

**ADSORPTIVE REMOVAL OF ALUMINIUM (III) USING  
CHEMICALLY MODIFIED SUGARCANE BAGASSE FROM  
AQUEOUS SOLUTION**

**A DISSERTATION SUBMITTED FOR  
THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR  
THE MASTER OF SCIENCE DEGREE IN CHEMISTRY**

**SUBMITTED BY:**

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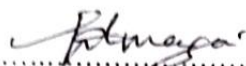
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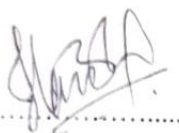
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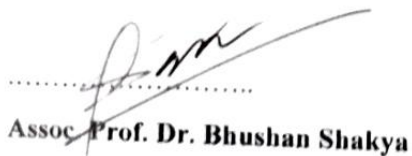


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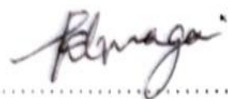
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## LETTER OF RECOMMENDATION

This is to recommend that this dissertation entitled “ADSORPTIVE REMOVAL OF ALUMINIUM (III) USING CHEMICALLY MODIFIED SUGARCANE BAGASSE FROM AQUEOUS SOLUTION”, has been carried out by Mr. Diwash Nepal as a partial fulfilment for the requirements of M.Sc. Degree in Chemistry under my supervision. To the best of my knowledge, this work has not been submitted elsewhere for any other degree.



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## DECLARATION

I, Diwash Nepal, hereby declare that the work entitled “ADSORPTIVE REMOVAL OF ALUMINIUM (III) USING CHEMICALLY MODIFIED SUGARCANE BAGASSE FROM AQUEOUS SOLUTION”, presented herein is genuine work done originally by me under the supervision of Associate professor Dr. Puspa Lal Homagai and has not been published or submitted elsewhere for the requirement of a degree program. Any literature, data and works done by others and cited in this dissertation has been given due acknowledgement and listed in the reference section.

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Diwash Nepal  
December, 2022

## LIST OF ABBREVIATIONS

FTIR	Fourier transform-infrared
XRD	X-ray diffraction
SEM	Scanning electron microscope
CSB	Charred sugarcane bagasse
XSB	Xanthanized sugarcane bagasse
CSBB	Charred sugarcane bagasse before adsorption
CSBA	Charred sugarcane bagasse after adsorption
WHO	World health organization
PPM	Parts per million
$R^2$	Correlation coefficient
$C_i$	Initial concentration
$C_e$	Equilibrium concentration
W	weight of adsorbent in gram
$K_1$	Pseudo-first-order rate constant
$K_2$	Pseudo-second order rate constant

## ABSTRACT

A major concern for both humans and aquatic life can result from the presence of several metal ions in an aquatic environment that exceeds the allowed limit. The most efficient way to remove minute levels of hazardous metals from wastewater is through adsorption. The primary goal of this thesis work is to chemically modify sugarcane bagasse in order to create a low-cost, highly effective adsorbent for the removal of Al (III) from an aqueous solution. Both xanthated and charred sugarcane bagasse have been prepared as adsorbents. Adsorbents are characterised using FTIR, EDS, and SEM. For analysis, batch experimental method was carried out. Utilizing both CSB and XSB, the effect of pH, Al (III) concentration and contact time have been investigated using both CSB and XSB adsorbents. For both adsorbents, a 150-minutes maximum duration and a pH of 4 are found to be ideal. The Langmuir isotherm model is best fitted for equilibrium sorption data, and maximum adsorption capacities of CSB and XSB are determined to be 50.9 mg/g and 81.0 mg/g, respectively. Studies on kinetic modelling showed that a pseudo-second-order kinetic model best fit the experimental data. These findings show that XSB can be an alternative bio-adsorbent for the elimination of Al(III) from an aqueous solution.

**Keywords:** Sugarcane bagasse, Adsorbents, Aluminium ion, Langmuir Isotherm, Charred

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# Chapter 1

## 1. INTRODUCTION

### 1.1 Background of the study

Aluminium is a light, conductive, corrosion-resistant metal with a strong affinity for oxygen. This combination of properties has made it a widely used material, with applications in the aerospace, architectural construction and marine industries, as well as many domestic uses (Josefa & Gandara, 2013). Corrosion resistance and protection against UV light combined with moisture and odour containment plus the fact that Al is non-toxic and will not leach or taint the products has resulted in the wide spread use of Al foils in food packaging and protection (Josefa & Gandara, 2013).

With the increment on the uses of aluminium and due to its abundant availability on earth crust, contamination of aluminium on the water sources has been increased. The potentially dangerous contamination is related to a great extent because of atmospheric acidification of the soil due to acid rain, followed by a massive export of aluminium from the crust of the earth to surface waters (Crisponi et al., 2019). The use of aluminium based coagulant for drinking water treatment often leads to higher concentration of aluminium in the treated water than in the raw water (Singh et al., 2006). Another major reason for the water resources contamination due to aluminium is industrial waste. There has been many evidence reported that aluminium has a toxic environmental impact of considerable importance (Rajwanshi et al., 1997).

Aluminium has been reported the most beneficial, non-toxic and essential element for humans. However, adverse effects of aluminium on it's over dose are currently known. If aluminium is allowed to enter the bloodstream it could be neurotoxic. And, long term exposure of patients to dialysis water containing aluminium may cause encephalopathy and /or bone mineralization disorders. Furthermore, aluminium could be potential cause of Alzheimer's disease and other forms of senile dementia (Al-Muhtaseb et al., 2008). Not only for humans, the elevated levels of aluminium on water bodies may have serious ramifications for fish living in these waters as well as birds whose diets are made up of insects from the shoreline of affected streams and lakes (Singh et al., 2006). Presence of aluminium ion also effect nutritional uptake of plants (Mariano & Keltjens, 2005). The prevalence of aluminium ion under acidic conditions inhibits primary root elongation and hinders plant growth and productivity (Sade et al., 2016)

## **1.2 Introduction of metal**

Aluminium (Al) is the most abundant metal present in the earth crust in the form of ore. The chief ore of Al is bauxite found in rocky form and contains the minerals such as gibbsite, diaspore and boehmite. Pure aluminium is soft, ductile, corrosion resistant and has high electrical conductivity (Josefa & Gandara, 2013)

The versatility of aluminium makes it the most widely used metal after iron. Aluminium and its alloy offers good strength and light weight due to which it is a leading construction material likewise for the construction of light weight utensils, aircrafts, siding and motor vehicles (Long et al., 2017). Not only pure metal but also its salts are being extensively used. The aluminium salts are widely used in water treatment applications to facilitate coagulation of pollutants such as sediments, nutrients, microbes and dissolved organic compounds. Aluminium sulphate and aluminium chlorides are used as ingredients in drugs, cosmetics, such as antiperspirants and topical creams (Downs, 1993).

## **1.3 Effects of Aluminium**

Extensive use of Aluminium and its salts in various industries has been leading recently. Moreover, the Aluminium and its salts have great importance and beneficial activities against human lives. However, its over dose may lead to the adverse effect. Also, the minimum dose of the Aluminium could have adverse effect for the aquatic lives. The industrial discharges/effluents possess a noticeable amount of Aluminium ions and if proper care is not envisaged in removing them, the Al compounds get into the nearby water bodies. This could lead bio-amplification and that may results the enhanced level of Aluminium ions in the water bodies (Kumari & Ravindhranath, 2012). Moreover, the earth crust has about 8% of Al and the acidic conditions resulting due to intensive human activity, volcanic eruptions and improper disposal of effluents from industries leach trivalent Aluminium ions into the nearby water bodies. Thus the concentration of Aluminium ion is progressively increasing in water bodies (Campbell, 2002).

The over dose of Al(III) in water bodies are highly objectionable as they effect the crop production and harmful to fish, zooplankton, cyanobacteria, algae and water weeds (Ghazy et al., 1988).

Further, it is implicated in bone softening, renal insufficiency, pulmonary fibrosis and microcytic anaemia in human beings. As per WHO and US drinking water standards, the permissible limit is 0.20 mg/L (Al-Muhtaseb et al., 2008). Therefore it is important to

remove the Al (III) from water before being used as drinking water or letting it to be collected in water sources.

#### **1.4 Removal methods**

Several methods of waste water treatment are in practice these days. Several treatment processes such as chemical precipitation (Brbooti et al., 2011), ion exchange (Akieh et al., 2008), membrane filtration, coagulation, ultra filtration, reverse osmosis (Fenglian & Wang, 2011), adsorption and electrochemical technologies (Segneanu et al., 2013) have been developed over the years to remove heavy metals dissolved in industrial waste water. However, these of the techniques have some disadvantages, such as complicated treatment process, high cost and energy consumption. Adsorption technique is found to be one of the best processes in removal of contaminants from aqueous effluents. Modified carbon is one of the popular adsorbent in the adsorption process because of having high surface area, high adsorption capacity and high degree of surface reactivity. Regarding the cost of treatment process, scientists have attempted to investigate the inexpensive and efficient adsorbent material.

The common techniques are any of the other listed process, adsorption method for the waste water treatment is the best. It could be applied for wide range of compounds. It is cost effective and the materials used in the process are biodegradable too. However, the cost of activated or modified carbon is yet to be addressed. So, many investigators have studied the feasibility of economical, commercially available materials as its possible replacements (Homagai et al.,2010). Bio sorption based on binding capacities of different low-cost adsorbents includes natural, agricultural, and industrial by-product wastes. They are found to be more promising and attractive because of their abundant availability at low or no cost, their good performance in removing metal ions from aqueous solutions as well as minimum volume sludge to be disposed (Al-Kaim, 2007). Numerous investigations have been taken place in order to protect the environment and living creatures through new methods due to the image caused by the water pollution (Hassan & Abdulhusein, 2015). Adsorption is a surface phenomenon, the accumulation of a gas or liquid on a liquid or solid. Adsorption can be defined further based on the strength of the interaction between the adsorbent (the substrate onto which chemicals attach) and the adsorbed molecules. Depending upon the nature of the forces involved, Adsorption can be classified into:



- Physical adsorption: In physical adsorption, the forces of attraction between the molecules of the adsorbate and the adsorbent are of the weak Vander Waals' type. It is also known as Vander Waals' adsorption. Physical adsorption on activated or modified carbon and carbonaceous adsorbents is widely used for the separation and purification of gases (Song et al., 2013)
- Chemical adsorption: In chemical adsorption, the forces of attraction between the adsorbate and the adsorbent are very strong; the molecules of adsorbate form chemical bonds (usually covalent) with the molecules of the adsorbent present in the surface. It is also known as Langmuir adsorption. Chemical bonds involved (covalent bonds usually) in sticking the adsorbate to the adsorbent. Chemical adsorption involves more energy than physical adsorption.

The extent of adsorption of metal ions depends upon the following factors (Lofrano, 2012):

- Adsorbate and adsorbent's nature
- Total surface area of the adsorbent
- Modification/activation/xanthation of adsorbent
- Experimental conditions like temperature, pressure, time etc.

In this research work, the experiment has been carried out for CSB (charred sugarcane bagasse) is physical adsorption and XSB (xanthated sugarcane bagasse) is ion exchange complexation.

