L values of BOD and COD

BOD		COD	
Initial concentration	R_L	Initial concentration	R_L
479(mg/L)	0.15	1250(mg/L)	0.8113
679(mg/L)	0.114	1500(mg/L)	0.7873
879(mg/L)	0.09	1750(mg/L)	0.76

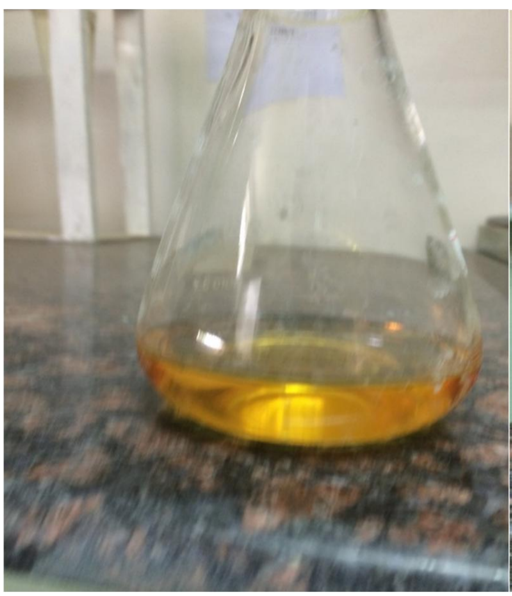
APPENDIX: B

Laboratory picture

a) b) c)

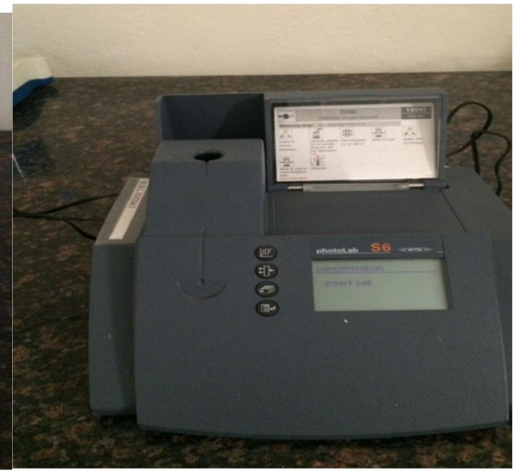
a) After and before H2SO4 added b) Wastewater with DO c) wastewater with no/less DO

a) b)



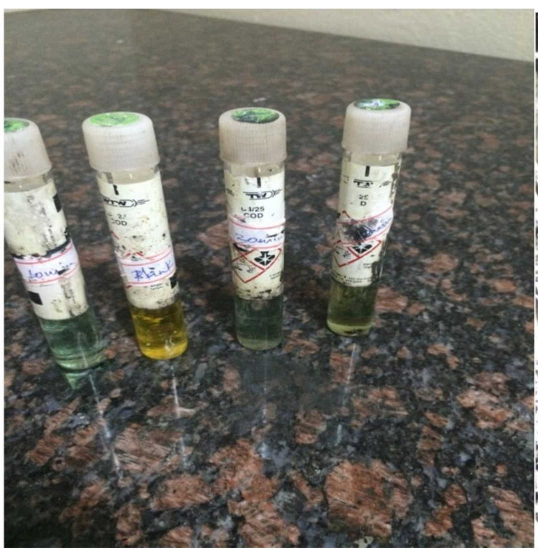
a) Before indicator addition b) After indicator addition

a) b)



a) COD digester b) photo lab

b) b)



a) COD digester tubes b) SBFA