### **1.5 Bio-materials for absorption**

In recent years, various low-cost adsorbents from agricultural wastes/by-products have been used for removal of metal ions from aqueous solution. These adsorbents are very economical, eco-friendly, and are renewable, with excellent metal ion removal ability, and are abundantly available. For this many researchers have tried to prepare adsorbent from agricultural wastes, such as orange peel (Abdelhafez & Li, 2016), banana peels (Li et al., 2016), date pits (Al-Muhtaseb et al., 2008), tea leaves (Shrestha et al., 2016), plum kernels (Pap et al., 2017), oil palm shell (Rahman et al., 2014), sawdust (Meena et al., 2008), wheat bran (Renu et al., 2017), coffee grounds (Davila-Guzman et al., 2016), coconut husk (Song et al., 2013), jackfruit peel (Ranasinghe et al., 2018), rice husk (Sobhanardakani et al., 2013) and sugarcane bagasse (Homagai et al., 2010). Utilization of

these as an adsorbent precursor is highly recommended to moderate the solid waste disposal issue, as well as to generate local economy. These bio-materials can be further modified by physical and chemical methods to obtain charcoal. Herein we report a low cost adsorbent sugarcane bagasse for removal of Aluminium ion from the aqueous solution. The method of removal is eco-friendly, energy efficient, rapid and cost effective.



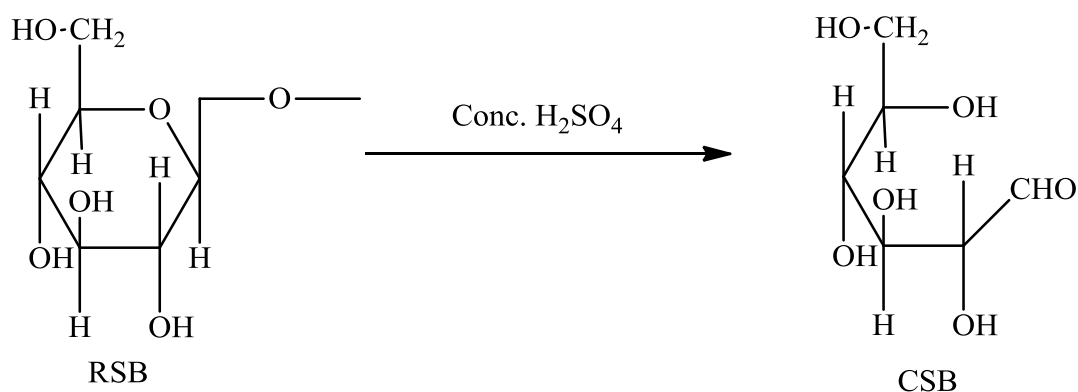
Figure 1.1: Sugarcane bagasse

### **1.6 Significance of Bio-adsorption**

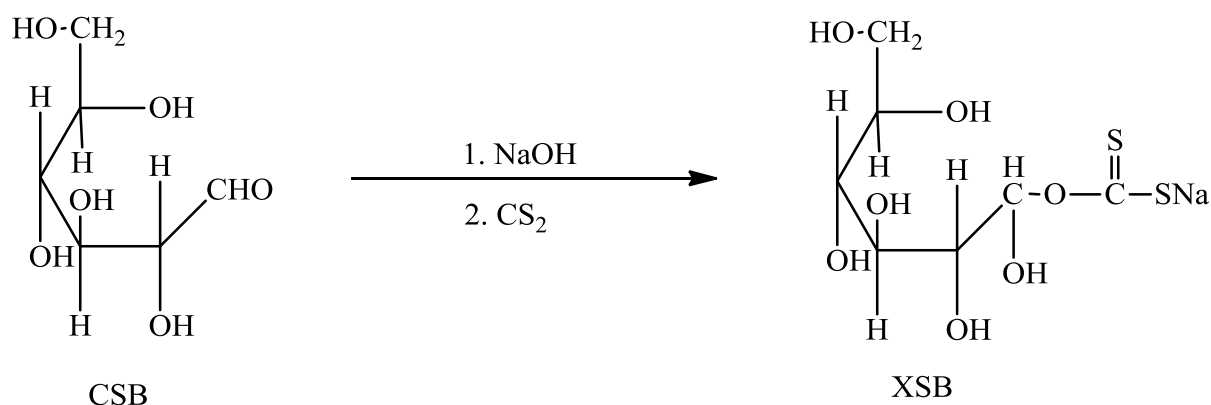
Adsorbents are the substances that attract other particles (adsorbates) to its surface. It can be also defined as adsorbents are substances such as activated charcoal and, clay which have ability to adsorb adsorbates (Isene et al., 2007). Many adsorbent materials have been developed and evaluated, but none has emerged as being economically. In the recent decade study on the exploration of application of biomass as an adsorbent has been made. Among all the biomass, sugarcane fractions (bagasse, ash, and trash) as an low cost adsorbent for the removal of heavy metals and dyes have been studied (Rodriguez-Diaz et al., 2015). Many polar groups like carbonyl, carboxyl, and hydroxyl etc. on the adsorbents prepared from sugarcane bagasse has been reported. These polar functional groups could adsorb many organic and inorganic compounds. Based on the characteristics, it could be used as adsorbent for both organic (e.g., dyes, phenols, etc.) and inorganic (e.g., heavy metals) compounds (Rodriguez-Diaz et al., 2015). In this study, aluminium has been removed from aqueous solution by using raw and modified sugarcane bagasse as an adsorbent.

## 1.7 Surface Enhancements of Bio-adsorbents

Raw bio-waste is prepared just by grinding the collected bio-waste in the powder form. The raw bio-waste can have low surface area and removal percentage of contaminants could be minimum. It is hypothesized that charring followed by chemical or thermal modification of the bio-waste could increase the surface area consequently the high removal percentage of contaminants. Chemical activation of the char by various activating agents like NaOH, ZnCl<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub> etc helps to enhance the surface area. Likewise, thermal activation of the char by heating it in the tube furnace at higher temperature could increase the surface area. Either of the methods could be applied but the selection of the modification methods depends on the nature of adsorbate to be removed. Furthermore, the addition of functional group on the modified carbon may also apply to increase percentage removal of the contaminants. In this work, the charred carbon is xanthated by carbon disulfide. The mechanism of modification is explained in the below schemes (Homagai et al., 2022).



Scheme 1: Synthetic route of CSB from RSB



Scheme 2: Synthetic route of XSB from CSB

## 1.8 Adsorption study

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid (adsorbate) to a surface (adsorbent) (Abdelhafez & Li, 2016). Adsorption occurs naturally in physical, biological and chemical systems. Industrialists have perfected adsorption methods to clean up hazardous wastewater or purify drinking water. Adsorption is superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants (Ahalya et al., 2003). The removal of metal ions from aqueous solution is usually studied by column or batch experiments.

### 1.8.1 Column adsorption

In the column adsorption method, a column of particular internal diameter and length is set up to determine the effect of operating parameters such as flow rate, bed depth, pH, and concentration. Glass wool is kept at the bottom of the column to improve the flow distribution and prevent the loss of adsorbent. The effluent is allowed to flow from top of the column at constant rate using a flow controller. Effluent samples are collected from the exit of the column at certain intervals and are used for analysis of the metal ion concentration. The metal ion concentration is measured before and after the adsorption as it helps to determine the efficiency of the adsorbent. The analysis of the metal ion is done with the help of available instrument (Spectrophotometer or Atomic Absorption Spectrophotometer) (Ali & Gupta, 2006).

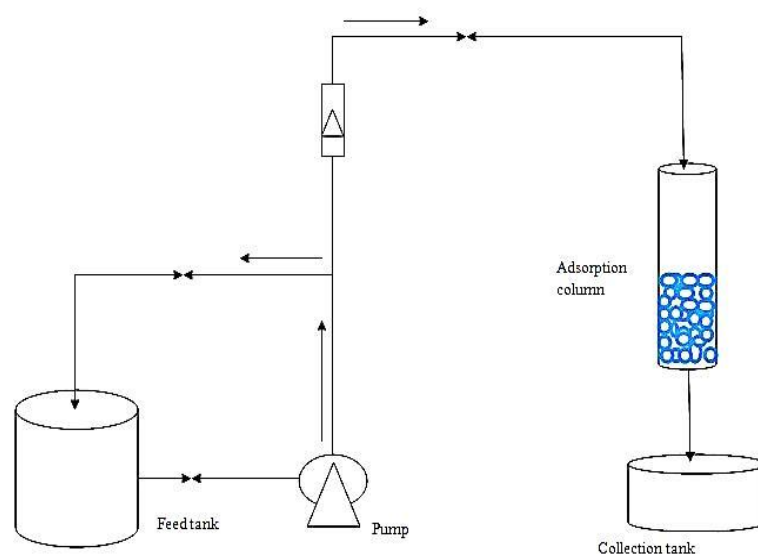


Figure 1.2: Schematic diagram of fixed bed column adsorption.

### 1.8.2 Batch Adsorption

Batch adsorption is used to measure the isotherms of metal ion adsorption onto the surface of the adsorbent. In the batch adsorption method, a known amount of adsorbent is combined with the required amount of solvent, and the concentration and pH of the solution are then adjusted. The next step is to reach adsorption equilibrium using continuous agitation for 24 hours at room temperature in a mechanical shaker. The initial and equilibrium concentration of metal ions are measured using a pertinent technique (like AAS) in order to evaluate the level of adsorption. Several factors, including the pH of the solution, the initial concentration of the aluminium solution, contact time, and adsorbent dose, affect how much  $Al^{3+}$  is able to bind to different adsorbents. As a result, while keeping the other parameters constant, one parameter is altered to better understand the principle and efficiency of adsorption (Ghimire et al., 2002). The amount of metal adsorbed at equilibrium per unit mass is calculated as;

$$q = \frac{C_i - C_e}{W} \times V \quad (1)$$

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Where ' $C_i$ ' is the initial concentration ' $C_e$ ' is the equilibrium concentration, ' $V$ ' is the volume of adsorbate solution in milliliter and ' $W$ ' is the weight of adsorbent in milligram. The percentage of metal ion adsorption (% A) is calculated using the equation (Acharya et al., 2018).

### 1.9 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the most powerful and useful tools for the examination and characterization of surface morphologies, fracture surfaces, microstructures of the activated carbon. SEM images obtained at microscopic level through SEM are primarily used to observe the structure and distribution of the pores present on the surface of the activated carbon. The presence of mesopores and micropores on the surface of activated carbon can be seen through the high resolution magnification of SEM. Activated carbon possessing more pores and irregular surface is considered to have high surface area and good adsorption capacity.

### 1.10 Fourier Transform Infrared Spectroscopy

FTIR is an analytical technique which can be used for identifying the types of functional groups present at the surface of adsorbent. The surface functional groups detected by FTIR would give the knowledge on the adsorption capability of certain adsorbate at the

surface of adsorbent. Fourier transform refers to a fairly recent development in the manner in which the data are collected and converted from an interference pattern to a spectrum. By interpreting these spectrum different functional groups present in the surface of adsorbent can be determined. More complex molecular structures lead to more absorption bands and more complex spectra.

### **1.11 Atomic absorption spectroscopy**

Atomic absorption spectroscopy (AAS) uses the absorption of optical radiation (light) by free atoms in the gaseous state as a spectroanalytical method for the quantitative measurement of chemical elements. The foundation of atomic absorption spectroscopy is the light absorption of free metallic ions.

The method is employed in analytical chemistry to establish the concentration of a specific element (the analyte) in a sample that will be subjected to analysis. AAS is utilized in pharmacology, biophysics, archaeology, and toxicology studies to identify over 70 distinct elements in solution or directly in solid samples using electrothermal vaporisation.

The clinical measurement of metals in biological fluids and tissues, such as whole blood, plasma, urine, saliva, brain tissue, liver, hair, and muscle tissue, is one application of atomic absorption spectrometry in several fields of chemistry. Both qualitative and quantitative analyses can be conducted using atomic absorption spectrometry.

### **1.12 Adsorption Isotherms**

Adsorption isotherm describes the equilibrium of the adsorption of material at a surface at a fixed temperature since the surface coverage of adsorbate depends on adsorptive adsorbents. As a function of the substance present in the gas phase or solution, it represents the volume of material bound at the surface. The Freundlich isotherm and the Langmuir isotherm are two often utilized adsorption isotherms in empirical models.

#### **1.12.1 Langmuir Adsorption Isotherm**

This isotherm is generated from the suggested kinetic mechanism and is semi-empirical in nature. The Langmuir isotherm, which describes sorption the best of all isotherms, has been successfully applied to many sorption processes because it assumes that all adsorption sites are equivalent, adsorbed molecules do not interact with one another, all adsorption occurs via the same mechanism, and at maximum adsorption only a monolayer is formed. Adsorbate molecules do not deposit on other adsorbate molecules that have

previously been adsorbed; rather, adsorption only takes place on the adsorbent's free surface.

$$\frac{1}{q_c} = \frac{1}{q_m b c_e} + \frac{1}{q_m} \quad (3)$$

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \quad (4)$$

Where  $q_e$  = amount of metal ion adsorbed per unit weight of adsorbent (mg/g)

$c_e$  = Equilibrium concentration of the adsorbate in a solution after adsorption (mg/L)

$q_m$  = Langmuir constant related to monolayer sorption.

$b$  = Langmuir constant related to the equilibrium constant and represents enthalpy of sorption.

The standard slope of  $\frac{c_e}{q_e}$  versus  $\frac{1}{q_m}$  gives the value of  $\frac{1}{b}$  from which the value of  $b$  can be determined. The intercept gives the value of  $\frac{c_e}{q_m}$  from which the value of  $q_m$  can be determined.

The equilibrium constant  $b$ , like all chemical processes, depends on temperature and is connected to Gibb's free energy, which in turn affects the process's enthalpy change.

$$G^\circ = RT \ln b \quad (5)$$

Where,  $R$  = universal gas constant in  $J K^{-1} mol^{-1}$ .

And Langmuir parameter  $K_L$  which is given by the following equation

$$K_L = \frac{1}{1 + b c_o} \quad (6)$$

If  $K_L = 1$  linear and  $C_o$  = initial concentration of adsorbate (mg/L)

And  $K_L = 0$  indicates the shape and nature of the adsorption process.

If  $K_L > 1$ , unfavourable,  $K_L < 1$ , favourable and  $K_L = 0$  indicates an irreversible type of adsorption.

### 1.12.2 Freundlich Adsorption Isotherm

Freundlich provided an empirical connection in 1909 that represented an isothermal fluctuation of the amount of adsorbate adsorbed by unit mass of adsorbent with pressure; this process is known as the Freundlich adsorption isotherm equation.

$$q_e = \frac{kc_e}{n} \quad (7)$$

$$\text{Or, } \log q_e = \log K + \frac{1}{n} \log C_e \quad (8)$$

Where  $q_e$  = amount of adsorbed per unit weight of adsorbent (mg/g)

$c_e$  = equilibrium concentration in (mg/L)

$K$  = adsorption constant roughly gives adsorption capacity (mg/g)

$n$  = Freundlich constant characteristic of adsorption system

Plot of  $\log q_e$  versus  $c_e$  gives a straight line with an intercept of  $\log K$  and slope of  $\frac{1}{n}$ .

Experimentally, it was found that the exact of adsorption varies directly with pressure till a saturation pressure is reached beyond that point, rate of the adsorption saturates even after applying higher pressure. The value of  $\frac{1}{n}$  lies between 0 to 1 and indicates the favourable adsorption of metal ions. This isotherm does not indicate that the sorbent will be saturated by the sorbet. Thus, mathematical predictions for infinite surface coverage indicate multilayer adsorption on the surface. Therefore, in addition to a highly non-ideal sorption that involves a homogeneous surface, adsorption on a heterogeneous surface is also appropriate. The batch technique can be used to carry out sorption experiments. To ascertain the rate at which metal ions bind to the adsorbents in a reagent bottle, batch studies are conducted. A steady rate of shaking was applied to the reagent bottles to give the adsorption equilibrium enough time to occur. It is expected that throughout the experiment, the applied shaking speed enables all of the surface area to come into contact with metal ions. In order for the study to be representative of environmental relevant conditions, it can be conducted at room temperature. A pH metre is used to determine the pH of the solution. In order to prevent pH fluctuations brought on by the exchange of gases during the experiment, the reagent bottles will be sealed and kept closed. By adjusting contact time, adsorbent concentration, temperature, and solution pH, the impact of different parameters on the rate of the adsorption process will be seen. (Kundu et al.,



2004) Keeping one parameter changing and another parameter constant, the effect of each parameter can be studied. The solution volume ( $V$ ) is kept constant. The amount of metal adsorbed per unit mass is calculated by using formula as,

$$q_t = \frac{c_i - c_e}{W} \times V \quad (9)$$

$$R\% = \frac{c_i - c_e}{W} \times 100 \quad (10)$$

Where  $C_i$  and  $C_e$  is the initial and equilibrium concentration (mg/L) is the mass of the adsorbent (g) and  $V$  is the total volume of the solution taken (mL). Removal of Aluminium ions in percentage (R) was calculated by using the relation 10.

### 1.13 Adsorption Kinetics

The study of adsorption kinetics is crucial to waste water treatment because it not only sheds light on the mechanisms and reaction pathways of sorption processes but also explains the solute uptake rate, which in turn affects the amount of time sorbate is retained at the solid-solution interface. (Kamar et al., 2015). Two widely used kinetic models—pseudo-first-order and pseudo-second-order kinetic models—can be used to analyse the kinetic data resulting from the adsorption of Al (III) onto sugarcane baggase. The linear regression correlation coefficient ( $R^2$ ), a metric for how well a forecast model's predicted values match the experimental data, is used to determine which model has the best fit.

#### 1.13.1 Pseudo-first order kinetics model

Lagergren's first-order rate equation (1898) has been referred to as the pseudo-first-order kinetic model in order to distinguish kinetics of equation based on the sorption capacity of solid form and concentration of solution (Yuh-San, 2004). The rate of sorption site occupation is assumed to be proportional to the quantity of vacant sites in the pseudo-first-order kinetic model. The pseudo-first-order equation is written as,

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (11)$$

Where,  $q_e$  = amount of metal adsorbed at equilibrium (mg/g)

$q_t$  = amount of metal ion adsorbed at any time (mg/g)

$K_1$  = Lagergren's rate constant for first-order adsorption ( $\text{min}^{-1}$ )

On integrating, the equation becomes,

$$\log(q_e - q_t) = \log q_e - \log \frac{K_1 t}{2.303} \quad (12)$$

The plot of  $\log(q_e - q_t)$  versus  $t$  gives a straight line from which  $K_1$  and  $q_e$  can be determined from slope and point of interception respectively.

$$\text{Hence, } K_1 = -\text{slope} \times 2.303 \quad (13)$$

$$q_e = C \quad (14)$$

### 1.13.2 Pseudo-second order kinetic model

The pseudo-second order is based on the presumption that chemical sorption, which involves valence forces through the sharing or exchange of electrons between metal ions and adsorbent, may be the rate-limiting step. The equation for the pseudo-second-order kinetic rate is expressed as (Acharya et al., 2018).

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (15)$$

Integrating this equation at boundary condition gives,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (16)$$

$$\text{Let, } P = K_2 q_e^2 \quad (17)$$

$$\frac{t}{q_t} = \frac{1}{p} + \frac{1}{q_e} \times t \quad (18)$$

The linear plot of  $\frac{1}{q_t}$  versus  $t$  gives values of  $q_e$  and  $K_2$ . By examining the kinetics at various time points, it is possible to examine the validity of kinetic models. The equilibrium metal uptake needs to match the experimental equilibrium. If not, the response is unlikely to match the model (Kamar et al., 2015).

## 1.14 Objective of the study

### 1.14.1 General Objective

The general objective of the research work is to prepare bio-adsorbent from low-cost bio-waste (sugarcane baggase) followed by chemical modification to charred and xanthate forms for investigating the adsorption capacity to remove Aluminium ions. The main objective of the research is to develop efficient and selective adsorbent from locally

available agricultural waste by simple chemical modification, which can replace expensive synthetic adsorbent.

#### **1.14.2 Specific Objective**

1. Preparation of powdered form of sugarcane bagasse.
2. Modification of the adsorbents from the raw form using concentrated Sulphuric acid.
3. Xanthation of charred sugarcane bagasse powder with NaOH and CS<sub>2</sub>.
4. Characterization of adsorbent using SEM and FTIR for adsorptive removal of Aluminium ions from aqueous solution.
5. Determination of various physiochemical controlling factors affecting adsorption including pH, adsorbent concentration and time of contact.
6. Finding out the kinetics and isotherm model for adsorption process.
7. Comparative study for the percentage removal of Aluminium ions between charred and xanthated adsorbent.

#### **1.15 Research gap and novelty of the work**

There are several standard ways for removing Aluminium (III), but they are expensive and environmentally unfriendly, so they may not be appropriate for impoverished nations like Nepal. Because of its widespread availability, low cost, and relatively high carbon content as well as the existence of porous structure, agro-wastes are one of the most commonly utilised methods for adsorption. Here, a promising material to close the research gap is created from sugarcane bagasse: a low-cost adsorbent. In the literature, a variety of agricultural bio-mass materials including fruit peels or shells have been utilised as adsorbents to remove aluminium. To the best of my knowledge, chemically activated, charred and xanthated bio-adsorbent sugarcane bagasse is a new material that is not studied yet for the preparation of adsorbent for the removal of Aluminium ions from aqueous solution. More interest have been drawn to this bio-adsorbent is due its successful removal of several heavy metal ions and dyes from the aqueous solution.

## Chapter- 2

### 2. LITERATURE REVIEW

#### 2.1 Literature review

Singh et al., (2005) investigated the charred rice husk's adsorption behaviour. Data on adsorption equilibrium came from batch trials. The activated rice husk char had a lower adsorption capacity than the inactivated rice husk char. The adsorption was significantly impacted by the pH of the solution. Aluminium was most effectively removed when the pH was between 4.2 and 4.4. As the concentration of aluminium increased, the rice husk char's ability to adsorb more aluminium diminished. Rice husk char is ineffective at removing aluminium when there is a concentration of more than 10 mg/l. Adsorption data was organised according to Langmuir adsorption isotherms.

Al-Mustaseb et al., (2007) investigated how well date-pit activated carbon adsorbs aluminium. The adsorption was 0.305 mg/g at low starting concentrations of Al and low pH. The adsorption data were consistent with the Dubinin-Radushkevich (D-R) and Langmuir adsorption models. pH 4 was discovered to be the ideal level for Al adsorption.

Homagai et al. (2010) synthesised the unique charred xanthanized sugarcane bagasse with CS<sub>2</sub> under alkaline conditions and investigated the adsorption behaviour with heavy metals such as Cadmium, Lead, Nickel, Zinc, and Copper. Adsorption data were fitted with the Langmuir isotherm and pseudo-second order kinetics was implemented to control the reaction. The pH range that worked best was between 4-6.

Kumari and Ravindhranath., (2012) studied the adsorption behavior of Al by using bio-adsorbents derived from *Moryngea millingtonia* and *Cygium arjunum* plants parts like leaves and barks. According to the study, adsorption amount can be affected by pH fluctuation, sorbent dosage, and duration. Both *Moryngea millingtonia* and *Cygium arjunum* had an optimal pH of 6 at which 100% adsorption took place, it was discovered. At a fixed pH, it was discovered that the % of adsorption increased with time until becoming constant after a certain period.

Ghani.,(2014) investigated the removal of aluminium (Al) from waste water using an adsorbent made from rice hulls. The Langmuir isotherm was followed by the adsorption. After 180 minutes of contact time, the adsorption rate was found to be at its peak. The highest adsorption (82%) occurred at pH 4, and the adsorption kinetics was of the pseudo order.

Denzili and Ridvan., (2001) in order to remove Al (III) ions from drinking and dialysis water, magnetic dye poly(2-hydroxyethylmethacrylate) (mPHEMA) adsorbent beads was produced and tested its applicability. Al (III) adsorption from aqueous solutions was examined by batch system. The study discovered that at pH 5.0, the maximum Al (III) adsorption was  $722 \text{ molg}^{-1}$  polymers. Additionally, the beads' Al (III) adsorption capacity may be reused without suffering a major loss.

El-nahaas et al., (2021) examined the aluminium adsorption from sugarcane bagasse activated carbon and compared it with activated carbon that is easily available on the market. This investigation shows that their activated carbon removes aluminium successfully, reaching 80% at high starting concentrations, just like commercial activated carbon ( $10 \text{ mgL}^{-1}$ ). Additionally, the price of the exothermic adsorption method when activated carbon was made from sugarcane bagasse was \$40 per tonne.

Cherifi et al., (2009) evaluated the impact of initial water content and temperature on the electrokinetic removal of aluminium from drinking water sludge. The study found that the mobility of aluminium species is stimulated when 10 V is applied for 10 days to drinking water sludge at temperatures of  $20^\circ$  or higher. Starting water content was 100 mL of tap water/75 g of sludge in weight. By flushing the acid created at the anode over the specimen, Al (III) is released. As a result, Al (III) desorbs, moves through the electroosmotic flow, and is advected.

Mortada et al., (2017) in order to remove aluminium, they synthesised cellulose that has been treated with gallic acid with microwave aid. The produced adsorbent had a maximum adsorption capacity of  $59.8 \text{ mg g}^{-1}$  and exhibited a strong affinity for adsorption to  $\text{Al}^{3+}$ . Additionally, the method was used to preconcentrate  $\text{Al}^{3+}$  from samples of water, rocks, blood, and soil. It was also exothermic and the adsorbent could be easily reused.

Aly et al., (2013) prepared polyacrylonitrile beads and employed it for the adsorption of  $\text{Al}^{3+}$  ions from aqueous solutions. The prepared adsorbent was characterised by IR, X-ray diffraction, SEM, and the effects of pH, contact time, kinetics, and adsorption isotherms were investigated. The investigation discovered that the highest adsorption occurred at pH 4 at 30 min of contact time with an efficiency of 65% at  $10 \text{ mgL}^{-1}$  starting concentration. Additionally, the adsorption adhered to the Langmuir monolayer adsorption isotherm and pseudo-second order kinetics.

Humelnicu et al., (2021) used modified hydroxyapatites for the adsorption of  $\text{Al}^{3+}$  ions and performed the batch technique. The adsorption followed Langmuir adsorption isotherm and adsorption rate was described by a pseudo-second order kinetic model. The result indicated that hydroxyapatite treated with pluronic P123 had more adsorption capacity ( $117.65 \text{ mgg}^{-1}$ ) than treated with pluronic F127 ( $109.89 \text{ mgg}^{-1}$ ) and untreated hydroxyapatite ( $104.17 \text{ mgg}^{-1}$ ).

Nasseh et al., (2019) developed a kind of ceramic foam that was applied over polyurethane sponge for the removal of  $\text{Al}^{3+}$  ions from aqueous solution. The maximum adsorption capacity of the ceramic foam was found  $3.0639 \text{ mgg}^{-1}$  at  $25^{\circ}\text{C}$ . After 10 times of adsorption/desorption cycle, the efficiency of ceramic form was reduced to 19.7%. The regeneration tests were performed using 0.01M HCl solution.

Virolinen et al., (2021) used aminomethylphosphonic acid functional chelating resin (Lewatit TP260) for removing Fe, Al, Mn, and Cu from leach solutions of lithium-ion battery waste. The two step elution procedure was followed in which Cu and Mn was first with sulphuric acid solution followed by Fe and Al with potassium oxalate solution. The optimum pH for the removal of these metals was 4.

Peydayesh et al., (2019) developed a membrane technology based on amyloid fibrils for the removal of  $\text{Al}^{3+}$  from its aqueous solution. Amyloid- based membrane demonstrated outstanding removal efficiencies around 98% at pH 3.5 to 4.5.

Cayllahua and Torem.,(2010) studied the biosorption capacity of  $\text{Al}^{3+}$  ions by *Rhodococcus opacus* from waste water. The maximum adsorption capacity was found to be  $41.59 \text{ mgg}^{-1}$  at pH 5.0 (initial concentration of  $50 \text{ mgL}^{-1}$ ) and temperature  $25^{\circ}\text{C}$ . The maximum uptake was obtained in 20 minutes of contact time. The kinetic data were well fitted by pseudo second order also the reaction was found to be exothermic in nature.

Sari and Tuzen ., (2009) conducted a research for the biosorption of  $\text{Al}^{3+}$  ions from the aqueous solution by brown algae (*Padina pavonica*) biomass. The biosorption capacity was found as  $77.3 \text{ mg g}^{-1}$ . The adsorption of  $\text{Al}^{3+}$  ions onto *P.pavonica biomass* was spontaneous and endothermic. The reaction followed pseudo second order kinetics. Furthermore, the efficiency of the biomass was reduced by 20% after 10 times of adsorption-elution. The metal ions were desorbed by using 1 M HCl solution.

Samy et al., (2022) performed a research using natural clay such as bentonite and combining bentonite-cationic polymer as coagulant to remove aluminium salts from lean sludge. 0.6 ppm concentration of bentonite was sufficient for the 98.8% removal of  $\text{Al}^{3+}$

ions. The reaction followed pseudo-second order with rate constant of  $11.922 \text{ mol}^{-1}\text{S}^{-1}$ . The adsorption capacity was  $1.48 \text{ mg g}^{-1}$ .

Lodeiro et al., (2010) investigated marine algae, obtained from beach cast seaweed as a adsorption material for the adsorption of  $\text{Al}^{3+}$  ion from waste water. The optimum pH value was 4 with a maximum adsorption capacity of  $22.5 \text{ mg g}^{-1}$ . The reaction followed Pseudo-second order kinetics.

Abdel-Ghani et al., (2009) used *Typha domindensis* leaf powder for the removal of Al, Fe, Zn and Pb ions from aqueous solution. The removal process increased with the contact time and attained saturation in about 120 minutes. The adsorption kinetics followed pseudo second order. The reaction followed Langmuir adsorption isotherm for  $\text{Al}^{3+}$  ions adsorption.

Tangsathitkulchai et al., (2012) removed aluminium ions by making a aluminium dye complex from natural dye solution using activated carbon obtained from coconut shell and again with eucalyptus-based activated carbon. Pseudo-second order kinetics were used to guide the adsorption. Both activated carbon followed the Langmuir adsorption isotherm in terms of adsorption. With the help of these carbonaceous materials, almost 80% of the initial  $\text{Al}^{3+}$  content was eliminated.

Homagai et al., (2022) evaluated the efficiency of charred xanthated sugarcane bagasse and charred sugarcane bagasse in the removal of mercury ions from the aqueous media and found that charred sugarcane bagasse was more efficient in removing the mercury ions. According to their findings, maximum adsorption was found to be  $125 \text{ mg g}^{-1}$  and  $333.34 \text{ mg g}^{-1}$  for charred sugarcane bagasse and charred xanthated sugarcane bagasse respectively at pH 4.5. Furthermore, the adsorption process was found to be endothermic.

## Chapter-3

### 3. MATERIALS AND METHODS

#### 3.1 Materials and Methods

All the experiments were carried out using charred and xanthated sugarcane bagasse which was prepared from the sugarcane bagasse collected from the local market in Thamel, Kathmandu, Nepal in 2021 March. All the chemicals used were LA/AR grade and were used as received.

#### 3.2 Instruments & Chemicals or Reagents Used

The instruments that have been used during the research are listed below:

1. Laboratory mill (grinder)
2. Sieve number 150 (India)
3. Weighing Balance
4. Mechanical shaker
5. Digital pH meter (Labotronics-11, India)
6. AAS (Nova 350, Analytica)
7. Double beam UV-VIS spectrophotometer (Labotronics LT-2802 )
8. Hot air oven
9. Desiccator

Table 3.1: Chemical employed in the work

S.N	Name of the chemicals	Manufacturer name	%Purity
1	Sodium Hydroxide (NaOH)	Loba Chemie	98
2	Aluminium Chloride (AlCl <sub>3</sub> )	Fisher Scientific	99.9
3	Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> )	Fisher Scientific	98
4	Hydrochloric acid (HCl)	Qualigens fine chemicals	97
5	Buffer Tablets of pH 4 & 7	Qualigens fine chemicals	-

#### 3.3 Preparation of raw adsorbent material

In Falgun of 2077, sugarcane bagasse was collected from Thamel, a neighbourhood market in Kathmandu, Nepal (March, 2021). To completely remove any loosely held particles from the collected bagasse, it was chopped into small pieces and rinsed with distilled water. After being thoroughly washed, sugarcane bagasse was exposed to the sun



for about three days to completely dry it out. Using a 6000 rpm ball mill, bagasse made from fully dried sugarcane was processed into a fine powder. The entire dry powder is identified as raw adsorbent material on the label.

### **3.4 Preparation of charred sugarcane bagasse**

350 g of the raw adsorbent material was placed in a bucket with a 5 L capacity for the preparation of the charred sugarcane bagasse powder. 400 mL of concentrated sulfuric acid (Fisher Scientific, Sp.gr. 1.834-1.836 g, % purity 98) was then added to the bucket, and the mixture was thoroughly stirred under a fume hood until it turned completely black. A small amount of concentrated  $H_2SO_4$  was added incrementally while it was charring until it reached a deep, dark colour. Thus, the bagasse of sugarcane that had been obtained was left over for 24 hours. The charred sample was repeatedly washed in deionized water until the pH of the water approached neutral, or pH 7, and then dried in a hot air oven for 24 hours at 40 °C to completely remove the moisture from it. As a result, the acquired adsorbent was completely crushed and sieved with 150 m. The 250 g charred sample was then placed in an airtight bottle after one hour in a desiccator.

### **3.5 Preparation of xanthate sugarcane bagasse**

150 g of the charred sugarcane bagasse was placed in a 1000 mL beaker to create xanthate sugarcane bagasse. Following that, 500 mL of a 15% NaOH solution was added, and it was magnetically stirred at a speed of 200 RPM for three hours. After that, 40 mL of carbon disulfide was added, and the mixture was once more agitated for 10 hours using a magnetic stirrer before being left overnight. To neutralise the sample, the solution was first rinsed with distilled water and then with double distilled water. To completely remove the moisture from the material, it was then shade dried for two days and then oven dried for 15 hours at 40 °C. Finally, the xanthated sugarcane bagasse (130 g XSB) produced was kept in a desiccator for one hour and then placed in an airtight container for storage.

### **3.6 Preparation of reagents**

#### **3.6.1 Preparation of 1000 ppm of aluminium (III) solution**

4.94 g of aluminium chloride was dissolved in a 1000 mL volumetric flask to create a stock solution of aluminium chloride with a 1000 ppm concentration. A volumetric flask containing a 1000 ppm stock solution of the aluminium solution was used to generate working solutions at various concentrations using the serial dilution procedure.

### **3.6.2 Preparation of buffer solutions**

The pH 4 and pH 7 tablets were each individually dissolved in 100 mL of distilled water to prepare the standard buffer solutions.

### **3.6.3 Preparation of 15 % of sodium hydroxide (NaOH) solution**

75 g of sodium hydroxide was dissolved in 500 mL of water to produce a 15% NaOH solution.

### **3.6.4 Preparation of 1M sodium hydroxide (NaOH) solution**

1M NaOH solution was prepared and diluted as needed.

### **3.6.5 Preparation of 1M hydrochloric acid (HCl) solution**

Hydrochloric acid from the Amrit campus chemistry laboratory was used to make a 250 mL solution of 1M HCl, which was then diluted further as needed.

## **3.7 Characterization of adsorbent**

For the efficient removal of aluminium, charred sugarcane bagasse and charred sugarcane bagasse that has undergone chemical modification were prepared. Both of them were characterized in order to analyze the surface structure, morphology, and functional groups present in the bio-adsorbent, which demonstrate the modified adsorbent's capacity for adsorption. For which the following characterization tools were used.

### **3.7.1 Fourier- transform infrared spectroscopy**

The functional group study was carried out using Fourier transformed infra-red radiation (FTIR, Perkin Elmer Spectrum 10.5.1 USA). The FTIR spectra of RSB, CSB, and XSB were examined. Among the IR radiation passed through the sample in FTIR spectroscopy; some of the radiation is absorbed by the sample and some of the radiation is transmitted by the sample. The spectrum that resulted served as a representation of the molecular adsorption and transmission, forming the sample's molecular signature. By examining the shifting of the FTIR peaks following the adsorption experiment, it was possible to examine the impacts of the surface functional group's presence on the adsorption of aluminium.

### **3.7.2 Field Emission Scanning electron microscopy (FE-SEM)**

The morphology of as-prepared activated carbon was studied using field emission scanning electron microscopy (FE-SEM, Carl Zeiss Supra-40, VP Germany) at an accelerating voltage of 5.0 kV. A field emission source releases electrons, and they are

then accelerated in a strong electrical field gradient. These so-called primary electrons are focused and refracted by electronic lenses within the high vacuum column to create a narrow scan beam that bombards the target. Each point on the item therefore emits secondary electrons. These secondary electrons' angles and velocities are related to the object's surface structure. The secondary electrons are captured by a detector, which then generates an electrical signal. A video scan-image is created by amplification and transformation of this signal.

### **3.8 Adsorption study**

The working solution of aluminium chloride, CSB, and XSB was used as an adsorbent in an adsorption investigation. Using the stock aluminium solution with a concentration of 1000 ppm, the working solutions with the necessary concentrations were prepared. To ensure complete adsorption, 25 mg of the adsorbent and 25 mL of the aluminium solution were separately combined in a reagent bottle and agitated for three hours on a mechanical shaker. Whatman filter paper was used to filter the solution in order to remove the adsorbent and produce pure liquid. Utilizing AAS, the absorbance of the filtrate was measured both before and after adsorption, and the adsorption capacity of the various adsorbents was examined.

#### **3.8.1 Effect of pH**

The pH of the solution under investigation affects the removal of metal ions using an adsorbent. It is important to determine the aqueous solution's ideal pH before studying the effects of contact time, starting concentration, and adsorbent dose. Aluminium is removed using CSB and XSB in a batch adsorption test. By utilising sodium hydroxide solution and hydrochloric acid, the solution's initial pH was maintained. In this experiment, 25 mL of 50 ppm aluminium chloride solutions were taken individually in various reagent bottles with pH values ranging from 1 to 8. Then, 25 mg of the adsorbent (CSB and XSB) was added to the reagent bottles that contained the solutions with the various pH levels (1 to 8). To achieve equilibrium, each reagent bottle was then shaken mechanically for approximately 5 hours at room temperature at 200 rpm. After agitation, the solutions were left standing for an hour before being filtered using filter paper. AAS was used to measure the filtrate's absorbance. The ideal pH of the solution is that at which metal adsorption was greatest for CSB and XSB. The pH has an impact on the ability of functional groups like carbonyl, phenol, hydroxides, amino groups, and hydrocarbons of the cell wall to dissolve in the metal ion ionization state. The ideal pH for both CSB and

XSB adsorbents can be the same or different.

### **3.8.2 Kinetic studies of adsorption of aluminium**

The influence of the contact time at room temperature on the amount of time needed by the adsorbents for the maximum removal of the aluminium utilising CSB and XSB was evaluated. For this study, 25 mL of the metal (aluminium) solution with an ideal pH and a concentration of 50 ppm was taken in a reagent bottle. The individual bottles received 25 mg of the adsorbent, which was then added and mechanically shaken at a speed of 200 rpm. Adsorption data were collected at regular intervals of time, including 30, 60, 120, 150, 180, and 210 minutes. The sample was then taken, filtered, and analyzed. The absorbance of the aluminium metal was measured by AAS until the metal's adsorption quantity reached a constant value, at which point no further adsorbate was adsorbed. In order to ascertain the metal's adsorption kinetics, the adsorption process' kinetic characteristics were examined for contact times ranging from 30 minutes to the period required for full adsorption. Pseudo-first-order and pseudo-second-order kinetic models developed by Lagergren were used to assess the data acquired by computing the percentage absorbance of the aluminium at each time for CSB and XSB. By plotting the data obtained after the specified period, the removal kinetics of the aluminium were examined.

### **3.8.3 Adsorption isotherm study**

The amount of un-adsorbed adsorbate still present in the solution at equilibrium time is related to the amount of adsorbed per unit mass of the adsorbent by the adsorption isotherm curve. In order to do this, 25 mL of an aluminium solution with an optimal pH balance and various initial concentrations were taken in a separate bottle, to which 25 mg of adsorbent was added, and the bottle was sealed airtight. The solution was shaken at 200 rpm for three hours and then refrigerated for twenty-four hours. Adsorption was evaluated in Atomic absorption spectroscopy (AAS) on the agitated sample after filtering, and adsorptions at various initial concentrations were examined both before and after adsorption. The results from the investigation into the impact of the metal's initial concentration were used to analyse the adsorption isotherm model.

## Chapter-4

### 4. RESULTS AND DISCUSSION

#### 4.1 Characterization of charred and xanthated sugarcane bagasse

##### 4.1.1. FE-SEM

Field-Emission Scanning Electron Microscopy (FE-SEM) was used to observe the surface morphologies of RSB, CSB and XSB before adsorption whereas CSB and XSB after adsorption. The surface of RSB was found to be smooth whereas the fiber surface of CSB was found to be relatively rough and non-uniform most probably due to hydrolysis reaction on the surface of CSB by the action of concentrated sulphuric acid. SEM images of CSB revealed its non-uniform and rough surface that changed into irregular honeycomb structure. It can be seen that external surfaces of XSB is full of cavities like a honeycomb structure. The XSB showed apparently isolated and irregularly distributed pores, which are supposed to be formed due to the increase in effective diffusion surface area that helps to expose more surface-active binding sites and finally enhance adsorption capacity of the modified sugarcane bagasse. Hence, the xanthation process had not only enhanced the morphology of charred sugarcane bagasse but also its physical and chemical characteristics. Similarly the charred sugarcane bagasse after adsorption (CSBA) and xanthated sugarcane bagasse after adsorption (XSBA) showed that after adsorption of metal ion, the honeycomb surface like structure is completely filled which indicates that the adsorption has taken place properly. The surface morphology of RSB, CSB and XSB characterized by SEM are shown in figure 4.1. Similarly, the morphological images of CSBA, and XSBA characterized by SEM are shown in figure 4.2.

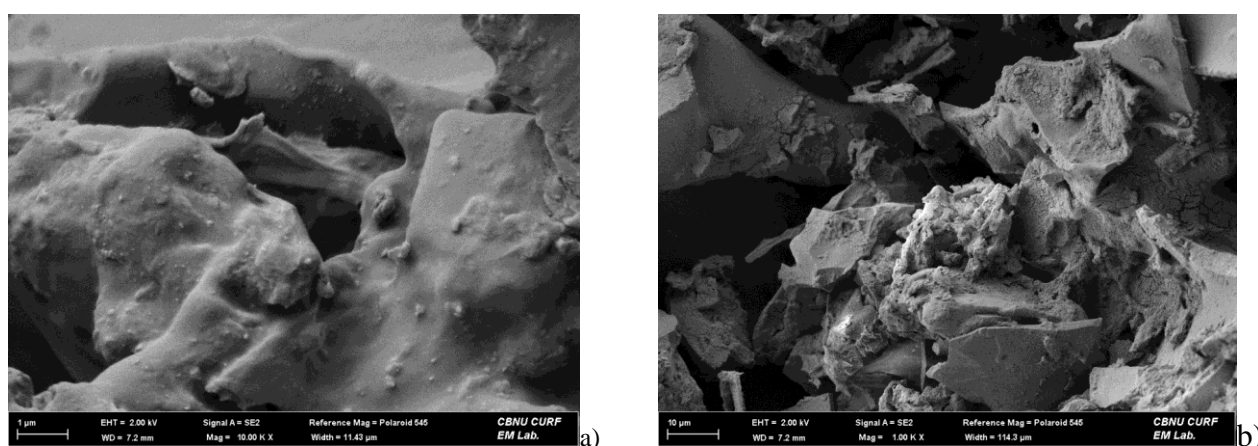
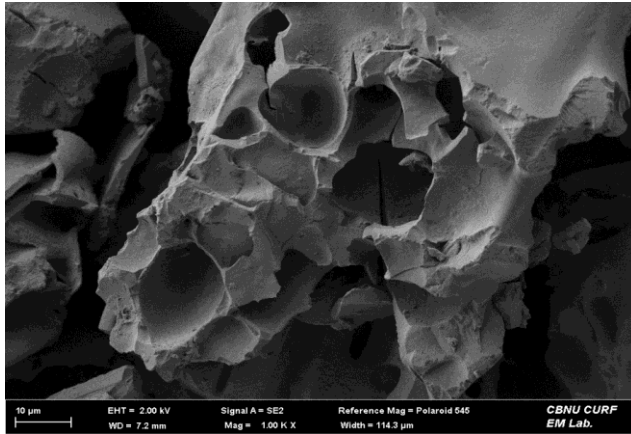
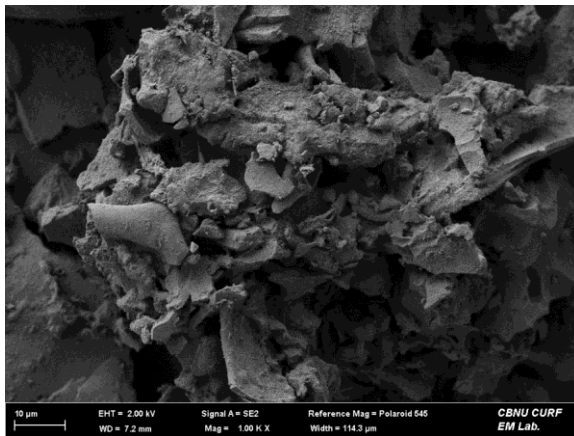


Fig. 4.1: SEM image of a) raw sugarcane bagasse(RSB)

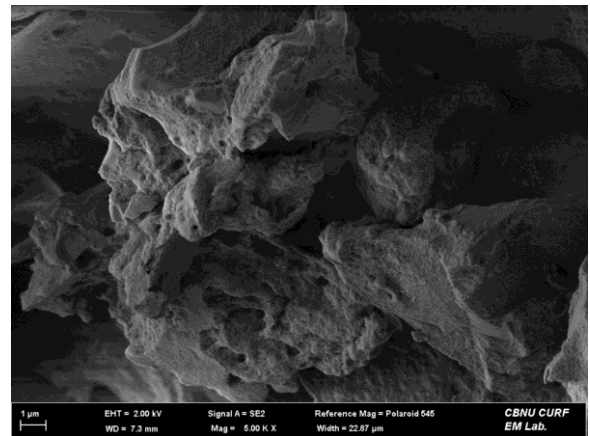
b)charred sugarcane bagasse (CSB)



c) xanthated sugarcane bagasse(XSB) before adsorption.



(a)



(b)

Figure 4.2: SEM image of a) charred sugarcane bagasse(CSB) and b) xanthated sugarcane bagasse(XSB) after adsorption

The EDS spectra in fig. 4.3 showed the presence of carbon, sulphur, aluminium and sodium in the xanthated sample after adsorption. Additionally, the presence of oxygen could be due to the presence of oxides forms. The EDS spectra explicitly showed the successful xanthation and the adsorption process.

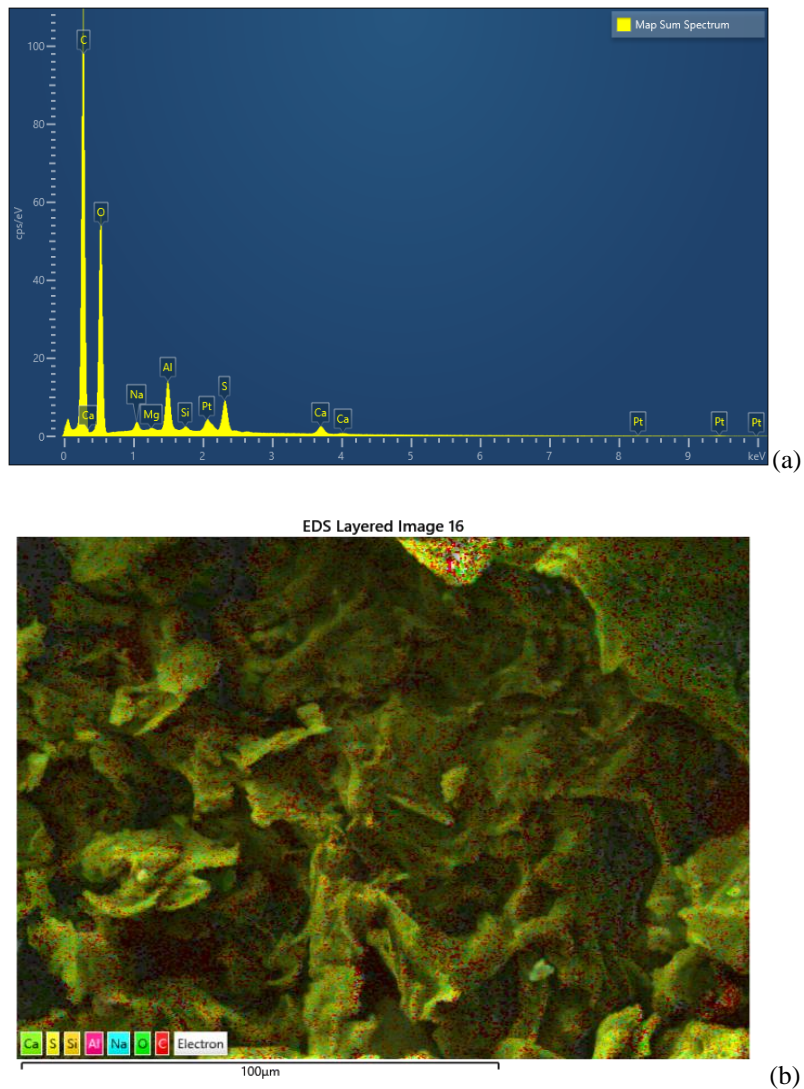


Figure 4.3: a)EDS spectra and b) elemental mapping image

The EDS spectra in fig. 4.3 (a) showed the presence of carbon, sulphur, aluminium and sodium in the xanthated sample after adsorption. Additionally, the presence of oxygen could be due to the presence of oxides forms. The EDS spectra explicitly showed the successful xanthation and the adsorption process. The EDS image in fig. 4.3 (b) showed the presence of carbon, aluminium, sulphur and sodium in the mapping. Additionally, the presence of oxygen could be due to the presence of oxides forms. The elemental mapping clearly showed the successful xanthation and adsorption process.

Table 4.1: EDS Table showing different adsorbed elements in the sample

Element	Line Type	Apparent concentration	k Ratio	Wt%	Atomic %
C	K series	22.75	0.22748	59.45	67.35
O	K series	22.16	0.07456	35.81	30.46
Na	K series	0.54	0.00227	0.42	0.25
Mg	K series	0.09	0.00059	0.08	0.04
Al	K series	2.22	0.01592	1.85	0.93
Si	K series	0.18	0.00146	0.15	0.07
S	K series	1.81	0.01557	1.57	0.66
Ca	K series	0.82	0.00733	0.68	0.23
<b>Total:</b>				<b>100.00</b>	<b>100.00</b>

#### 4.1.2 Fourier Transform Infra-Red (FTIR) Analysis

The FTIR spectrum of RSB, CSB and XSB are shown in the figure 4.4. The FTIR spectrums of adsorbents were taken in the range of 400-4000 $\text{cm}^{-1}$  using IR tracer. In fig 5.8 spectrum of RSB has many peaks for different functional groups. It means many organic compounds are present in the RSB. No peaks are seen at the range around 1000 $\text{cm}^{-1}$ , which indicates the absence of sulphur in RSB. In fig 4.4 Spectrum of CSB shows comparatively less number of peaks that refers most of the organic compounds are destroyed during charring process. A broad peak is seen at the range of 3397.5 $\text{cm}^{-1}$  that indicates the presence of hydroxyl group for both CSB and XSB.



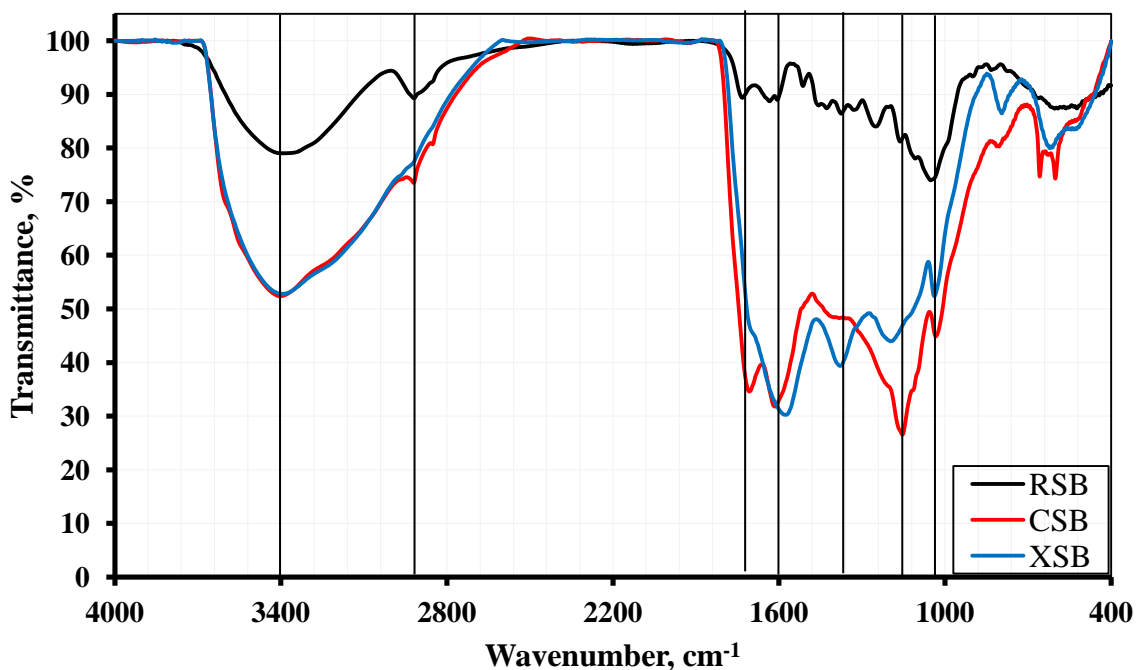


Figure 4.4: FTIR spectrum of RSB, CSB and XSB

## 4.2 Adsorption Study

Adsorption study was performed with respect to the effect of pH, effect of contact time, and effect of initial concentration. Percentage removal increased with the initial concentration and increased with an increase in contact time of modified sugarcane bagasse. As initial pH increased, percentage adsorption increased till pH 4 and then gets decreased. Percentage adsorption of chemically modified XSB was found more than that of CSB because of more adsorption sites present in chemically modified XSB than that of CSB. Thus XSB could be employed as the best alternative adsorbent than commercial activated carbon for effluent treatment containing aluminium ions.

### 4.2.1 Effect of pH

The pH of the solution is the most important parameter which influences the metal ion speciation and surface properties of adsorbent and hence controls the adsorption of ionic species. In this section, the influence of pH on the adsorption process with their adsorption efficiency has been analyzed at different pH. Figure 4.5 shows the effect of pH on adsorption of aluminium by CSB and XSB. For this study, 50 ppm of the metal solution was taken and required pH (1 to 8 in each bottle) was maintained using a pH meter at room temperature. Then 25 mg of the CSB, and XSB was taken in a reagent bottle along within pH maintained metal solution. Adsorption study for effect of pH by bio adsorbent i.e. CSB and XSB was done separately in reagent bottle from pH 1 to pH 8.

From the pH studies, it was seen that the optimum pH for the adsorption of metal ions for both CSB and XSB was found to be pH 4 i.e. maximum removal of aluminium ion solution was found at pH 4. Below and above the pH 4, the adsorption of aluminium by the activated carbon was low. This could be associated with the surface charge of activated carbon which is greatly influenced by pH of the media. The % removal of the aluminium metal ion by CSB increased from 9% at pH 1 to 73.83% at pH 4 then again decreased up to 55% at pH 8 whereas for XSB % removal of aluminium ion solution increased from 21% at pH 1 to 97.72% at pH 4 and then again decreased up to 76% at pH 8.

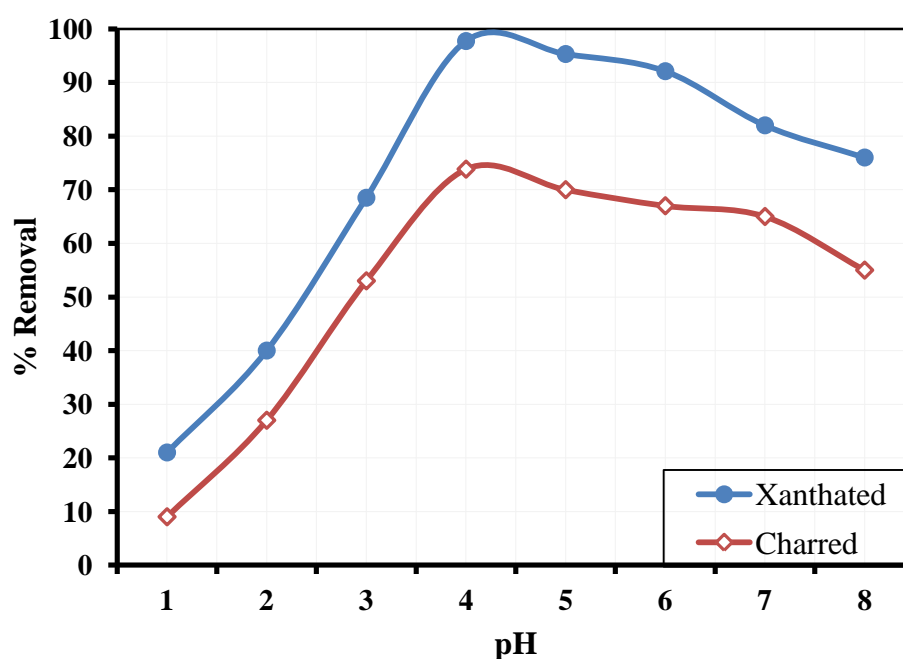


Figure 4.5: Effect of pH on the adsorption of  $Al^{3+}$  by using xanthated and charred sugarcane bagasse.

From the pH studies, it is seen that the optimum pH for XSB and CSB was found to be 4.0. It can be seen from fig. 4.5 that the maximum percentage removal of the aluminium metal ion was found to be 73.83% and 97.72% for CSB and XSB, respectively. The metal removing ability of the XSB was found more efficient than that of the CSB probably due to the addition of the chelating group i.e. S-atom of the sulfur group which enhances the ability of the activated carbon more metal ion on the XSB. Thus, it can be concluded that the optimum pH for adsorption of aluminium ions by CSB and XSB is 4.0. This obtained result is in the agreement with the adsorption of Aluminium ions with the help of adsorbent prepared from date-pit seeds (Al-Muhtaseb et al., 2008).

#### 4.2.2 Effect of contact time

The contact time is an important parameter for performing the batch adsorption experiment. In this section, the amount of adsorbate uptake by both of adsorbents at different time intervals has been investigated which is shown in the plot of  $q_t$  versus time in the figure 4.6. The effect of contact time for adsorptive removal of  $Al^{3+}$  was studied in the range of 0-210 min. The experiment was set using 25 mL of solution of aluminium of 50 ppm at pH 4 for both CSB and XSB with an agitation speed of 200 rpm for 5 hours at room temperature.

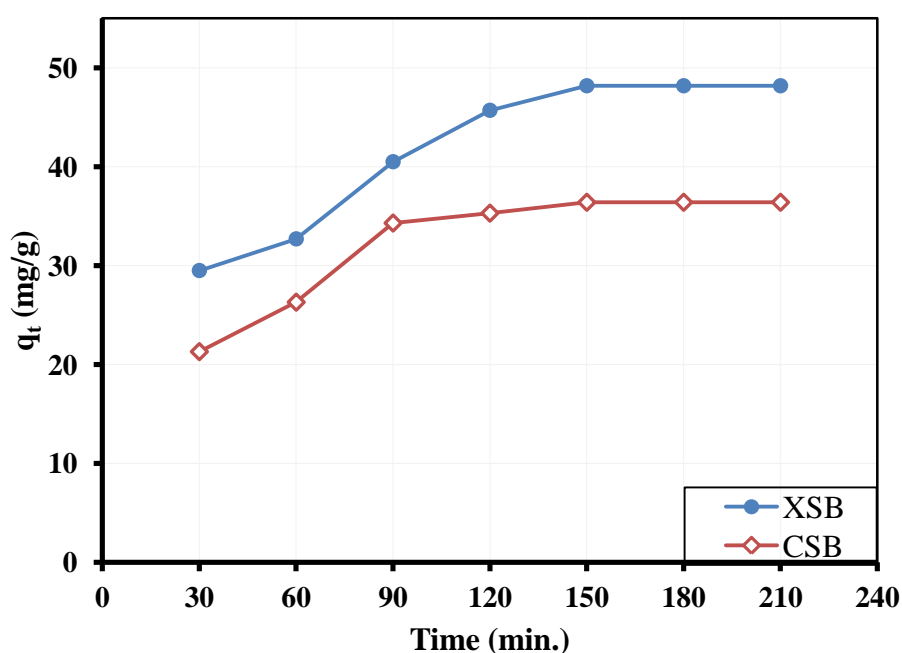


Figure 4.6: Effect of contact time on the adsorption of  $Al^{3+}$  by using xanthated and charred sugarcane bagasse.

Figure 4.6 above shows that the equilibrium contact time for the adsorption of Al (III) by adsorbent CSB and XSB reached within 150 minutes at pH 4 with adsorbate uptake of 36.4 mg/g and 48.18 mg/g respectively. The adsorption of  $Al^{3+}$  was initially increased with the increase of contact time up to the certain time and remained constant. The increase in adsorption initially is due to the availability of the large surface area of adsorbents for the adsorption. After the equilibrium has reached, the adsorption rate slows down and finally becomes constant due to difficulty in occupying the vacant surface. The above result concludes that chemically modified XSB has more  $Al^{3+}$  uptake than CSB at this optimum time.

### 4.2.3 Effect of initial concentration

The effect of initial concentrations on adsorption of Al (III) was studied by varying the concentration of an aqueous solution from 10 mg/L to 800 mg/L with the chemically modified sugarcane bagasse i.e. CSB and XSB at optimum pH 4. The plot of  $C_i$  vs.  $q_e$  for the adsorption of Al is shown below.

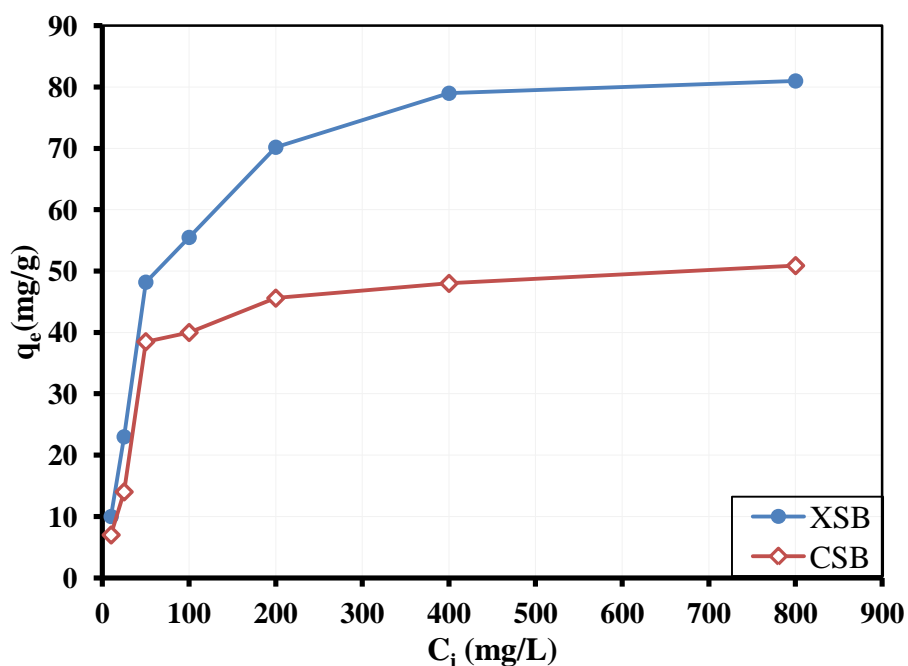


Figure 4.7: Effect of initial concentration on the adsorption of  $Al^{3+}$  by using xanthated and charred sugarcane bagasse.

The experimental data showed that the maximum adsorption capacity of CSB and XSB was 50.9 mg/g and 81.0 mg/g, respectively which are shown in figure 4.7. It is found that the adsorption capacity of XSB is better than that of the CSB. This curve indicates that the sorption capacity will increase with the increase in the initial concentration gradient. At lower initial concentration, sufficient sorption sites are available for the sorption of the metal ions but, at higher initial concentration, the numbers of metal ions are relatively higher than adsorption sites; hence the removal percentage depends on the initial concentration. This occurs due to the increase in the rate at which Aluminium ions pass from the bulk solution to the particle surface along with the increase in the concentration of the solution that would result in the higher adsorption.

### 4.3 Adsorption Isotherm Studies

The adsorption isotherms help to determine the design of the adsorption mechanism between adsorbate and adsorbent systems. To evaluate the best-fit isotherm model for Aluminium ions adsorption, the experimental data of Al adsorption onto CSB and XSB were analyzed using the well-known Langmuir and Freundlich isotherm equation. Linear plots were obtained in both models which are illustrated in figures 4.8 and 4.9. In figure 4.8, the plot of  $C_e/q_e$  vs  $C_e$  showed the straight line that indicates the experimental data of Langmuir linearized isotherm for Al (III) onto adsorbents i.e. CSB and XSB. Here, the maximum adsorption capacity ( $q_m$ ) for CSB and XSB were found to be 50.9 mg/g and 81 mg/g, respectively. Similarly  $R_L$  values from the Langmuir isotherm modes were found to be 0.99 and 0.99 for CSB and XSB. These values were found to be in the range of  $0 < R_L < 1$  which indicates that the process is favorable and adsorption data fit well in the Langmuir adsorption isotherm.

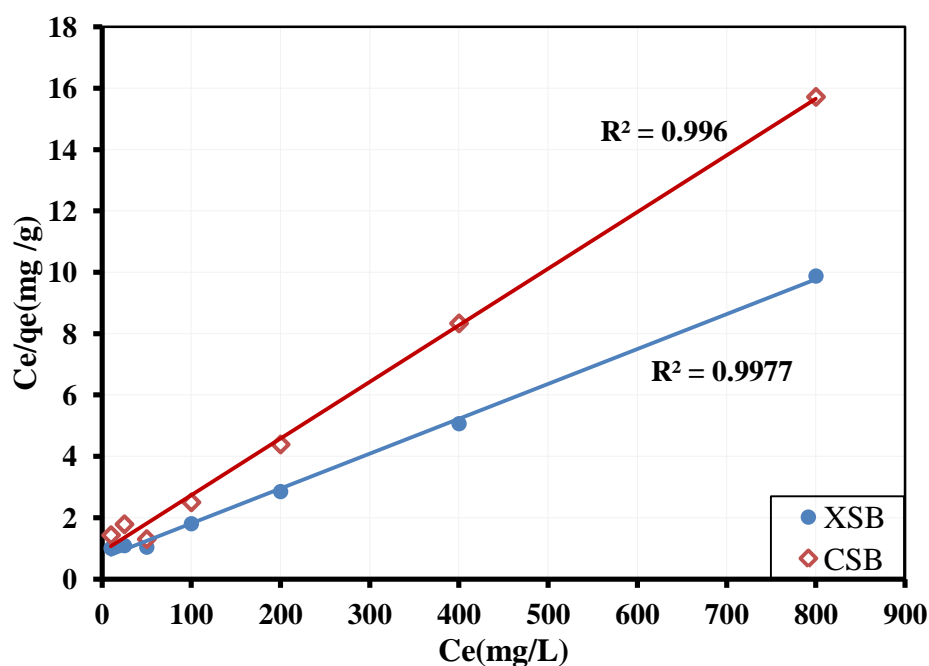


Figure 4.8: Langmuir adsorption isotherm for adsorption of  $Al^{3+}$  onto CSB and XSB

Table 4.2: Langmuir parameter for adsorption of  $Al^{3+}$  onto CSB and XSB

Metal	$q_e$ (mg/g)	$R^2$
$Al^{3+}$ ions onto CSB	50.9	0.996
$Al^{3+}$ ions onto XSB	81.0	0.997

The plot of  $\log q_e$  versus  $\log c_i$  showed the straight line that indicates the straight line that indicates the experimental data of Freundlich linearized isotherm and provides the value of  $1/n$  as 0.78 and 0.85 for CSB and XSB respectively. Here the value of  $n/1$  lies in between 0 and 1, which indicated that Freundlich isotherm, is also followed by the resulting data. But the experimental data presented in the figures 4.8 and 4.9 revealed that the Langmuir isotherm model for both adsorbents showed a better fit than the Freundlich isotherm.

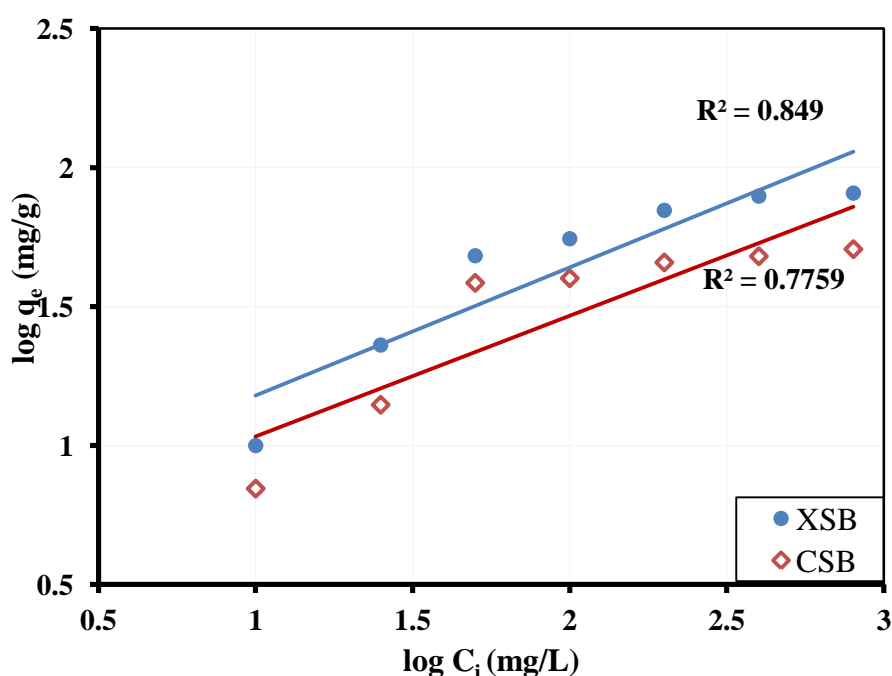


Figure 4.9: Freundlich adsorption isotherm for adsorption of  $Al^{3+}$  onto CSB and XSB.

Table 4.3: Freundlich parameter for adsorption of  $Al^{3+}$  onto CSB and XSB.

Metal	$q_e$ (mg/g)	$R^2$
$Al^{3+}$ onto CSB	50.9	0.78
$Al^{3+}$ onto XSB	81.0	0.85

#### 4.4 Batch Kinetics Studies

The experimental kinetic data for the adsorption of Al onto CSB and XSB were studied by using different kinetic models such as pseudo-first-order and pseudo-second-order kinetic models.

Pseudo-second order plot of  $\frac{t}{q_t}$  versus  $t$  gave the perfect straight line for adsorption of

Aluminium metal ions onto CSB and XSB simultaneously indicating that the adsorption reaction followed the Pseudo order kinetic model. In this study, the  $R^2$  value was found to be 0.991 and 0.993 and equilibrium concentration  $q_e$  for the adsorbents were found to be 38.5 mg/g and 48.2 mg/g for CSB and XSB respectively.

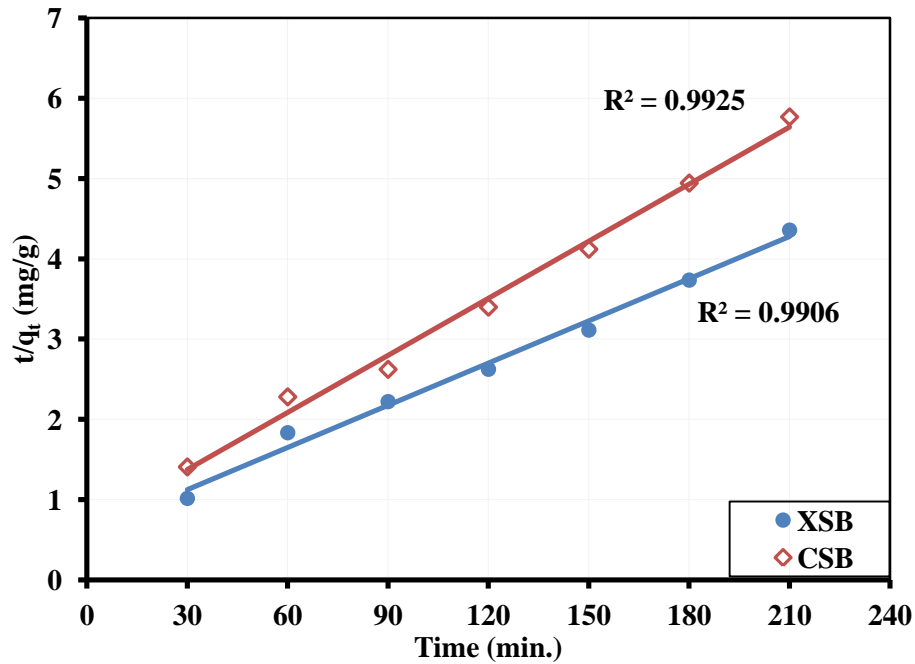


Figure 4.10: Pseudo second order kinetics model for adsorption of  $Al^{3+}$  ions onto CSB and XSB.

In the figure 4.10 the experimental kinetics data for adsorption of Al (III) were studied, and the plot of  $\log (q_e - q_t)$  versus time showed downward straight line which indicates the pseudo-first-order reaction with respective slope, intercept and correlation coefficient  $R^2$ . In this study, the  $R^2$  was found to be 0.95 and 0.91 for CSB and XSB respectively.

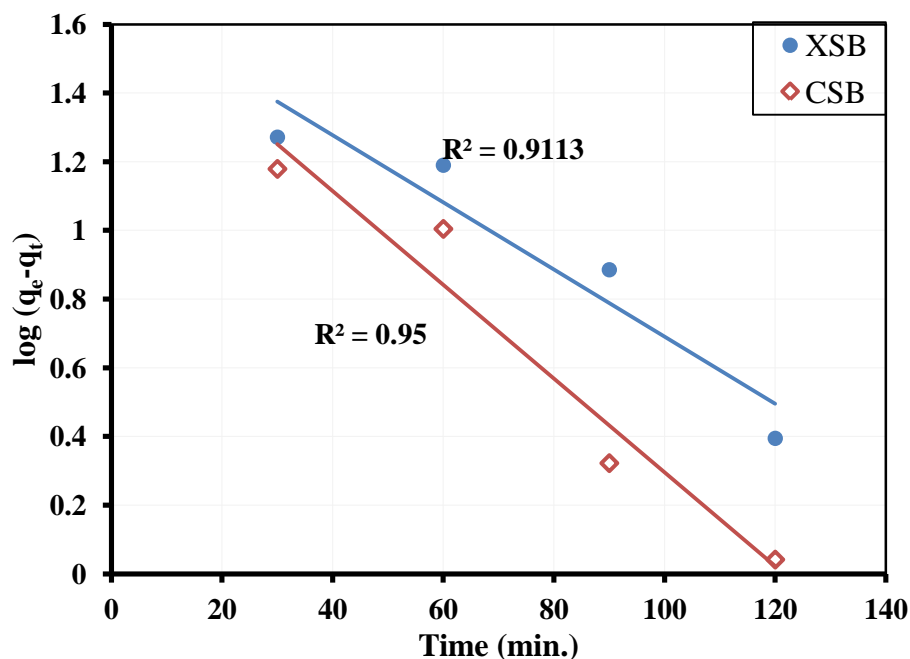


Figure 4.11: Pseudo-first order kinetics model for adsorption of  $\text{Al}^{3+}$  ions onto CSB and XSB.

From the kinetic data for the adsorption of  $\text{Al}^{3+}$ , a straight line with the best fitting and high correlation coefficient value was observed for the pseudo-second-order than pseudo-first-order. The experimental data followed pseudo-second-order for both adsorbents.

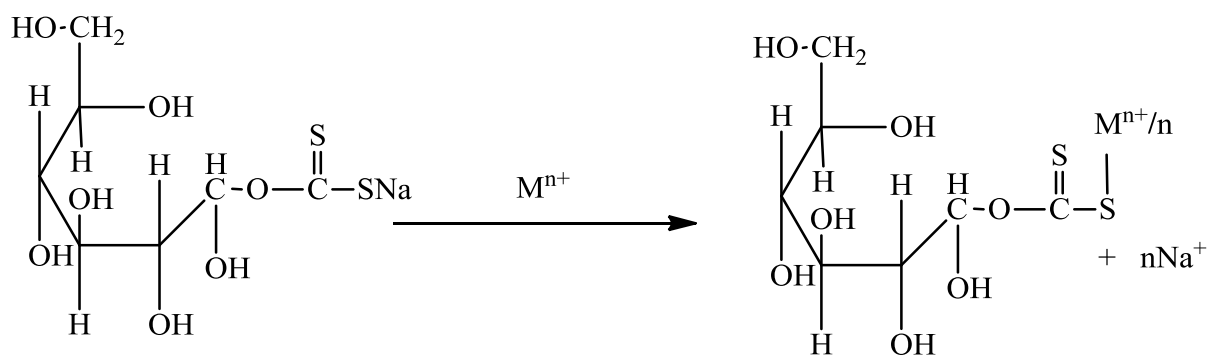
Table 4.4: pseudo-first and pseudo-second order kinetics model for adsorption of  $\text{Al}^{3+}$  onto CSB and XSB

Adsorbent	Pseudo-first-order			Pseudo-second-order		
	Slope	$q_e(\text{mg/g})$	$R^2$	Slope	$q_e(\text{mg/g})$	$R^2$
CSB	-0.0136	38.5	0.95	0.0237	38.5	0.99
XSB	-0.0098	48.2	0.91	0.0175	48.2	0.99

#### 4.5 Plausible adsorption mechanism

The probable mechanism between Al (III)-XSB interaction could be electrostatic, ion exchange, and/or specific chemical reaction. The adsorption sites for Al (III) are at sulphur atoms attached to the xanthate groups. The cation from the xanthate group contained in the monomeric unit has been exchanged at the cost of Al (III) present in the solution. A schematic representation of the complexation mechanism of the Al (III) with the xanthate group which had taken place through ion exchange process is shown below in the scheme 3.





Scheme 3: Plausible adsorption mechanism of  $M^{n+}$ (Al) ion onto monomeric cellulose unit contained in XSB.

## Chapter-5

### 5. CONCLUSIONS AND RECOMMENDATIONS

#### 5.1. Conclusion

In the present work, sugarcane bagasse was successfully charred and xanthated. Different physicochemical properties of the as developed bioadsorbents were investigated. Its efficiency for removal of Al (III) was determined by varying different parameters. The functional group present in bio adsorbent was characterized by FTIR analysis. The adsorption of Al (III) was found to be strongly dependent upon the pH of the solution and the optimum pH value for the adsorption was determined to be 4 for both CSB (with 73.83% adsorption) and XSB (with 97.72% adsorption). At the optimum pH value of 4, CSB leads to 73.83% removal of Aluminium ions from the aqueous solution whereas XSB was found to be tremendously effective with 97.72% removal. Hence, it could be concluded that the XSB adsorbent was by far better at removal of the Aluminium ions from aqueous solution than CSB adsorbent.

The equilibrium time for adsorption of Al onto both CSB and XSB was found to be 150 min. The maximum adsorption capacity of CSB and XSB was found to be 50.9 mg/g and 81.0 mg/g, respectively. The adsorption isotherm study revealed that the Langmuir adsorption isotherm can best explain the adsorption of Al onto both CSB and XSB. The kinetic data were analyzed using pseudo-first-order and pseudo- second-order kinetic models. It was found that the obtained data were best fitted for the pseudo-second-order kinetic model. This research work concludes that the sugarcane bagasse can be used as a potential bio-adsorbent for the removal of Aluminium (III) from an aqueous solution.

#### 5.2 Limitation of the Study

Every experiment in this research was performed carefully and wisely as far as possible to minimize errors and limitations. However, the following limitation of the study is subjected.

- a. Chemicals were not subjected to further purification before the experiment.
- b. Characterization like XPS and TEM were not performed due to time and budgeting constraints.
- c. The experiment in column mode was not performed.

### **5.3 Suggestion for further study**

Activated carbon prepared by chemical modification of sugarcane bagasse has shown a good ability to remove aluminium from aqueous solution. Thus, sugarcane bagasse can be used to remove a variety of different heavy metal ions, including cadmium, lead, mercury, copper, zinc, etc., as well as dyes found in industrial waste water, including methylene blue, Congo red, malachite green, etc. It is possible to prepare the adsorbent physically. To investigate the impact of the additional parameter, the experiment can also be run in column mode.

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